ACTIVITY AND CHARACTERIZATION STUDIES IN METHANOL REFORMING CATALYSIS: Cu AND Cu-ZnO CATALYSTS AND THE ROLE OF NANOMATERIALS

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To Pop
There are some things which cannot be learned quickly, and time, which is all we have, must be paid heavily for their acquiring. They are the very simplest things and because it takes a man's life to know them the little new that each man gets from life is very costly and the only heritage he has to leave.

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ACTIVITY AND CHARACTERIZATION STUDIES IN METHANOL REFORMING CATALYSIS: Cu AND CuO-ZnO CATALYSTS AND THE ROLE OF NANOMATERIALS

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Major: Chemical Engineering

Hydrogen storage is a major barrier to commercialization of proton exchange membrane (PEM) fuel cell powered automobiles. The problem can be circumvented by storing a liquid hydrogen source and then using a reforming reaction to generate hydrogen onboard the vehicle. Methanol is the preferred liquid hydrogen source for onboard generation. Methanol steam reforming is a convenient way to generate large amounts of clean hydrogen at reasonable temperatures and atmospheric pressure. Cu and CuO-ZnO reforming catalysts on Al₂O₃, ZrO₂/Al₂O₃, and CeO₂/Al₂O₃ nanoparticle oxide supports were investigated in this work. These systems ranged from traditional impregnated CuO-ZnO/Al₂O₃ to more complex CuO-ZnO on mixed nanoparticle ZrO₂/Al₂O₃ supports. Finally, binary CuO/ZrO₂ systems were constructed using a reverse microemulsion procedure.

Detailed reaction studies were performed and kinetic reaction data was examined and compared to surface, structural and electronic characterization data in order to determine both structural and valence state information of the catalyst system before and after reaction. In all cases it was determined that a reasonable Cu surface area is necessary to catalyze the reforming reaction but that high Cu surface area is not the critical criterion for highly active reforming
catalysts. It was shown that using nanoparticle Al₂O₃ supports can greatly increase catalyst surface area but that Al₂O₃ has a retarding effect on catalytic activity which partially offsets any benefits. Therefore it was concluded that Al₂O₃ should only be used in relatively low concentrations or in conjunction with another oxide support.

It was determined that an electron deficient Cu species formed due to an interaction with the nanoparticle ZrO₂ support which was highly beneficial for catalyst performance. This electron deficient Cu species promoted the methanol reforming reaction while also apparently suppressing CO production via the reverse water gas shift. This work demonstrates that the Cu-ZrO₂ synergy can be exploited by using binary reforming catalysts and is increased by using calcination temperatures above 300°C, despite a slight loss of Cu surface area at high calcinations temperatures.
1.1 Introduction and Motivation for Research

Fuel cells have been the subject of intense research over the past decade as an environmentally friendly alternative to the rather dirty and inefficient internal combustion engines. Fuel cells have several distinct advantages as mobile power sources when compared to combustion engines. First, since a fuel cell is an electrochemical power source and not a thermal power source, fuel cells of any type are not restricted by the Carnot efficiency, which states that the maximum theoretical efficiency for internal combustion engines is around 40%, with actual working efficiencies closer to 25% [1]. Freedom from the Carnot limitation means that the maximum theoretical efficiency of a fuel cell is 100%.

Nearly every car in existence today is powered by the combustion of hydrocarbons, and even with today’s catalytic converters in cars and filters on diesel engines, this is still a relatively dirty business. Gasoline powered engines emit sulfur oxides, nitrogen oxides, and volatile organic carbons, and the emissions from their diesel counterparts also contain their share of sulfur oxides as well as fine particulates. PEM fuel cells, by contrast, emit only water.

There are many types of fuel cells, and most are named by the type of electrolyte used to carry electric charge through some type of membrane or separation. The most common types are solid oxide, direct methanol, phosphoric acid, and proton exchange membrane (or polymer electrolyte membrane) fuel cells. Direct methanol fuel cells are perhaps the most desirable since the fuel cell uses methanol itself as the fuel and thus there is no need for methanol reforming to produce hydrogen as is the case for proton exchange membrane fuel cells. However, direct methanol fuel cells have notoriously poor anode kinetics and are not suitable for the high power requirements which would be necessary in automotive applications [2].
Alternatively, PEM fuel cells have much better (faster) anode kinetics and can meet the power requirements of automotive applications [1,2]. The first practical use for PEM fuel cells was in the 1960’s in the Gemini space missions [1]. One notable problem with PEM fuel cells is that onboard high pressure hydrogen storage is neither safe nor practical in a commercial application. An alternative is to store a hydrogen source in liquid form and generate the hydrogen on board. One method of great interest in recent years is hydrogen production from methanol via steam reforming over copper-based catalysts. Methanol is the preferred fuel for the reforming process given that it has a high H:C ratio, can be reformed at reasonably low temperatures (200-300°C) and produces low amounts of CO [3]. One of the major challenges with the steam reforming reaction is to avoid CO formation. Even small amounts (levels greater than 10 ppm) of CO present in the hydrogen fuel will result in lower fuel cell efficiencies due to CO poisoning of the PEM fuel cell anode [1]. The generally accepted limit on CO concentration which can be tolerated by the anode catalyst is below 100 ppm [1,4]. Consequently, not only are high yields of hydrogen at low temperatures important, a CO-free or near CO-free hydrogen also has to be produced. This is a great challenge to the heterogeneous catalyst community.

1.2 General Literature Review

The first documented instance of hydrogen generation from steam reforming of methanol was in 1921 [5]. Reforming was achieved using pure copper metal. Since that time, the trend in methanol reforming, and heterogeneous catalysis in general, has been towards more durable catalysts which generally incorporate some combination of an active metal (copper), plus a “support” to increase surface area, as well as a stabilizing component, also called a promoter. The most common promoter for Cu-based methanol steam reforming catalysts is ZnO [6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23]. The ZnO is added to improve the dispersion of the Cu, increase the so-called “spill over” effect, and to improve the reducibility of
the CuO precursor [12,13,14,16,19,20,24]. The adsorption of methanol is generally thought to occur on the copper metal, and hydrogen atoms dissociate from the adsorbed methanol and move ("spill over") from the copper onto the ZnO, where they are loosely bound [24].

Alumina has long been a popular support for copper-based steam reforming catalysts due to its high surface area [6,7,8,10,11,12,13,14,15,16,17,18,19,22]. It has also been shown that the alumina can reduce the vulnerability of copper to sintering [12,15,16,19]. Additionally, since methanol is a Lewis base, it should not be surprising that alumina, which is a strong Lewis acid, would support a strong electronic interaction between the methanol reactant and the catalyst surface [11,25]. Despite the common use of alumina as a support in these reactions, it has been shown that the H\textsubscript{2} yield decreases with increasing alumina concentration and that Al\textsubscript{2}O\textsubscript{3} actually hinders the reforming reaction [16]. It is therefore not surprising that recently work has been done moving away from the traditional alumina support to alternative supports such as CeO\textsubscript{2} and ZrO\textsubscript{2} [14,16,18,26,27,28,29]. Other references suggest that a mixed oxide support would be better still [18,28,30]. The main advantages of CeO\textsubscript{2} and ZrO\textsubscript{2} supports appear to be that the support oxides themselves are more easily reduced than the traditional Al\textsubscript{2}O\textsubscript{3} supports, and furthermore, that increasing Al\textsubscript{2}O\textsubscript{3} content tends to decrease the reducibility of the CuO species [15,26,31,32]. The role of ZrO\textsubscript{2}, CeO\textsubscript{2}, and ZrO\textsubscript{2} nanoparticles in methanol reforming catalysis will be examined in Chapters 3 and 4.

Not long after the Gemini space missions and with evidence that methanol reforming was potentially useful in power generation, efforts were made to model the catalytic reforming reaction. Most models assume that the steam reforming of methanol involves three main reactions, shown here in equations 1-1 to 1-3. These include: 1-1) steam forming of methanol to
form hydrogen and carbon dioxide; 1-2) the water-gas-shift (WGS) reaction and 1-3) the decomposition of methanol.

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2 \] 1-1

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2 \] 1-2

\[ \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} \] 1-3

It has been demonstrated that the equilibrium of reaction 1 is over 99\% in the presence of excess steam at 500 Kelvin and 1 atmosphere [33]. Among the earliest model was that of Santacesaria and Carra [34]. These researchers developed a Langmuir-Hinshelwood type expression that fit their reaction data but did not involve a specific surface mechanism. An Arrhenius-type kinetic equation for the rate of methanol conversion in the reforming reaction was later developed by Amphlett in 1985 [35]. This model is shown in equation 1-4 using the author’s notation:

\[ -r_{\text{CH}_3\text{OH}} = \frac{k' P_{\text{CH}_3\text{OH}} - k_P \text{P}_{\text{CO}} P_{\text{H}_2}}{k_c \text{P}_{\text{CO}}} \] 1-4

In this equation \( P_{\text{CH}_3\text{OH}}, P_{\text{CO}} \) and \( P_{\text{H}_2} \) are the partial pressures of \( \text{CH}_3\text{OH}, \text{CO}, \) and \( \text{H}_2, \) respectively. The \( k \) terms are Arrhenius type rate constants. It is worth noting that the partial pressures of \( \text{H}_2\text{O} \) and of \( \text{CO}_2 \) do not appear anywhere in this equation. A more well-accepted model was developed in 1993 by Jiang, et al [36]. His kinetic expression is more complex and demonstrates the nonlinear nature of the methanol reforming reaction net work. This model is shown in equations 1-5 and 1-6.

\[ -r_{\text{CH}_3\text{OH}} = k' P_{\text{CH}_3\text{OH}}^{0.26} P_{\text{H}_2O}^{0.03} P_{\text{H}_2} \] \( P_{\text{H}_2} < 7kPa \) 1-5

\[ -r_{\text{CH}_3\text{OH}} = \frac{k' P_{\text{CH}_3\text{OH}}^{0.26} P_{\text{H}_2O}^{0.03} P_{\text{H}_2}^{0.2}}{P_{\text{H}_2}^{0.2}} \] \( P_{\text{H}_2} > 7kPa \) 1-6
This model was fairly well accepted and is heavily cited in the methanol reforming literature. However, in this work no effort was made to develop an actual surface mechanism, only to empirically fit reaction data to an Arrhenius expression.

In 1998 a very ambitious study by Peppley and coworkers developed a detailed surface mechanism for copper and zinc oxide on alumina catalysts. Their goal was to develop a comprehensive model for the entire reforming network [7,8]. Many later models cite this work. Peppley et al. insisted that the methanol decomposition reaction (equation 1-3 above) had to be considered for an accurate and comprehensive kinetic model [7,8]. The authors based this conclusion, in no small part, on the work of Vanderborough, et al. [6]. In their study Vanderborough et al. used a CuO-ZnO/Al₂O₃ catalyst which exclusively contained radio labeled oxygen atoms (¹⁸O). The authors were able to show that C¹⁸O¹⁸O and CO¹⁸O are immediately detectable after the start of the reforming reaction, whereas C¹⁸O is never detected [6]. This is direct evidence that the carbon-oxygen bond in methanol was never broken and that carbon monoxide therefore is formed via methanol decomposition and not via the reverse water-gas-shift reaction.

Peppley and coworkers performed the reforming reaction and studied the equilibrium of the water-gas-shift reaction. They showed that at very low methanol conversions the CO partial pressure is higher than can be achieved through equilibrium of the water gas shift. Peppley states that the “only explanation” for this result is that the rate of the decomposition reaction must be significant with respect to the rates of the steam reforming and water gas shift reactions [7].

With the information in the preceding three paragraphs, Peppley made two key conclusions: 1) the reaction pathway for CO production must be different from the pathway for
CO₂ production. This means that there must be one distinct type of active site for CO production and a separate type of active site for CO₂ production, and 2) the direct decomposition of methanol must be included in a kinetic model. The latter conclusion is of greater relevance in this dissertation. The Peppley work has one distinct disadvantage in that it is extremely cumbersome. The model involves dozens of rate constants, active site and intermediate species concentrations, fitting parameters and equilibrium coefficients. When employed, it is almost exclusively used in an abbreviated and simplified form.

In contrast to the work by Peppley et al., Agrell and coworkers found that the CO formed in the steam reforming reaction over their catalysts was below the water gas shift equilibrium concentration at every temperature in the study and furthermore that CO production decreased to the point where it was a negligible product at very short contact times [9]. These observations do not support the assertion that CO is a primary product, as stated by Peppley. This is in agreement with a study by Purnama, et al. who stated that their data indicates that CO is a secondary production produced exclusively through the reverse water gas shift [10]. It is interesting to note that Turco, et al. found that it is possible to attain decent methanol conversions through the direct decomposition of methanol, but only in the absence of both steam and O₂ [11]. The authors reported that the activation energy for the reforming reaction is considerably lower than that of the decomposition reaction and therefore in the presence of steam methanol reacts via reaction (1-1) to form H₂ and CO₂ [11]. This is in agreement with results of Choi and Stenger [37]. Recent work by Mastalir, et al. agrees that the model which best fits the data includes the methanol decomposition [4]. Mastalir stated that the contribution of the decomposition reaction was only significant at low conversions [4], which agrees with the findings by Peppley [8]. However, Mastalir concluded that CO was predominantly formed
through the reverse water gas shift, although methanol decomposition does play some role at low contact times [4]. Evidently the reaction is very sensitive to the reaction conditions and catalyst in use. The role of methanol decomposition and the equilibrium of the water gas shift will be covered in detail in this work. When reviewing the literature it is evident that despite the number of articles on the copper-based steam reforming catalysts, there is still some controversy in the literature on the actual reaction mechanism and, furthermore, a detailed picture of the chemical and electronic characteristics of the active sites is to this date not available.

Recent work has noted an increase in catalytic activity of Cu metal in the methanol reforming reaction when a “reducible oxide” such as CeO$_2$ or ZrO$_2$ is used as the catalyst support [27,29,38,39,40,41,42,43]. There has been a discussion of “synergy” in the Cu/Zr catalysts that is credited for an increase in catalytic activity [29,42]. The possible advantages of using nanoparticle ZrO$_2$ in methanol reforming catalysts have not been investigated at the date this dissertation was published. The nature of the interaction between the ZrO$_2$ support and the Cu metal in methanol reforming catalysts is investigated in Chapter 3. The Cu-Zr electronic interaction in the catalyst is covered in detail in Chapter 4.

In order to exploit the synergy of the Cu/Zr system, novel microemulsion catalyst preparation techniques have been used by Ritzkopf, et al. [44]. The utility of the microemulsion preparation procedure has previously been demonstrated for Cu/ZnO [45] and Pd/ZnO systems [46] by other researchers. The apparent advantage of the microemulsion preparation technique for Cu/ZrO$_2$ reforming catalysts is that the resultant catalysts have a lower CO selectivity than is attainable with catalysts from more traditional preparation techniques [44]. However, the possible advantages of using nanoparticle supports in conjunction with microemulsion catalyst
preparation procedure have yet to be examined. This new area of methanol reforming research will be covered in Chapter 5.

In the present work, we have investigated the consequences of using nanomaterials in the methanol reforming catalyst fabrication. Specifically, this work employs nanoparticle Al$_2$O$_3$ and ZrO$_2$ supports in the catalysts that have not been investigated previously. A more detailed literature review will be included in the chapter where it is most relevant to the topic at hand.

1.3 Catalytic Reaction System Design and Construction

1.3.1 Reactor System Design

Since the initiation of this project, a complete reactor system for testing catalytic activity has been constructed. Figure 1-1 shows the reactor system diagram for the catalyst testing system.

![Catalytic Reactor system](image)

Figure 1-1 Catalytic Reactor system
The system uses an internal (inert) standard of Argon as the calibration reference. Argon is introduced to the system by an MKS series M100 mass flow controller (MFC). The gas travels through a series of valves used to isolate different parts of the system depending on the type of experiment being performed. In the case of methanol reforming, the argon flow is directed to a KDS series 101 syringe pump which dispenses the desired volume of methanol and water. The argon/methanol/water mixture travels a short distance to the in house built evaporator, which is maintained at 220 degrees C by an Omega brand model CN616TC2 PID type controller. For the studies covered in Chapters 3 and 4, this in-house built evaporator was replaced by a more sophisticated Barnstead Thermolyne model F21125 tubular furnace. The effluent temperature from the evaporator is monitored via an Omega 1/8” type K thermocouple to make sure that there is single phase flow to the reactor. The reactant mixture then travels a short distance in heated tubing to the catalytic reactor. The reactor consists of a ½” stainless steel tube which houses the catalyst bed. The catalysts used in this study were pressed into pellets in a ½” diameter pellet die under two tons of force exerted by a Carver press. For all reactor experiments in this study, the catalyst pellet of the sample to be loaded into the reactor was crushed and sieved to obtain particles with sizes between 500 μm and 1 mm for activity testing. The reactor is loaded by simply disconnecting the compression fittings on either side of the reactor and removing the reactor tube from the furnace. Sieved catalyst particles are loaded in the effluent (downstream) side of the reactor. The catalyst particles are held in place by two plugs of quartz wool which take no part in the reaction. The size of the bed (weight of catalyst) can be varied as desired. The downstream side of the catalyst bed is supported by an Omega ¼” type K thermocouple. From the reactor, the effluent gas again travels through a length of heated pipe into an ice bath condenser where unreacted CH₃OH and H₂O are removed. It was determined
early in this study that introduction of liquid species into the chromatograph was problematic. The different temperatures in different parts of the instrument give rise to rapid condensation and evaporation of the liquid species, which likewise results in huge swings in the flow rate. This gives rise to problems in reproducibility. After the ice bath the non-condensable species travel a short distance to the GC for analysis.

1.3.2 Gas Chromatograph Design and Operation

The main piece of analytical instrumentation for all of these tasks is a custom built Agilent 6890 gas chromatograph (GC). All reaction products can be measured in a single sample of product gas injected automatically to the GC. The GC is programmed to take a sample of a known volume of gas through an automatic sampling valve when prompted. Manual injections are also possible. From the sampling valve, the different components of the product gas are separated by two capillary columns in series inside the GC oven. The oven is set at 30°C at the start of the run in order to separate the permanent gases, and ramps up to 65°C to elute the remaining components. Permanent gases, except for CO₂, first travel through an Agilent polar “Plot Q” column, and then onto a molecular sieve (mol. sieve) for further separation. Methanol vapor, CH₂O and CO₂ could potentially get “hung up” on the mol. sieve, and are adequately separated by the Plot Q column. Therefore, after the permanent gases besides CO₂ pass onto the mol. sieve, it is isolated by means of a column isolation valve which prevents the other species from entering this column. Instead, any methanol vapor, CH₂O, and CO₂ are sent straight towards the detectors. Just before entering the flame ionization detector, CO and CO₂ pass over a nickel catalyst (methanizer) which reduces them to methane so that they can be detected on the flame ionization detector.
There are two detectors in series in this GC, a thermal conductivity detector (TCD) and a flame ionization detector (FID). The FID is used to measure the concentrations of any species which contains a carbon-hydrogen bond (methanol, methane, plus CO and CO₂ after reduction). For all experiments in this study the FID temperature is set at 400°C, and the H₂, air, and N₂ make-up gas flow rates to the FID are set to 40, 450, 6 sccm, respectively. The FID is operated in “Constant Make-Up” mode, where the make-up N₂ flow to the detector is held constant. These settings give a baseline signal of ~6.0 pA.

The TCD performs the same task but on all chemical species. Although these measurements could be performed with the TCD alone, the additional detector provides higher sensitivity and a level of redundancy for the hydrocarbon species. The FID is also able to detect the presence of trace amounts of CO that may not be detectable with the TCD alone. Further details of how the detectors work can be found elsewhere [47]. For all experiments in this study the TCD temperature is set at 250°C. The reference He flow is set at 33.0 sccm and the make-up He flow is set at 4 sccm. The TCD is operated in “Constant Make Up” mode for all experiments. These settings give a baseline signal of ~40 μV. After exiting the detectors, the product gas travels to the fume hood for ventilation.

The direct line of helium to the GC serves as both the carrier gas and the reference gas for the TCD (see Figure 1-1). The direct air, hydrogen, and nitrogen lines to the GC serve as oxidant, fuel, and make up gas, respectively, for the FID.

1.3.3 Gas Chromatograph Calibration

After the complete construction of the system, the next step before catalytic activity testing was a complete calibration of the analytical equipment. This was accomplished by sending a
known flow rate of the gas to be used in the calibration and a known flow of the internal (argon) standard to the GC. The signal area from the detector(s) was then noted and the ratio of the signal areas of the calibration gas to argon was recorded. Since the concentration of the calibration gas sent to the GC is known, a plot can be constructed of the concentration (volume percent) of the gas in question as a function of the gas to argon signal area ratio. TCD and FID calibration plots for several of the gases present in the reforming reactions are shown in Figure 1-2.

The TCD response to hydrogen is obviously very nonlinear towards the upper end of the detection limit. The data are fit with a logarithmic expression and the measurement appears reproducible. A slightly more accurate calibration curve can also be used which is linear over the low H$_2$/Ar ratio signal range. It is also worth noting that the detector does not have the exact same response for a sample containing 20% CO$_2$ as it would for a sample containing 20% CH$_4$. This calibration takes into account that the detector has a different response for each component.

In Figure 1-2 B it is evident from the overlap of the CH$_4$ and CO curves that essentially all of the CO sent to the methanizer is reduced to methane. Therefore the detector sees all CO as CH$_4$ and does not report a difference. However, the CO and CH$_4$ peaks are easily identifiable since they have different elution times. The fact that the CO$_2$ curve is further to the left on the plot reflects the fact that CO$_2$ is more difficult to reduce than CO and consequently the methanizer does not reduce the entire volume of CO$_2$ in the sample to methane, as it does in the case of CO. The details from the calibration curves generated from these plots are displayed in Table 1-1.
Figure 1-2 Calibration curves. A. Calibration Curves for the thermal conductivity detector (TCD) response to various gases. B. Calibration curves for the flame ionization detector (FID) response to various gases. H₂, CH₄, CO₂, CO. For all calibrations the flow of the argon internal standard was constant at 15 sccm.

Some non-linearity in the detector response is to be expected, especially at the upper and lower limits of detection [48]. Sources of non-linearity in chromatographic systems result from
interactions with inlet linings, valve lubricants, or other components in the system which can incur some sample losses [48]. The non linearity is not necessarily a problem as long as it is both reproducible and quantifiable. Developing a mathematical relationship between the signal response and the concentration takes this non-linearity into account. Manual curve fitting is also possible in regions where the mathematical relation differs notably from the data. Note that the linear fits for most gases are adequate, but relationships which take into account the non-liner (quadratic) contributions at the upper and lower end of the concentration range give the best fit. From this table it is evident which calibration curve should be used for each species.

CH$_2$O is difficult to detect with a GC [49]. It is also difficult to prepare a calibration curve for this species. In this study, CH$_2$O vapor calibration was performed using a saturation chamber, since the vapor pressure (and total system pressure) is known at a set temperature. Condensate analysis was performed via liquid injections into the same chromatograph. The condensate analysis showed that even at the highest CH$_2$O production rates, the water in the condenser had either no CH$_2$O at all, or only negligible amounts of dissolved CH$_2$O. In either
case the tiny amount of CH$_2$O in the condensate does not change the shape of the methanol conversion curves shown in the following chapters since the amount of CH$_2$O dissolved in the condensate is several orders of magnitude less than the amount of CO$_2$ produced in the reactor. Calibrations for liquid CH$_2$O in the condensate were performed using a saturated CH$_2$O solution (Fisher Scientific) and diluting it to known concentrations of CH$_2$O. There is also no evidence of coking of the catalysts (measured via carbon content of the surface via XPS), which would further complicate calculating an accurate conversion via a carbon balance. All chromatography data is analyzed using the Cerity 3.0 software, which is the same software used to operate the GC.

1.4 Water Gas Shift Equilibrium

The water gas shift, shown in equation 1-2, has been studied by generations of chemists. It is of particular interest in this study to elucidate the source of CO. To this end, equilibrium calculations were performed to compare the partial pressure of CO in the reactor effluent to the equilibrium partial pressure of CO for the reverse water gas shift reaction. The thermodynamic equilibrium constant for the water gas shift was calculated according to equation 1-7:

$$ K_{eq}^{WGS} = \frac{P_{eq}^{CO} * P_{eq}^{H_2}}{P_{eq}^{CO} * P_{eq}^{H_2O}} = \exp \left( \frac{-\Delta G_{WGS}^{WGS}}{R*T} \right) 1-7 $$

In this equation $P_{eq}^{CO}$, $P_{eq}^{CO}$, $P_{eq}^{H_2}$, and $P_{eq}^{H_2O}$ are the equilibrium partial pressures of the species involved in the water gas shift reaction. $\Delta G_{WGS}^{WGS}$ is the free energy change associated with the water gas shift reaction, $R$ is the ideal gas constant and $T$ is the temperature in Kelvin. The free energy change $\Delta G_{WGS}^{WGS}$ is itself a function of temperature. The temperature dependence is given by the van’t Hoff equation:
\[
\frac{d(\Delta G^\circ / RT)}{dT} = -\frac{\Delta H^\circ}{RT^2} \tag{1-8}
\]

It is commonly assumed that the standard enthalpy change of reaction, \(\Delta H^\circ\) is independent of temperature. If equation 1-7 is solved for \(\Delta G^\circ\) and this result is substituted into equation 1-8, the result is:

\[
\frac{d(\ln(K_{eq}^{WGS}))}{dT} = -\frac{\Delta H^\circ}{RT^2} \tag{1-9}
\]

Thus, by integrating from the reference temperature \(T'\) to the temperature of interest, \(T\) the result is:

\[
\ln\left(\frac{K_{eq}^{WGS}}{K_{eq}^{WGS}'}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T'}\right) \tag{1-10}
\]

Using equations 1-7 and 1-10, the water gas shift equilibrium constant can be calculated at any temperature given \(\Delta G^\circ\) and \(\Delta H^\circ\). \(K_{eq}^{WGS}\) can in turn be used to determine the source(s) of CO in the system at a given set of reaction conditions by defining the function \(\Phi\), as shown in equation 1-11:

\[
\Phi = \frac{1}{K_{eq}^{WGS}} \cdot \frac{P^{CO_2} P^{H_2}}{P^{CO} P^{H_2O}} \tag{1-11}
\]

Equation 1-11 shows that \(\Phi\) is defined as the inverse of the water gas shift equilibrium constant at the temperature of interest times the ratio of partial pressures of the products of the water gas shift reaction divided by the partial pressures of the reactants as measured in the reactor effluent. If the ratio of the partial pressures is equal to the equilibrium partial pressure ratio shown in equation (7) then the system is at equilibrium with respect to the water gas shift reaction and \(\Phi=1.0\). If the CO concentration in the effluent is above the water gas shift
equilibrium concentration, then this is indicative that there is CO production via the methanol decomposition reaction in addition to the reverse water gas shift. In this case $P^{CO}_{eq}$ is relatively large (greater than $P^{CO}_{eq}$) and therefore $\Phi$ is less than unity. The condition of $\Phi$ being less than unity is therefore indicative of CO being produced via the methanol decomposition reaction.

This same procedure was originally used by Graaf, et al. in their study of the water gas shift reaction [50]. The procedure was later used by Peppley, who concluded that methanol decomposition, though undesirable, had to be included in the model of the reaction network for a complete picture [7,8].

### 1.5 Catalyst Characterization Techniques

#### 1.5.1 Catalyst Activity Testing

The primary objective in the course of this investigation is to fabricate and test highly active methanol reforming catalysts using nanomaterials. The fabrication techniques used in this study varied according to what property of the catalyst was to be examined. Detailed information of each of the fabrication techniques used can be found in the appropriate chapter.

This section contains a general overview on the methods used to examine catalytic activity and characterize the physical and electronic properties of these catalysts.

#### 1.5.1.1 Catalyst pretreatment

In all reactor experiments in this study, the catalyst loaded in the reactor was reduced by dilute H$_2$ before being exposed to the H$_2$O/CH$_3$OH feed. This reduction was accomplished by flowing ~15% H$_2$ in Ar over the catalyst bed at 300°C for 3 hours. The flow rates used were 7.5 sccm of H$_2$ and 40 sccm of Ar. After the reduction the catalyst was allowed to cool under a pure Ar flow before beginning an activity experiment. This is the pretreatment recommended by the catalyst manufacturer. It has also been used by other research groups [9].
1.5.1.2 Temperature dependent activity measurement

The primary method of determining the activity of a given catalyst in any reaction is to vary the temperature of the reaction and measure the corresponding activity of the catalyst. Catalytic activity is determined by measuring the composition of the reactor effluent and calculating methanol conversion and CO selectivity as described previously. In the present work this was accomplished by loading the reactor with a set mass of the catalyst to be tested as described in section 1.3.1. Generally this mass was approximately 340 mg unless otherwise noted. The catalyst was then reduced in situ as described in section 1.5.1.1. After reduction the reactor was cooled to 200°C and the experiment started. To begin an experiment, the syringe pump was loaded with a mixture of CH₃OH and H₂O. There is much discussion in the literature as to the proper H₂O/CH₃OH ratio for the methanol reforming reaction. It has been shown that excess H₂O suppresses the formation of undesirable species such dimethyl ether and methyl formate [37]. The H₂O/CH₃OH ratio used in each experiment is noted in the appropriate chapter, but was generally either 3.1 or 1.4. At the start of the temperature sweep, the reactor temperature was allowed to stabilize at 200°C, the condenser was loaded with ice water, the temperature of the evaporator coil was set at 200°C, the syringe pump was started, and all heating tapes are turned on at maximum output. The two detectors in the GC were set at the appropriate temperatures as described in section 1.3.2. The system generally reaches equilibrium approximately one hour after the initial power-up. Longer equilibration times were noted in Chapter 2 and 3 but changes in the power up procedure shortened this time in the later studies (Chapters 4 and 5). Equilibrium was said to be attained when the measured output of the GC was no longer changing with time at a given temperature. Six gas samples are taken at each temperature, which are averaged to give the methanol conversion, CO selectivity and any other information from the reaction. If the data was seen to be stable and there are no changes in the
measured outputs then the temperature is increased by 15-20°C and the process is repeated. In order to ensure reproducibility, it was often necessary to repeat the high temperature points in order to demonstrate that time on stream has not impacted the catalyst performance. In order to do this, the same procedure was followed except that the temperature sweep was started at 300°C or higher. This generates a second activity curve, which should overlap with the first curve if time on stream does not deactivate the catalyst. Because unreacted CH$_3$OH was not introduced into the GC, methanol conversion was calculated by performing a carbon balance. That is, the moles of CO, CO$_2$ and CH$_2$O (if any) measured in the outlet are subtracted from the moles in CH$_3$OH in the influent.

1.5.1.3 Contact time activity measurement

In addition to temperature sweep, contact time sweeps were also performed on selected catalysts to determine what effect the residence time of the reactant had on catalytic activity. In homogeneous catalysis, space time, $\tau$, is generally used to measure the residence time of the reactants. Space time is defined as the volume of the reactor divided by the volumetric flow rate of the reactant feed to the reactor, as shown in equation 1-12.

$$\tau = \frac{V_{\text{reactor}}}{\dot{V}_{\text{feed}}}$$  \hspace{1cm} 1-12

The complication in heterogeneous catalysis is that the reactor volume is not necessarily the same as the packed bed volume, and to know the actually bed volume, the density of the catalyst must be known. This is simple enough to measure but not always included in the literature. Hence, contact time (CT) is very often used instead of space time in methanol reforming studies [7,9,10,12,28,38]. In order to facilitate comparison of the data in this research to the available literature, the common definition of contact time has been used:
In equation 1-13, \( W \) is the mass of the catalyst in kg and \( \text{\dot{F}} \) is the feed rate of methanol in mmol/sec. This gives units of CT as kg*sec/mmol CH\(_3\)OH. It is worth noting here that the most common definition for space time includes the total reactant flow (H\(_2\)O + CH\(_3\)OH) while the common definition of contact time is only in terms of CH\(_3\)OH. In Chapter 2 the Figures are shown using space time as the independent variable and the density of each catalyst is also reported so that the reader can convert between the two.

In order to perform a contact time sweep, the reactor is loaded with a known mass of catalyst as described previously and the system is initialized as described in section 1.5.1.2. The syringe pump is started at a known flow rate and six gas samples are taken at this flow rate. In order to probe other contact times, the flow rate on the syringe pump is changed after data collection at one inlet flow is completed. The low flow rate (high contact time) data points are difficult to measure and the system often takes long periods of time to equilibrate since the system is very sensitive to perturbations at low flow rates. In any case, in order to ensure that the data is indeed reproducible, contact times sweeps are repeated in a similar manner as temperature sweeps, with the catalyst bed reloaded and the sweep started at a different (generally higher) flow rate.

1.5.2 Brunauer-Emmett-Teller (BET) Surface Area Analysis

Brunauer-Emmett-Teller (BET) surface area measurements were performed on either a Quantachrome NOVA 1200 instrument or a Quantachrom ChemBET 3000 instrument. Further details are given in each chapter.
1.5.3 Temperature Programmed Reduction Experiments

Temperature Programmed Reduction (TPR) measurements were performed in a Quantachrome ChemBET 3000 instrument. For these measurements, 55 milligrams of the catalyst was loaded in a quartz tube reactor and secured with plugs of quartz wool on both ends. An Omega K-type thermocouple monitored the temperature in the catalyst bed. Reduction was carried out at a heating rate of 5°C per minute up to a temperature of 400°C under a flow of 5% H₂/N₂ mixture at a total flow rate of 70 sccm until the catalyst was fully reduced and did not consume additional hydrogen. The hydrogen uptake was continuously monitored using a TCD detector during the reduction.

1.5.4 N₂O Decomposition Experiments

The copper surface area was measured on a ChemBET 3000 instrument (QuantaChrome Corporation) using the N₂O decomposition method, as is typically done for copper based reforming catalysts [14,26,51]. The catalysts were loaded in a quartz tube reactor and held in place by quartz wool. Prior to each measurement the samples were reduced in 5% H₂ at 300°C (20 sccm) and then cooled overnight to room temperature under helium. During the measurements helium gas flowed over the samples at a rate of 70 sccm, and the reactive adsorption of N₂O was performed by titrating known amounts of N₂O over the catalyst surface and monitoring the N₂ evolved using a thermal conductivity detector. With this instrument unreacted N₂O is removed from the system through use of a liquid argon cold trap, which condenses out N₂O but allows N₂ to pass on to the TCD. In this way N₂O is titrated over the sample until no signal is recorded on the TCD. At this point the surface is saturated and no further N₂O reacts to N₂. The total amount of N₂ formed (or N₂O consumed) was determined
and used to calculate the amount of copper surface atoms according to the stoichiometry in Equation 1-14.

\[ 2Cu + N_2O \rightarrow N_2 + Cu_2O \quad 1-14 \]

The copper surface area was calculated from these results assuming a copper surface density of 1.47x10^{19} copper atoms per square meter [26,51]. The dispersion is defined as the ratio of copper atoms on the surface of the catalysts to the total number of copper atoms in the catalyst. The error in this measurement has been estimated by other researchers to be approximately 15% [26], which is reasonable in the current investigation as well. This procedure was used in each of the following chapters.

### 1.5.5 Catalyst Density Measurements

For the calculations of space time (volumetric flow rate divided by the volume of catalyst), the catalyst densities were measured on a Quantachrome Ultrapyc 1000 Gas Pycnometer.

### 1.5.6 X-ray Diffraction Analysis

The XRD data was gathered on a Philips powder X-ray diffractometer using Bragg-Brentano geometry with Cu-Kα radiation (\( \lambda = 1.54 \) Å). The XRD spectrum was recorded in a 2\( \theta \) range of 20° to 80° at ambient conditions. Diffraction patterns were obtained for all samples after calcinations and for selected samples after reductive pretreatment and after reaction. Average particle sizes were calculated from the line-broadening of the XRD peaks using the Scherrer equation, show here in equation 1-15.

\[ d = \frac{K \cdot \lambda}{FW \cdot \cos(\theta)} \quad 1-15 \]
Instrument broadening effects were neglected. In this equation $K$ is a constant generally taken as unity, $\lambda$ is the wavelength of the incident radiation, $FW$ is the full width at half maximum and $\theta$ is the peak position.

1.5.7 X-ray Photoelectron Spectroscopy Analysis

The X-ray Photoelectron Spectroscopy (XPS) data presented in Chapter 2 was collected using a Kratos XSAM 800 XPS instrument equipped with a hemispherical analyzer. This instrument was located in the Major Analytical Instrumentation Center (MAIC) at the University of Florida. Incident radiation was from an aluminum anode with $h\nu = 1486.6$ eV. Charge shift corrections were made by assuming a C 1s signal of 284.5 eV unless otherwise noted. Some of the XPS data used in Chapter 2 and all of the XPS data in Chapter 4 were taken using a second XPS instrument located in Gar Hoflund’s lab in the Chemical Engineering department at the University of Florida. This system has been described in detail elsewhere [52]. In either case the atomic percentages of each element on the surface were calculated from the areas under the peaks taking into consideration the atomic sensitivity factor for each element. Further details on the procedures used in collecting and analyzing XPS data can be found in the appropriate chapter.
2.1 Introduction and Literature Review

As mentioned in Chapter 1, the earliest catalysts used in methanol reforming were the simple binary Cu/ZnO systems similar to the one used in the study by Amphelett [35]. Since then use of Al₂O₃ and other oxide supports have become common. Al₂O₃ concentrations as low as 1% were used in the past [6], but later works generally included a higher Al₂O₃ concentration [53]. In these instances the alumina is included both as a binding agent and an oxide support. More recently, the trend in heterogeneous catalysis in general and reforming catalysts in particular has been to develop highly dispersed catalysts where the promoter or support/promoter complex may be 90% or more of the catalyst mass [12,26,31,54]. In this chapter we explore the role of nanoparticle Al₂O₃ supported Cu/ZnO reforming catalysts which have not been previously investigated in the literature. More specifically, it is of interest to determine if the drawbacks of high Al₂O₃ content published by Matter, et al. [16] are inherent in the use of Al₂O₃ as a support or can be avoided if nanoparticle Al₂O₃ supports are used in place of traditional impregnated supports.

While investigating the role of the nanoparticle support, a closely related area of interest which has received considerable attention in the literature is the nature of the active sites, in particular the oxidation state of the copper in methanol steam reforming catalysts. It is generally agreed that Cu²⁺ is inactive and Cu⁺ as well as Cu⁰ are active species in the steam reforming reaction [20,26,27,28]. While some authors do not attribute any activity to Cu⁺[55], other groups have found that stabilizing Cu₂O with “reducible” oxides, such as ZrO₂ and CeO₂, results in
highly active methanol reforming catalysts [20,26,27,28]. Stabilization of Cu$_2$O with an Al$_2$O$_3$ support has never been reported in the literature.

Catalyst characterizations of supported Cu-ZnO steam reforming catalysts have indicated the formation of spinel-type compounds, either CuAl$_2$O$_4$ or ZnAl$_2$O$_4$ [11,21,23,31,32,56]. Several groups have identified the spinel phase as CuAl$_2$O$_4$ [21,31,32,56], while other authors report that ZnAl$_2$O$_4$ forms in the bulk and that CuAl$_2$O$_4$ exists only as a surface species [11,23,56]. Formation of surface CuAl$_2$O$_4$ results in the presence of inactive Cu$^{2+}$ species and is undesirable given that the total number of active Cu$^{0}$ or Cu$^{+}$ atoms is decreased. On the other hand, ZnAl$_2$O$_4$ has been found to be a very efficient catalyst support in the methanol steam reforming reaction [57]. Therefore, determination of the type of spinel phase formed is critical.

The above summary of previous results reveals the complexity of Cu-ZnO-based methanol steam reforming catalysts. These catalysts are further complicated by the fact that a high Cu surface area is not always a sufficient requirement for a high catalytic activity. Recent studies indicate that characteristics other than the Cu surface area, such as introducing micro-strain in the active metal phase, can improve the catalytic activity [12,13]. Consequently, engineering catalysts at the nanometer scale to achieve higher catalytic activities is important in these reactions. It is our hypothesis that starting with nanoparticle alumina as the support, it is possible to prepare highly active Cu particles on the catalysts. Therefore, the goals of this study are to prepare catalysts using nanoparticle alumina supports and determine how they compare with a more traditionally prepared reforming catalyst. The present study will focus on the following:

1) Investigate if Al$_2$O$_3$ is a retardant in the reforming reaction, or if it is possible to make high performance reforming catalysts with copper and zinc oxides deposited onto nanoparticle Al$_2$O$_3$.

2) Determine if there are advantages to using nanoparticle precursor materials in catalyst synthesis.
3) Determine if CO is produced solely via the water-gas-shift, or if methanol decomposition also plays a role over the nanoparticle catalysts.

4) Determine if the surface and structural characteristics of the nanoparticle-supported catalysts differ from those reported in the literature and how they affect the catalytic activity.

2.2 Experimental Methods

Most of the experimental methods used in this chapter are covered in detail in Chapter 1. However, the catalyst preparation method used in this study is unique to this chapter and is described herein. Also, a detailed overview of the reactor operation is included. The details provided for density measurements, BET, and XPS experiments also represent experimental procedures unique to this chapter. TPR, N₂O titration experiments and XRD data collection were performed as described in Chapter 1.

2.2.1 Catalyst Preparation

Catalysts in this study are named according to the concentrations of the active metal oxides, promoter, and support as mass percentages. Labels are assigned according to the concentrations of CuO, ZnO, and Al₂O₃, respectively, in the catalyst sample. For instance, the 35/35/30 sample is 35% CuO, 35% ZnO, and 30% Al₂O₃ by mass. The 35/35/30 and 42/47/11 catalysts were prepared via a sequential wet impregnation method with the goal of attaining 2.0 grams of the finished catalyst sample. For these catalysts, a mass of commercial nanoparticle Al₂O₃ (NanoScale, surface area ~650 m²/g) was dispersed in deionized water. A solution of Zn(NO₃)₂ (Alfa Aesar) was then added to the mixture. The total volume of water used was 50 ml, which resulted in dispersions with nitrate concentrations of 0.18 M for the 35/35/30 and 0.21 M for the 42/47/11 samples. The water was boiled off until a paste consistency was formed. The pastes were dried overnight at 105°C and calcined at 350°C for 3 hours. The resultant ZnO/Al₂O₃ samples were ground and redispersed in water. The copper was then added as an
aqueous solution Cu(NO₃)₂ (Alfa Aesar) to the dispersion (water added = 50 ml and the molar concentration of the copper nitrate precursor: 0.18 M copper nitrate for the 35/35/30 catalyst and 0.24 M for the 42/47/11 catalyst). The water was boiled off and the paste was dried in the same manner as in the previous step. The sample was then calcined a second time at 350°C for 3 hours.

For the sequentially precipitated 5/5/90 catalyst 1.8 g of the nanoparticle Al₂O₃ support was dispersed into 50 ml of deionized water and a solution of Zn(NO₃)₂ added, which resulted in a 0.025 M zinc nitrate dispersion as described above. The mixture was titrated with a 50% stoichiometric excess (i.e. 50 ml of 0.0375 M) solution of NaOH and then aged overnight before it was filtered and washed by stirring in deionized water again overnight. The catalyst dispersion mixture was filtered a second time and the resulting catalyst dried in an oven at 105°C over night and calcined at 450°C for 3 hours. A calcination temperature of 450°C was used instead of 350°C for this catalyst since the lower calcination temperature resulted in higher CO selectivities. The lower calcination temperature would also give less reproducible results, in that the conversion and the selectivity would change with time on stream. The calcined 5/5/90 sample was then ground and again dispersed in water. The precipitation and calcination procedures were repeated exactly as described above with a solution of Cu(NO₃)₂.

The commercially available Süd-Chemie catalyst is approximately 42% CuO, 47% ZnO and 11% Al₂O₃ by mass according to the manufacturer. This catalyst was designed as a low temperature shift catalyst, which is typical for commercially available reforming catalysts.
2.2.2 Reactor Operation and Data Collection

The GC and the catalytic reactor were initialized and operated as described in Chapter 1. Catalyst samples were activated in situ in 15% H₂ in Ar at 300°C for 3 hours before being exposed to the reactant mixture.

Gas samples from the reactor were taken after the system had reached steady state, approximately two hours after system start-up. The concentrations of CO, CO₂ and H₂ were measured as a function of temperature by starting at 200°C and increasing the temperature in increments of approximately 15°C for each data point. At least six gas samples were taken for each data point, and all data was seen to be reproducible. Points plotted in the figures are the average of these samples. An average standard deviation is ±6% for the methanol conversion and ±1% for the CO selectivities was calculated for the reference catalyst, and is typical compared to the other samples. Likewise, in cases when space time was the independent variable, the reactor feed was started at a low flow rate and the flow was gradually increased to examine decreasing space times. The curves were repeated by starting with a fresh sample and taking measurements at high flow rates and decreasing the flow to examine increasing space times. This procedure ensures the curves were reproducible and that catalyst aging could be ruled out in the analysis. The catalyst behavior, even the sharp changes in activity, was verified by repeated experiments in each case using fresh catalysts. In all cases catalyst deactivation due to time on stream for relevant time lengths (~40 hours) was not found to affect the analysis or conclusions in this study.

2.2.3 BET Surface Area Analysis

Brunauer-Emmett-Teller (BET) surface area measurements in this chapter were performed on a Quantachrome NOVA 1200 instrument. Samples were outgassed under vacuum for 3 hours
at room temperature for fresh catalysts and at 105°C for spent catalysts. The BET was performed over five isotherms, which gave roughly linear fits.

2.2.4 Catalyst Density Measurements

For the calculations of space time (volumetric flow rate divided by the volume of catalyst), the catalyst densities were measured on a Quantachrome Ultrapyc 1000 Gas Pycnometer as described in Chapter 1.

2.2.5 X-ray Photoelectron Spectroscopy Analysis

The preliminary XPS data was collected using a Kratos XSAM 800 XPS instrument equipped with a hemispherical analyzer. The samples were supported on double-sided tape during the measurement. Incident radiation was from an aluminum anode with $h\nu = 1486.6$ eV. The pass energy settings on the instrument were set to “low” for the survey spectra and “medium” for the scans of the individual element peaks. Pressure was maintained at $10^{-7}$ Torr or less during the entire measurement. Charge shift corrections were first made by assuming a C 1s signal of 284.5 eV. The data collected from this instrument using the C 1s as the shift reference resulted in binding energies 2 eV above what is expected for the Cu 2p peaks. To test if the observed high binding energies were due to differential charging, i.e. different sections of the XPS spectrum experience a different charge, the fresh 35/35/30 catalyst was selected for analysis using a different XPS instrument. In the second system, the catalysts are pressed into an aluminum cup before entry into the UHV chamber [52]. The binding energies for the Cu 2p peaks obtained from the fresh 35/35/30 catalyst in this system is centered at 933.6 eV as expected for CuO, which is also in agreement with the XRD data and the conclusions from the XPS data obtained from the other system. Consequently, the XPS peaks, such as the Cu 2p peaks, obtained from the 35/35/30 catalyst using the Kratos system were shifted to match the
binding energies obtained from the same catalyst in the second system. The shift difference was then used to adjust the peak positions from the other catalysts (5/5/90 and 42/47/11) in this study. The atomic percentages of each element on the surface were calculated from the areas under the peaks taking into consideration the atomic sensitivity factor for each element and specified peak.

2.2.6 Thermodynamic Calculations

Water gas shift equilibrium calculations are also performed as described in Chapter 1 using equations 1-7 through 1-11. The main difference between the calculations done in this chapter and those of subsequent chapters is that in this chapter the thermodynamic equilibrium constant for the reverse water gas shift reaction, $K_{eq}^{\text{rWGS}}$, is plotted as a function of temperature and this is compared with the ratio of the partial pressure of the products of the reverse water gas shift over the reactants. This is the same method that was used in the publication this chapter was based on. In later chapters the $\Phi$ function is used.

2.3 Results and Discussion.

2.3.1 Methanol Conversion.

Figure 2-1 shows methanol conversion as a function of temperature at constant liquid feed flow rate (0.80 ml/h) for each catalyst tested. It is evident from the conversion plot that the reference catalyst is more active at a lower temperature than any of the nanoparticle supported catalysts, although the activities of the reference and the 42/47/11 catalysts are fairly similar below 280°C. It is also evident that no catalyst is even close to approaching the equilibrium conversion (>95%) under these conditions (see Figure 2-1). However, at higher temperatures, both the reference catalyst and the 42/47/11 catalyst lose activity very rapidly. The 42/47/11 catalyst exhibits severe deactivation at only 280°C. The reference catalyst does not exhibit significant deactivation until 20°C higher. No reaction data for the reference catalyst could be
obtained above approximately 320°C due to severe deactivation. Significant deactivation of the 5/5/90 catalyst does not occur until over 400°C, whereas significant loss of activity for the 35/35/30 catalyst did not occur in the temperature range investigated in this study. The deactivation of the catalysts is irreversible. After a second reduction in dilute H₂ none of the deactivated catalysts could be returned to their original activity levels. The fact that no catalyst achieved over 65% conversion at the space time used in Figure 2-1 regardless of temperature reflects a kinetic limitation (since the equilibrium conversion of the methanol steam reforming reaction is 95% or higher in this temperature range). Higher conversions can be achieved with these catalysts by increasing the space time of the reactants, which is discussed in the next paragraph. Two curves are displayed for the 5/5/90 sample to differentiate between total CH₃OH reacted to all products (CO₂, CO and CH₂O), and CH₃OH reacted specifically to CO₂ and CO. No CH₂O was produced by any other catalyst.

Figure 2-1. Conversion of methanol as a function of temperature at constant liquid feed flow rate (0.8 ml/h). ■-■: catalyst 5/5/90 total conversion, ——: catalyst 5/5/90 conversion to CO and CO₂, ★—★: catalyst 35/35/30, ▲—▲: catalyst 42/47/11, ○—○: reference catalyst, ♦—♦: blank run (no catalyst or support) and –––: conversion to CO and CO₂ over nanoparticle alumina.
Methanol conversion as a function of space time at 280°C is presented in Figure 2-2. The curves for the nanoparticle supported catalysts in Figure 2-2 show the classic sigmoidal growth shape asymptotically approaching a conversion of 100% at the highest space times. It is interesting to note that the curve for the reference catalyst does not display this shape, but rather goes through a very sharp change in the shape of the curve about halfway through the range of space times investigated. It is not evident what is responsible for the differences between the shapes of these curves. Purnama has also noted a “change in controlling kinetics at conversions higher than 70%” in his space time study of a commercially available Cu-ZnO/Al₂O₃ catalyst at 250°C [10]. In the present experiment the distinct change in kinetics appears to occur at conversions of approximately 60%, but the jump in the curve does suggest a change in reaction mechanism. Conversions above 90% can be achieved rather easily at moderate temperatures for the 35/35/30 catalyst as well as the reference catalyst given sufficiently long space times. High conversions are also evident for the 5/5/90 sample, but a large amount of undesired CH₂O is produced by this catalyst with increasing space time. The other disadvantage with increasing the

![Image](image.png)

Figure 2-2. Conversion of methanol as a function of space time, T=283°C. -■-: catalyst 5/5/90 total conversion, -▲-: catalyst 5/5/90 conversion to CO and CO₂, -★-: catalyst 35/35/30, -●-: catalyst 42/47/11, and -○-: reference catalyst.
temperature or the space time is that the CO selectivity increases dramatically for all catalysts (see Figures 2-3 and 2-4).

2.3.2 CO Selectivity

Figure 2-3 shows the CO selectivity as a function of temperature (liquid feed flow rate = 0.80 ml/h). Perhaps the most interesting feature of this figure is that the CO selectivity for the nanoparticle supported catalysts actually decreases with increasing temperature up to approximately 300°C (up to 260°C for the 42/47/11 catalyst). In this temperature range (220-300°C) the conversion is increasing rapidly with temperature for all catalysts (Figure 2-1). The decrease in CO selectivity with increasing temperature is unexpected given that both CO production routes (the methanol decomposition reaction and reverse water-gas-shift reaction) are endothermic, which means that CO formation via these routes are favored both kinetically and thermodynamically with increasing temperature. However, the steam reforming reaction is also endothermic and the equilibrium conversion very high in this temperature range. The fact that the CO selectivity decreases over this temperature range for all of the nanoparticle catalysts reveals that the rate of CO₂ formation is increasing more rapidly with increasing temperature than the rate of CO formation. Evidently, this is true for all nanoparticle catalysts, despite the significant differences in conversion in this temperature range. This may indicate that the catalyst surface is being altered at these temperatures, for example the Cu⁺/Cu⁰ ratio could be changing (see discussion in section 2.4.4). Since the conversion and the CO selectivity are both very dependent on the temperature, it is useful to compare the CO selectivities of different catalysts at a specific conversion, as well as at the maximum conversion (Table 2-1). At 50% conversion the commercial catalyst and the 42/47/11 catalyst exhibit similar CO selectivities, which are considerably lower than those of the other nanoparticle supported catalysts. More
importantly, both the CO selectivity and the temperature at maximum conversion for the 42/47/11 catalyst are lower than the corresponding values for the commercial catalyst. Even though the maximum conversion is slightly lower for the 42/47/11 catalyst compared with the commercial catalyst, the decreased CO selectivity at 50% conversion indicates that the catalysts in this study can be tuned to outperform the commercial catalyst. This is further demonstrated by altering the space times, as shown in Figure 2-4.

Figure 2-3. CO selectivity, CO/(CO₂+CO) as a function of temperature at constant liquid feed flow rate (0.8 ml/h). -□-: catalyst 5/5/90, -☆-: catalyst 35/35/30, -▲-: catalyst 42/47/11, -○-: reference catalyst.

The CO selectivity as a function of space time at 280°C is shown in Figure 2-4. A temperature of 280°C was selected since this temperature corresponds to the maximum conversion of the reference catalyst at a space time of 0.15 seconds. The figure shows that increasing the space time to the level needed for maximum conversion drastically increases the CO selectivity for all catalysts. Evidently, the reference catalyst has a higher CO selectivity at all space times than either the 35/35/30 or the 42/47/11 catalysts at this temperature. Only the
Table 2-1. Comparison of CO selectivity values at 50% and maximum conversion and fixed liquid feed flow rate, and CO selectivity at 65% conversion and 280°C and variable space times (liquid feed flow rates).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Selectivity [%] a</th>
<th>Temperature [°C]</th>
<th>ST [s] b</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/5/90</td>
<td>50</td>
<td>3.9</td>
<td>300</td>
<td>0.21</td>
</tr>
<tr>
<td>35/35/30</td>
<td>50</td>
<td>4.3</td>
<td>280</td>
<td>0.13</td>
</tr>
<tr>
<td>42/47/11</td>
<td>50</td>
<td>2.5</td>
<td>255</td>
<td>0.14</td>
</tr>
<tr>
<td>Commercial</td>
<td>50</td>
<td>2.8</td>
<td>230</td>
<td>0.16</td>
</tr>
</tbody>
</table>

| 5/5/90     | 65 (max)       | 7                 | 341              | 0.19    |
| 35/35/30   | 60 (max)       | 4.6               | 300              | 0.13    |
| 42/47/11   | 58 (max)       | 2.5               | 263              | 0.14    |
| Commercial | 62 (max)       | 4.1               | 280              | 0.15    |

| 5/5/90     | 65             | 6.5               | 280              | 0.40    |
| 35/35/30   | 65             | 5.3               | 280              | 0.31    |
| 42/47/11   | 65             | 6.4               | 280              | 0.40    |
| Commercial | 65             | 8                 | 280              | 0.39    |

a CO selectivity defined as in Equation 4.
b Space time.

5/5/90 catalyst exhibits a slightly higher CO selectivity than the reference catalyst at space times below 0.15 seconds. The CO selectivities of both the reference catalyst and the 42/47/11 catalyst also display a large increase at space times around 0.5 seconds. The same discontinuous increase in conversion was evident for the reference catalyst in Figure 2-2. Repeated tests verified that this step increase was neither due to catalyst aging nor an experimental artifact. The discontinuous change in conversion indicates a change in mechanism or reaction pathway for this catalyst at this specific value of the space time. The nanoparticle supported catalysts show superior performance over the reference catalyst at high space times in that they can achieve
increased methanol conversions without undergoing the jump in CO selectivity that is evident in the reference catalyst. In fact at a conversion of 65% (T=280°C), the CO selectivity of all catalysts in this study are below that of the commercial catalyst (Table 2-1). The CO selectivity curves clearly display a zero intercept with decreasing space time. This has been taken as an indication that CO is a secondary product in several articles [9,10].

![Figure 2-4. CO selectivity, CO/(CO₂+CO) as a function of space time at T=283°C.](image)

**Figure 2-4.** CO selectivity, CO/(CO₂+CO) as a function of space time at T=283°C. □: catalyst 5/5/90, ⋄: catalyst 35/35/30, ▲: catalyst 42/47/11, ◇: reference catalyst.

### 2.3.3 “Blank” Experiments.

The 5/5/90 catalyst produced CH₂O during the reforming reaction. No other catalyst showed detectable levels of CH₂O at any temperature. The fact that CH₂O is produced over the nanoparticle catalyst that contained 90% Al₂O₃ but not over the 30% or 11% Al₂O₃ catalysts suggests that the formation of CH₂O is a consequence of the high Al₂O₃ concentration. This was confirmed by performing a steam reforming experiment over bare nanoparticle alumina. The nanoparticle alumina produced relatively high levels of CH₂O, but the levels of CO and CO₂ were similar to those observed for the homogeneous reaction, i.e. a “blank” steam reforming.
experiment with no support or catalyst in the reactor (see Figure 2-1). Furthermore, the CH₂O produced over the nanoparticle alumina was higher than over the 5/5/90 catalyst, which is likely an effect of a lower alumina surface area on the 5/5/90 catalyst due to coverage of the alumina by copper and zinc oxide. These results indicate that Al₂O₃ is active in CH₂O production, but not in reactions 1-1 to 1-3. Other researchers have also reported formation of CH₂O from CH₃OH on SiO₂/Al₂O₃ supports [58].

Of the catalysts in this study, the 35/35/30 catalyst demonstrated the greatest thermal stability. The 35/35/30 catalyst is more stable and does not suffer from the same degree of deactivation with temperature as the commercial reference and the 42/47/11 catalysts. The low CO selectivity coupled with the high durability of the catalyst means that high CH₃OH conversions can be achieved while generating lower amounts of CO than would be possible with a commercially available catalyst.

2.4 Catalyst Characterization Results.

2.4.1 Surface Area Analysis

The BET surface areas before and after reaction, active copper surface areas, and turnover frequencies of the catalysts in this study are shown in Table 2-2. Evidently, the samples higher in alumina have a larger surface area. The nanoparticle supported catalysts rely almost entirely on the Al₂O₃ for the surface area of the catalyst. Therefore, when the concentration of Al₂O₃ is small in the sample, the surface area is relatively low. The reference catalyst has a larger surface area compared with the nanoparticle supported catalyst of the same composition. For the 5/5/90 and 35/35/30 nanoparticle supported catalysts the surface areas of the spent catalysts are notably lower than those of the fresh catalyst samples. It is interesting to note that as the copper and zinc content increases the difference in surface area before and after exposure to the reaction
conditions decreases. The surface area for the 42/47/11 catalyst is nearly unaffected by the reaction.

Table 2-2. Surface characteristics of reforming catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nominal CuO concentration [weight %]</th>
<th>Cu surface area [m²/g Cu]</th>
<th>Dispersion [%]</th>
<th>Fresh BET surface area [m²/g]</th>
<th>Spent BET surface area [m²/g]</th>
<th>Density [g/cm³]</th>
<th>TOF at 280°C [10³·sec⁻¹]¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>42</td>
<td>20.2</td>
<td>3.1</td>
<td>68</td>
<td>82</td>
<td>5.2</td>
<td>34.6</td>
</tr>
<tr>
<td>42/47/11</td>
<td>42</td>
<td>3.5</td>
<td>0.5</td>
<td>23</td>
<td>24</td>
<td>5.8</td>
<td>160.1</td>
</tr>
<tr>
<td>35/35/30</td>
<td>35</td>
<td>5.3</td>
<td>0.8</td>
<td>46</td>
<td>40</td>
<td>5.0</td>
<td>128.8</td>
</tr>
<tr>
<td>5/5/90</td>
<td>5</td>
<td>56.2</td>
<td>8.6</td>
<td>218</td>
<td>170</td>
<td>3.5</td>
<td>59.4</td>
</tr>
</tbody>
</table>

¹ TOF = Turnover frequency, defined as the molecules of hydrogen produced per surface copper atom per second.

The decrease in surface area of the 5/5/90 catalysts after exposure to reaction conditions most likely corresponds to a sintering effect that causes some of the pores in the alumina support to be clogged due to particle growth of the copper. The loss of surface area is not due to the sintering of the alumina itself, given that there is no significant change in the Al₂O₃ particle size on this sample before and after the reaction (see XRD section, below). In contrast, on the reference catalyst, it appears that there is a slight increase in surface area after reaction. This effect was unique to the reference catalyst. Despite the fact that the reference catalyst did not lose surface area during the reaction, there was strong deactivation of this sample at elevated temperatures. Consequently, there is no correlation between the overall surface area and the catalytic activity for these catalysts.

The results of the N₂O titrations data provide a quantitative view of the differences in the surface copper concentration of the catalysts. Table 2-2 clearly shows that very high copper surface areas can be attained by using a high concentration of nanoparticle Al₂O₃. The copper
surface area per gram of copper on the 5/5/90 sample is an order of magnitude higher than on the other nanoparticle catalysts, and more than double that of the reference catalyst. In comparing the data in Table 2-2 to the curves in Figure 2-1, another interesting trend is evident. Despite the fact that the copper surface area per gram of the 42/47/11 is a fraction of that in the reference catalysts, the two samples achieve similar maximum conversions. The difference is that the turnover frequency (TOF) of the 42/47/11 catalyst is dramatically higher than that of the reference sample. In fact, all nanoparticle-supported catalysts have higher TOFs than the reference catalyst. The surface copper of the nanoparticle catalysts is clearly more active than the copper on the surface of the reference catalyst. However, the activity does not correlate with the Cu surface area of the catalysts. In fact, the TOF appears to correlate with the nominal CuO concentration rather than the Cu surface area for the nanoparticle catalysts. Alternatively, it can be stated that the TOF decreases linearly with increasing Al₂O₃ content (Table 2). The highest Al₂O₃ concentration (and highest copper surface area) is the 5/5/90 catalyst, which also displays the lowest TOF. The catalyst with the lowest Al₂O₃ concentration (42/47/11) has the highest TOF. Past researchers using copper based methanol reforming catalysts have also noted that “properties other than copper surface area” affect the catalytic activity [14]. Obviously this is the case in the present study as well. It has been proposed that favorable morphology [59], increased reducibility [60], or simply higher “quality” [14] of the copper species in methanol reforming catalysts increases catalytic activity. In the samples used in this study, it is evident that increasing the alumina content of the samples tends to make the surfaces both less reducible and less active in the reforming reaction. This could be due to strong Cu-Al₂O₃ interactions at high Al₂O₃ concentrations, which in turn can alter the electronic properties of the Cu on the surface and also influence the Cu⁺/Cu⁰ ratios on the catalyst surfaces (see below). Hence, the “quality”
of the copper decreases with increasing Al\textsubscript{2}O\textsubscript{3} content despite the increase in Cu surface area, and high Al\textsubscript{2}O\textsubscript{3} concentrations ultimately result in a less active catalyst.

2.4.2 X-ray Diffraction Analysis

XRD spectra obtained from the fresh catalysts are shown in Figure 2-5.

![XRD spectra](image)

Figure 2-5. XRD spectra obtained from fresh catalysts: a) 5:5:90 CuO-ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst, b) 35:35:30 CuO-ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst and c) 42:47:11 CuO-ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst. +: γ-Al\textsubscript{2}O\textsubscript{3}, ∗: CuO, o: ZnO. Arrows indicate peaks due to ZnAl\textsubscript{2}O\textsubscript{4}.

The characteristic peaks of CuO are evident in all the spectra obtained from the fresh catalyst samples and a crystalline ZnO phase is present on the 35/35/30 and 42/47/11 catalysts, but not on the 5/5/90 catalyst. On the 5/5/90 the ZnO is below the detection limit or is present in amorphous form. No peaks due to alumina can be detected in the XRD spectrum obtained from the 35/35/30 or 42/47/11 catalysts. This is not surprising due to the low crystallinity and the lower alumina concentration of the catalysts compared to the 5/5/90 catalyst. There are small broad peaks visible in the spectrum of the 35/35/30 catalyst at 2θ = 31.3°, 37.1°, 44.6°, 55.6°, 59.2°, 65.1° which are not due to CuO or ZnO. The 2θ values of the peaks are consistent with...
those obtained from aluminate species such as CuAl$_2$O$_4$ [61] or ZnAl$_2$O$_4$ [62]. Since both the CuAl$_2$O$_4$ and ZnAl$_2$O$_4$ have nearly identical diffraction patterns is it difficult to distinguish between the two in the XRD spectrum obtained from the 35/35/30 catalyst [23,61,62]. An experiment was therefore designed to determine the type of aluminate formed during the catalyst preparation procedures used in our study. Two sample catalysts composed of ZnO-Al$_2$O$_3$ and CuO-Al$_2$O$_3$ were prepared using the catalyst preparation method described above, keeping the CuO:Al$_2$O$_3$ and ZnO:Al$_2$O$_3$ ratio the same as in the 35/35/30 catalyst (i.e. at 1.17 by mass), and characterized with XRD measurements. The presence of an aluminate phase was visible with XRD only in the ZnO-Al$_2$O$_3$ sample (not shown). This result suggests that the aluminate phase seen in the XRD spectra obtained from the 35/35/30 catalysts is ZnAl$_2$O$_4$ and not CuAl$_2$O$_4$ as has been assigned in the past [21]. However, due to the presence of copper in addition to zinc on these catalysts, the presence of CuAl$_2$O$_4$ cannot be ruled out completely. Our assignment of a ZnAl$_2$O$_4$ phase agrees with those made by Turco and coworkers [11].

Table 2-3 shows average crystal sizes of all species visible in the XRD spectra calculated using equation 1-15. The sizes of the CuO particles are slightly smaller on catalyst 42/47/11 (27 nm) compared with catalyst 35/35/30 (34 nm), despite the higher CuO concentration of the 42/47/11 catalyst. This contradicts the lower dispersion observed on the 42/47/11 catalyst (smaller particle sizes give larger surface areas and higher dispersions), and is likely due to more ZnO covering the CuO on catalyst 42/47/11 compared with catalyst 35/35/30. This may be expected due to the higher ZnO content on catalyst 42/47/11 and, the ZnO particle sizes are also considerably larger on catalyst 42/47/11 (58 nm) compared with those on catalyst 35/35/30 (32 nm). It is interesting to note that no CuAl$_2$O$_4$ or ZnAl$_2$O$_4$ can be detected on the 42/47/11 catalyst. Consequently, if present, the aluminates are either amorphous or below the detection
limit of the XRD instrument. Another interesting observation is that the particle sizes of the aluminate species are smaller than for the CuO and ZnO species. The Scherrer equation gives a value of 8 nm for the aluminate. The same behavior of the aluminate phase was observed in the study by Murcia-Mascarós et al. [21]. The small particle size observed is likely due to the strong metal-support interactions that result in formation of this compound.

Table 2-3. Particle sizes of the different compounds on the various CuO-ZnO/Al₂O₃ catalysts in the current work. The particle sizes have been determined from the XRD data using the Scherrer equation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Species</th>
<th>Cu</th>
<th>CuO</th>
<th>ZnO</th>
<th>ZnAl₂O₄</th>
<th>Cu₂O</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:5:90 Cu/ZnO/Al₂O₃ Fresh</td>
<td></td>
<td>--</td>
<td>13.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.5</td>
</tr>
<tr>
<td>5:5:90 Cu/ZnO/Al₂O₃ Spent</td>
<td></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>7.3</td>
<td>4.7</td>
</tr>
<tr>
<td>35:35:30 CuZnO/Al₂O₃ Fresh</td>
<td></td>
<td>--</td>
<td>33.6</td>
<td>32.1</td>
<td>7.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>35:35:30 CuZnO/Al₂O₃ Spent</td>
<td></td>
<td>35</td>
<td>--</td>
<td>33.4</td>
<td>6.9</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>42:47:11 Cu/ZnO/Al₂O₃ Fresh</td>
<td></td>
<td>--</td>
<td>26.9</td>
<td>57.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>42:47:11 Cu/ZnO/Al₂O₃ Spent</td>
<td></td>
<td>22.5</td>
<td>--</td>
<td>34.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

After reduction treatment and exposure to the reaction conditions no crystalline CuO is present on any of the catalysts (Figures 2-6A and B). The XRD spectra obtained from all catalysts exhibit features due to Cu metal after these treatments. In fact, the spectra obtained from the 35/35/30 and 42/47/11 catalysts after reductive treatment (not shown) are indistinguishable from those obtained after exposure to the reactions conditions. In addition to the peaks due to Cu metal, the XRD spectrum obtained from the spent 5/5/90 catalyst also exhibits peaks located at \( \theta = 36.8^\circ, 42.5^\circ, 61.7^\circ \) and \( 73.9^\circ \). These peak positions are consistent with Cu₂O [63]. The fact that the Cu₂O species can be detected with XRD is remarkable, since Cu₂O has only been detected previously using XRD on catalysts with significantly higher copper.
contents [27,43]. Furthermore, in those cases it appears that the ZrO$_2$ used as the support stabilizes the Cu$_2$O [27,43], and such support stabilization of Cu$_2$O is unlikely on Al$_2$O$_3$. Figure 2-6B shows that only Cu metal is present on the 5/5/90 catalyst after the reductive treatment. This unequivocally demonstrates that the Cu$_2$O is formed during the reforming reaction and is not a result of either the brief air exposure before analysis or incomplete reduction during the pretreatment. To our knowledge, Cu$_2$O has never been observed on Al$_2$O$_3$-supported spent reforming catalysts. This result also indicates that increasing the concentration of nanoparticle Al$_2$O$_3$ alters the redox properties of the surface (as indicated above), which in turn affects the surface activity. The Al$_2$O$_3$ makes the surface more difficult to reduce (see below), which apparently translates to a decrease in turnover frequency, as seen in the previous section.

The reduction treatment and exposure to the reaction conditions does not appear to affect the Al$_2$O$_3$ particle size on the 5/5/90 catalyst (see Table 2-3). The particle sizes of the Cu metal on the spent 35/35/30 catalyst are similar to those of the CuO particles on the fresh catalyst (~33 nm). This suggests that there is some sintering of the copper during the reduction (or reaction) [i.e. there are more Cu atoms per particle after reduction and reaction]. On catalyst 42/47/11 the Cu metal particles are slightly smaller (23 nm) than the CuO particles on the fresh catalyst (27 nm). Although some sintering is expected, this indicates that the sintering of copper is more severe on the 35/35/30 catalyst compared with the 42/47/11 catalyst. The ZnO appears to be unaltered after reduction and reaction on the 35/35/30 catalyst, while on the 42/47/11 catalyst they appear to be smaller after reduction and reaction (35 nm) compared to the fresh 42/47/11 catalyst (58 nm). The particle size of ZnAl$_2$O$_4$ on the 35/35/30 catalyst is not altered significantly, as expected. Other research groups have also noted that aluminates can be very difficult to reduce [31,32,64]. Even at elevated temperatures and under vacuum, a CuAl$_2$O$_4$
spinel phase is fairly stable and will not readily reduce to Cu and Al₂O₃ [64]. Hence, it is not surprising that under the reduction treatment and the reaction conditions of these experiments the ZnAl₂O₄ spinel phase is also rather stable.

Figure 2-6A

Figure 2-6B

Figure 2-6. XRD spectra obtained spent catalysts. A: a) spent 5:5:90 CuO-ZnO/Al₂O₃ catalyst, b) spent 35:35:30 Cu-ZnO/Al₂O₃ catalyst, and c) spent 42:47:11 Cu-ZnO/Al₂O₃ catalyst. B: a) fresh 5:5:90 Cu-ZnO/Al₂O₃ catalyst, b) reduced 5:5:90 Cu-ZnO/Al₂O₃ catalyst, and c) spent 5:5:90 Cu-ZnO/Al₂O₃ catalyst. +: γ-Al₂O₃, *: CuO, o: ZnO, l: Cu metal and ▲: Cu₂O.
Despite the fact that sintering of the Cu metal appears to be the highest on the 35/35/30 sample, this catalyst did not deactivate as rapidly as the 42/47/11 catalyst. Therefore the catalyst deactivation in the activity measurements is not simply due to sintering of copper in the samples (see section 2.4.4).

2.4.3 Temperature Programmed Reduction Measurements

TPR experiments provide further insight into these catalysts. Previous results indicate that the catalytic activity correlates with the reducibility of the copper species on the surface [29]. If this is true, then the commercial catalyst would be the easiest to reduce and the 5/5/90 the most difficult, which is indeed the case. The commercial catalyst starts to reduce below 200°C, which is 30°C lower than the nanoparticle catalysts (Figure 2-7). While reduction of the 5/5/90 catalyst starts at the same temperature as the other nanoparticle catalysts (i.e. 230°C), hydrogen consumption does not end until well above 400°C, long after the other catalysts are fully reduced. The high reduction temperature of the 5/5/90 catalyst is likely a result of the smaller copper particle size on this catalyst (14 nm versus 34 and 27 nm for the 35/35/30 and 42/47/11 catalysts, respectively) and stronger copper-alumina interactions. It has been previously reported that “reduction occurs at higher temperatures, or more reluctantly, as CuO particle size decreases” [65]. The TPR profiles of the 35/35/30 and 42/47/11 catalysts are similar, with reduction beginning at approximately 225°C and ending around 320°C. However, two differences can be observed; 1) the hydrogen consumption of the 35/35/30 catalyst peaks at approximately 265°C, while that of the 42/47/11 catalyst does not reach a maximum until 15°C higher and 2) the reduction for the 35/35/30 catalyst is not completed until 15-20°C higher than that for the 42/47/11 catalyst. Consequently, at high alumina concentrations, the CuO precursor on the nanoparticle catalysts is more difficult to reduce and this results in a less active catalyst,
i.e. the TOF is higher for lower Al₂O₃ concentrations. The observed correlation between catalytic activity (TOF) and ease of CuO reduction on the catalysts is consistent with the literature [29].

Figure 2-7. Normalized Temperature Programmed Reduction (TPR) Profiles. a) 5/5/90, b) 35/35/30, c) 42/47/11, and d) reference catalysts.

2.4.4 X-ray Photoelectron Spectroscopy Analysis

XPS measurements were performed to determine how the surface composition and the valence state of the surface copper vary between the different catalysts and between the fresh and spent catalysts. Part of the goal with these measurements is to determine if Cu₂O can be detected on the catalysts after exposure to the reaction conditions.
2.4.4.1 Fresh catalysts

The XPS survey spectra reveal that despite the higher CuO content, the Cu peaks obtained from the 42/47/11 catalyst have lower intensities compared to those obtained from the 35/35/30 catalyst, while the peaks due to ZnO are more intense. This is evident as a higher Cu/Al ratio on catalyst 35/35/30, while the Zn/Al ratio is higher on 42/47/11 (Table 2-4). Consequently, a higher fraction of CuO on the 42/47/11 catalyst is covered with ZnO compared with the 35/35/30 catalyst, which is in agreement with the conclusions from the XRD particle sizes and the Cu surface areas.

Figure 2-8

Figure 2-8. XPS spectra of the Cu 2p binding energy region obtained from catalysts: a) fresh 5:5:90 CuO-ZnO/Al₂O₃, b) spent 5:5:90 Cu-ZnO/Al₂O₃, c) fresh 35:35:30 CuO-ZnO/Al₂O₃ catalyst, d) spent 35:35:30 Cu-ZnO/Al₂O₃ catalyst, e) fresh 42:47:11 CuO-ZnO/Al₂O₃ and f) spent 42:47:11 Cu-ZnO/Al₂O₃. Vertical dashed lines mark the peak positions of the Cu 2p peaks in the current paper and the dotted lines mark the CuO or Cu₂O plus Cu metal peak positions.
Table 2-4. Relative surface concentrations of different elements calculated from the atomic concentrations at the surface. The atomic concentrations are based on the peak areas of the peaks listed in the table with adjustments made for the sensitivity factors of each peak.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>5/5/90</th>
<th>35/35/30</th>
<th>42/47/11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Spent</td>
<td>Fresh</td>
</tr>
<tr>
<td>Zn 2p / Cu 2p</td>
<td>0.6</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>C 1s / Al 2p</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu 2p / Al 2p</td>
<td>0.4</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Zn 2p / Al 2p</td>
<td>0.2</td>
<td>0.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The Cu 2p peaks obtained from the fresh and spent catalysts are shown in Figure 2-8. The presence of a Cu$^{2+}$ species on the fresh catalysts is evident from the intense satellite peak at a binding energy of 940-945 eV in the XPS spectra. The presence of the satellite peak is attributed to the interaction of the ejected photoelectron with another valence band electron, and/or to the metal-to-ligand charge transfer which has been demonstrated to occur in Cu$^{2+}$ [23,66]. Satellite peaks are not present in Cu$^0$ or Cu$^+$ spectra due to the full 3d bands [32,66]. The presence of a Cu$^{2+}$ species is in agreement with the XRD data, which indicates that CuO is the main Cu species before reduction and reaction. After charge corrections (see section 2.3.5) the binding energy of the Cu 2p peaks on the fresh catalysts are centered at 933.6 eV, which is the reported binding energy for CuO [66,67,68,69]. However, the peaks are broad with significant shoulders at 935 eV. This high binding energy may indicate the presence of CuAl$_2$O$_4$. The presence of this compound is further supported by the satellite-to-main peak intensity ratios (0.55-0.58), which are higher than that expected for CuO (0.45) although not as high as that expected for CuAl$_2$O$_4$. 

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(1.1). Only catalyst 5/5/90 has a slightly larger ratio (0.65), which indicates that more CuAl₂O₄ is present on this catalyst compared to the 35/35/30 and the 42/47/11 catalysts. This would be expected due to the higher dispersion on this catalyst (a larger degree of Cu-Al₂O₃ interface and thus stronger Cu-Al₂O₃ interactions). However, the main Cu species on all the calcined catalysts is CuO, which agrees with the XRD data.

**2.4.4.2 Spent catalysts**

After reductive treatment and exposure to the reaction conditions, the Zn/Cu ratio increases on all catalysts (Table 2-4). This indicates that after reaction more ZnO covers the active Cu phase compared to before the reaction. This explains at least part of the catalyst deactivation since the active Cu surface area is reduced. In contrast, the C/Al ratio is relatively constant before and after reaction on all catalysts. The absence of carbon build-up at the surface suggests that coking is not a deactivation pathway on these catalysts. After exposure to the reaction conditions the binding energy of the Cu 2p₃/₂ peak is shifted to a lower value revealing reduction of the CuO. The peaks are also narrower after exposure to the reaction conditions as is expected from reduction of CuO to Cu₂O or Cu metal. The binding energies of the spent catalysts (after charge correction) are located at 932.4 eV, which is in agreement with Cu₂O and Cu metal [70]. However, the peaks are broader than what would be expected for pure Cu₂O or pure Cu metal, which again suggests that more than one Cu species are present on the surface. The absence of satellites in the spectra obtained from the spent catalysts indicates that no significant quantity of Cu²⁺ species is left on the surface. This supports our assignment of a ZnAl₂O₄ phase on the 35/35/30 catalyst, although it does not exclude presence of CuAl₂O₄ in the bulk of the catalyst.

Differentiating between the Cu⁺ and Cu⁰ valence states of copper compounds using the Cu 2p peaks is rather challenging due to the relatively large Cu radius and thus electronic binding
energies are separated by only a small fraction of an eV [32,66,67,68,69, 74]. Therefore, in order to determine the valence state of the Cu on the surface, the kinetic energy of the ejected Auger electrons was examined (Figure 2-9) [69]. This energy does not depend on either the Cu 2p_{3/2} electronic binding energy or the energy of the incident radiation [71,74]. The Auger electron energy of Cu metal (918.6 eV) is higher than that of CuO (917.9 eV), while the Auger electron energy of Cu_{2}O is lower (916.7 eV). The signal to noise of the Auger electron energy region in the spectrum obtained from the fresh 5/5/90 catalyst is low and only a small feature at 916.2 eV can be observed. Although this electron energy would suggest the presence of CuAl_{2}O_{4} (electron energy 916.8 eV) rather than CuO (917.9 eV), it is known from the Cu 2p peaks that CuAl_{2}O_{4} is not the major species on the surface. Consequently, the low electron energy observed could be due to charging. In contrast, both the fresh 35/35/30 and 42/47/11 catalysts exhibit pronounced Auger features at 918.1 eV, which is the electron energy expected for CuO. After reduction and exposure to the reaction conditions, the Auger features shift to lower electron energies in all cases. This is indicative of Cu_{2}O formation rather than Cu metal formation. Consequently, the Cu metal on the reduced catalysts is oxidized to Cu_{2}O by steam during the reaction. However, the Auger peak is broad and the presence of Cu^{0} in the near surface region cannot be excluded, but the dominant species at the surface is not Cu metal.

It is possible that both Cu metal and Cu_{2}O are required for an active catalyst and that the specific Cu^{+}/Cu^{0} ratio determines the catalytic activity. For example, an oxygen-deficient surface is required for H_{2}O dissociation and formation of H_{2}, while an oxidized surface is necessary for methanol dissociation and oxidation [11,75]. This could explain why the activities are not a simple function of the Cu metal surface areas. Furthermore, it is also known that CO
binds strongly on Cu\(^+\), while it is adsorbed only weakly on metallic Cu \([11]\). Consequently, in the presence of Cu\(_2\)O the CO species will have time to react to CO\(_2\) (assuming sufficient oxygen present on the surface), while on a more reduced Cu surface the CO is not bound as strongly and can desorb before reacting. It has in fact been observed that the CO concentrations increase with increasing extent of reduction on the surface of Cu-based methanol reforming catalysts \([20]\).

The above could explain the trend in CO selectivity with temperature between 220 and 300°C.

The extent of Cu\(^0\) oxidation to Cu\(^+\) by the steam is likely to increase with the temperature in this

![Figure 2-9](image_url)

**Figure 2-9.** XPS spectra of the Cu Auger kinetic energy region obtained from catalysts: a) fresh 5:5:90 CuO-ZnO/Al\(_2\)O\(_3\), b) spent 5:5:90 Cu-ZnO/Al\(_2\)O\(_3\), c) fresh 35:35:30 CuO-ZnO/Al\(_2\)O\(_3\) catalyst, d) spent 35:35:30 Cu-ZnO/Al\(_2\)O\(_3\) catalyst, e) fresh 42:47:11 CuO-ZnO/Al\(_2\)O\(_3\) and f) spent 42:47:11 Cu-ZnO/Al\(_2\)O\(_3\). The dashed line marks the CuO peak position, the dotted line marks the Cu metal peak position and the dash-dotted line marks the Cu\(_2\)O peak position.
range, which would be expected to increase the CO₂ over the CO product. At elevated temperatures the oxidation of Cu to Cu₂O by steam is negated by the reductive properties of methanol that is reacting over the catalyst. Consequently, at higher temperatures the surface is likely in a more reduced state (lower Cu⁺/Cu⁰ ratio) and the CO selectivity increases with temperature above 300°C for all catalysts.

The Zn 2p, Al 2p and O 1s binding energy regions were also examined for all catalysts before and after reaction (not shown). However, these regions do not vary significantly between the catalysts and do not provide new information about the catalyst surface. For example, the Zn 2p peaks in ZnO and ZnAl₂O₄ are located at 1021.8 and 1021.7 eV, respectively and thus the XPS data alone cannot be used to differentiate between the two species [70]. The O 1s peaks are also not informative due to the presence of overlapping species. The O 1s peaks obtained from the 5/5/90 catalysts are dominated by the contribution from Al₂O₃ at 531.5 eV. The other catalysts 35/35/30 and 42/47/11 exhibit broad O 1s peaks due to Al₂O₃, CuO at 529.8 eV, Cu₂O and ZnO at 530.5 eV and potentially also CuAl₂O₄ at 530.8 eV or ZnAl₂O₄ at 531.4 eV.

In summary, all nano-alumina-supported catalysts contain Cu₂O at the surface after exposure to the reaction conditions. While some Cu⁺ likely is required for a high catalytic activity, it is possible that over-oxidation, i.e. formation of CuO or bulk Cu₂O, decreases the catalytic activity. This could explain the lower activity observed for the 5/5/90 catalyst. However, the strong Cu-Al₂O₃ interactions on the 5/5/90 also appear to result in formation of more inactive CuAl₂O₄, as well as a more difficult to reduce Cu₂O phase, compared to the other catalysts and may be the main reasons for the lower TOF observed for this catalyst.
2.5 Thermodynamic Calculations

The results in this study reveal that for the nanoparticle-supported catalysts the CO selectivity does not increase with increasing temperatures between 220°C and 300°C. The fact that the CO selectivity is not increasing over this temperature range indicates that neither the reverse water gas shift nor the methanol decomposition reaction rate is increasing faster than the rate of the reforming reaction (CO production is not increasing faster than the CO₂ production rate). To elucidate the source of CO in this study, equilibrium calculations (reverse water-gas-shift reaction) were performed to compare the partial pressure of CO in the reactor effluent to the equilibrium partial pressure of CO for the reverse water-gas-shift reaction. The general procedure is the same as was described in greater detail in Chapter 1. Briefly, the thermodynamic equilibrium constant for the reverse water-gas-shift was calculated according to equation 2-7:

\[
K_{eq}^{rWGS} = \frac{P^{CO} \times P^{H_2O}}{P^{CO_2} \times P^{H_2}} = \exp\left(\frac{-\Delta G^{rWGS}}{R \times T}\right)
\]

In this equation, \(P^{CO}, P^{CO_2}, P^{H_2}, \) and \(P^{H_2O}\) are the partial pressures of the components exiting the reactor. \(\Delta G^{rWGS}\) is the free energy change associated with the reverse water-gas-shift reaction, \(R\) is the ideal gas constant and \(T\) is the temperature in Kelvin. In this way the exiting concentrations of the reaction products can be compared with the thermodynamic equilibrium of the reverse water-gas-shift. The results for the 35/35/30 catalyst are typical of the catalysts in this study and are shown in Figure 2-10. Error bars indicate that even if there is 25% error in the measured gas pressures the conclusion that the CO concentrations are above levels which can be explained by the water-gas-shift equilibrium is still valid.
Figure 2-10. Comparison of Keq rWGS and ratio of measured partial pressures. $K_{eq}^{rWGS}$ and $P_{CO} \cdot P[H_2] / P[H_2O] \cdot P[CO_2]$ over the 35/35/30 catalyst. Reaction conditions are the same as for Figure 1.

At all temperatures the partial pressure of CO in the reactor effluent is higher than the equilibrium CO partial pressure of the water-gas-shift reaction. Below 300°C, the CO partial pressure approaches (decreases towards) the equilibrium value, but then sharply increases away from equilibrium above 300°C. CO levels higher than those attainable via the water-gas-shift equilibrium indicate that the source of the CO is not solely the reverse water-gas-shift reaction. CO production at these levels must occur via the decomposition reaction. This is reasonable particularly at higher temperatures given that the activation energy of the decomposition reaction is 170 kJ/mol [8] compared to 108 kJ/mol [10] for the reverse water-gas-shift. However, it appears that for the nanoparticle catalysts in this study, the decomposition reaction also must be taken into account at lower temperatures (and lower conversions) in agreement with the studies by Peppley and coworkers [7,8], Choi and Stenger [49] and Mastalir et al. [4].
2.6 Conclusions

The above results demonstrate that nanoparticle alumina can be used effectively as support in the preparation of highly active Cu-ZnO steam reforming catalysts. Very high copper surface areas can be attained on nanoparticle alumina and activities similar to those of commercial catalysts with much high copper contents can also be achieved. However, the activities of the catalysts do not scale with the copper surface area and high Al$_2$O$_3$ concentrations tend to retard the surface activity. Strong metal-support interactions between the small copper particles and the nanoparticle Al$_2$O$_3$ support on catalysts with high Cu dispersions, such as the 5/5/90 catalyst, appear to have a dramatic influence on the redox properties of the catalyst. The change in redox properties likewise appears to affect the methanol conversion, with less reducible nanoparticle catalysts having lower conversions. High Al$_2$O$_3$ concentrations also promote production of an undesired formaldehyde byproduct.

The results in this study demonstrate that novel catalysts prepared using nanoparticle alumina have the advantage of lower CO selectivities compared to a commercially available low temperature shift catalyst. In fact, below reaction temperatures of 300°C (260°C for the 42/47/11 catalyst) the CO selectivity over the nanoparticle catalysts decreases with increasing temperature. This is unexpected and observed only for the nanoparticle based catalysts, and must thus be due to changes in the surface composition of the nanoparticle systems, such as the Cu$^+$ to Cu$^0$ ratio, over this temperature range. It was also shown that use of a nanoparticle support results in a more active copper surface (evidenced by higher turnover frequencies) compared to a commercially available reference catalyst.

XRD reveals that Cu metal is present in the bulk of all the spent catalysts and XPS indicate that Cu$_2$O and perhaps a small amount of CuAl$_2$O$_4$ are present at the surface. Only on the 5/5/90
could the Cu$_2$O phase be detected with XRD. There is also evidence of a ZnAl$_2$O$_4$ spinel phase in the bulk of the 35/35/30 catalyst. The high stability of the 35/35/30 catalyst is likely due to a beneficial interaction between the zinc-aluminate species and the Cu species on the catalyst. Although it could also be due to the fact that there is less ZnO available that can migrate and cover the active Cu phase.

Permanent catalyst deactivation is likely due to ZnO covering part of the active Cu phase, although loss of activity, and increasing CO selectivities, at higher temperature may also be due to decreasing Cu$^+$/Cu$^0$ ratios.

The CO production levels are above what can be explained from the water-gas-shift equilibrium for the nanoparticle catalysts at all temperatures. This indicates that the methanol decomposition reaction is partly responsible for CO production. The results in this study suggest that it is the nature of the interaction between the copper and promoter or support, and not simply the copper surface area, which determines the catalytic activity. Our findings can be summarized as responses to the questions posed in the introduction:

1) Al$_2$O$_3$ is a retardant in the reforming reaction, but it is possible to make high performance reforming catalysts with copper and zinc oxides precipitated onto nanoparticle Al$_2$O$_3$ as long as the Al$_2$O$_3$ concentration is relatively low.

2) The apparent advantage to using nanoparticle precursor materials in reforming catalyst synthesis is that the surfaces of the nanoparticle catalysts are dramatically more active than more traditionally prepared reforming catalysts.

3) Methanol decomposition plays a role in the steam reforming reaction network over the nanoparticle catalysts.

4) The surface and structural characteristics of the nanoparticle-supported catalysts differ from those reported in the literature. More specifically, a high concentration of nanoparticle Al$_2$O$_3$ prevents CuO oxidation to Cu, instead resulting in Cu$_2$O formation in the 5/5/90 catalyst. This apparently decreases the activity of the surface in the reforming reaction.
The fact that Al₂O₃ was found to retard catalytic activity but that nanomaterials were useful in making highly active reforming catalysts was the basis for exploring alternative nanoparticle supports. This work is covered in the following chapter.

2.7 Acknowledgements.

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We also thank Dr. Gar Hoflund for letting us use his XPS system and Dr. Michael Everett for technical assistance with the XPS measurements.
CHAPTER 3
INCORPORATION OF REDUCIBLE OXIDES: STEAM REFORMING OF METHANOL OVER CeO2- AND ZrO2-PROMOTED Cu-ZnO CATALYSTS SUPPORTED ON NANOPARTICLE Al2O3

3.1 Introduction and Literature Review.

After investigating the effects of adding nanoparticle Al2O3 to the reforming catalyst matrix, the next study in this body of research was to investigate the effects of incorporating “reducible” oxides into the catalyst support. It has been shown in the preceding chapter that only small amounts of Al2O3 can be used in reforming catalysts, since higher concentrations can have a negative effect on the catalytic activity [16,76]. Due to the negative effects of Al2O3 supports in methanol reforming catalysts, the trend in recent years is to add another oxide to the Cu/ZnO/Al2O3 catalysts or simply use supports other than alumina. Reducible metal oxides, such as ZrO2 and CeO2, appear to be attractive alternatives or additions to Al2O3 [4,14,18, 27, 28,29,43,56,60,77,78,79,80,81]. For example, ZrO2 addition to Cu-based alumina-supported catalysts has been shown to increase methanol conversion and reduce CO yields [14,18,56,80]. The effects of ZrO2 on Cu-based catalysts appear to be similar to the effects of ZnO in that ZrO2 improves Cu dispersion and leads to more reducible catalysts [14,29,56,80]. However, it has been noted that the metal-support interactions in Cu/ZrO2 are different than in the more conventional Cu/ZnO catalysts [26]. The higher activity of Cu-ZrO2 catalysts has also been attributed to the stabilization of Cu2O on the surface of the reduced catalysts or during the reaction [14,27,43]. It is believed that the formation of Cu2O can lead to more active and also more durable catalysts, since Cu2O is less susceptible to sintering compared with Cu metal [27,43]. Cu+ species have also been observed in CeO2-containing Cu catalysts [77,82]. Addition of CeO2 to Cu/Al2O3 catalysts has also been shown to increase methanol conversion, decrease CO selectivity and increase catalyst stability [80].
Comparing results between reforming catalyst studies referenced above is challenging since the reaction evidently is very sensitive to the catalysts used and large differences in Cu loadings and catalyst compositions have been reported. For example, the copper concentrations on these types of catalysts have been varied from a few percent in some publications [77,81] up to 70% or above in others [29]. Some catalysts also contain ZnO and Al$_2$O$_3$ in addition to Cu and ZrO$_2$ [14,18,29,56]. Therefore, when comparing different methanol steam reforming catalysts it is important to include reference catalysts for comparisons. In order to further facilitate the comparison of results between this chapter and the previous chapter, the same Sud Chemie catalyst will be used as the reference catalyst.

Previous results from Chapter 2 have shown that using nanoparticle alumina as the support for Cu-ZnO-based methanol steam reforming catalysts leads to catalysts with lower CO selectivity and similar conversions compared to commercially available catalysts. The objective in the study presented in this chapter is to investigate if the catalytic activity (methanol conversion) and the CO selectivity of the nano-Al$_2$O$_3$-supported catalysts can be further improved by the addition of CeO$_2$ or ZrO$_2$. Another goal is to determine if the specific ZrO$_2$ precursor used (nitrate or nanoparticles) and the preparation method (co-impregnation and sequential impregnation) will affect the catalytic activity and the CO$_2$ (or CO) selectivity. Furthermore, the CO levels in the reactor effluent will be compared to the equilibrium CO concentrations from the water gas shift reaction to elucidate the most likely production pathway for CO (i.e. methanol decomposition or the reverse water-gas-shift). This procedure will also allow a simple comparison to the CO levels from the catalysts examined in Chapter 2. As Amphlette et al. [33] and Ritzkopf et al. [44] stated in their respective papers, the equilibrium conversion in the methanol reforming reaction is well over 95%, although conversions that high
can be difficult to attain in practice. Therefore, “clearly the thermodynamics offer the incentive for developing better catalysts” [33]. The search for better catalysts is continued here using nanoparticle reducible oxide supports.

3.2 Experimental Methods.

As in Chapter 2, the catalyst preparation technique used to fabricate the catalyst samples used in this study is unique to the data presented in Chapters 3 and 4. Also, details of the reactor operation are included for the reader’s reference. TPR, N₂O titrations, and XRD measurements and catalyst pretreatment were performed precisely as described in Chapter 1.

3.2.1 Catalyst Preparation.

Catalysts in this study are named according to the concentration of the active metal precursor, promoter, and support as a mass percentage. The concentrations of CuO and ZnO are kept constant at 14-15%. These concentrations were selected after careful consideration of optimum literature values [29,77,78]. In addition to the ZnO and CuO phases, either ZrO₂ or CeO₂ were used as promoter or support and the remainder of the material is nanoparticle Al₂O₃. The catalyst labels list the species present in the catalyst and the concentration of either ZrO₂ or CeO₂, as well as the preparation method employed. For instance, the CuZnZrAl-10-CI sample consists of 15% CuO, 15% ZnO, and 10% ZrO₂ by mass, with the balance (60 %) being Al₂O₃. The label CI indicates that the Cu, Zn, and Zr precursors were co-impregnated on the nanoparticle Al₂O₃, or Cu and Zn were co-impregnated on nanoparticle ZrO₂ or a mixture of nanoparticle ZrO₂ and nanoparticle Al₂O₃. All catalysts contain nanoparticle Al₂O₃ except the CuZnZr-70-NP, which is 15% CuO, 15% ZnO, and 70% nanoparticle ZrO₂ by mass. The label NP indicated when nanoparticle ZrO₂ is the zirconia precursor (as opposed to ZrO(NO₃)₂·6H₂O). The label “SQ” indicates sequential impregnation where the ZrO₂ was deposited onto the support
first. The CuO and ZnO were then co-impregnated on the ZrO\(_2\)/Al\(_2\)O\(_3\) (see below). This information is summarized in Table 3-1.

Table 3-1. Catalyst Preparation Summary

<table>
<thead>
<tr>
<th>Catalyst Label(^a)</th>
<th>Composition</th>
<th>Preparation</th>
<th>Zr or Ce Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuO</td>
<td>ZnO</td>
<td>ZrO(_2)</td>
</tr>
<tr>
<td>CuZnZrAl-10-CI</td>
<td>15%</td>
<td>15%</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZrO(NO(_3))(_2)·6H(_2)O</td>
</tr>
<tr>
<td>CuZnCeAl-10-CI</td>
<td>15%</td>
<td>15%</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ce(NO(_3))(_2)·6H(_2)O</td>
</tr>
<tr>
<td>CuZnZrAl-36-CI</td>
<td>14%</td>
<td>14%</td>
<td>36%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZrO(NO(_3))(_2)·6H(_2)O</td>
</tr>
<tr>
<td>CuZnZrAl-10-NP</td>
<td>15%</td>
<td>15%</td>
<td>10%</td>
</tr>
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<td></td>
<td></td>
<td>ZrO(NO(_3))(_2)·6H(_2)O</td>
</tr>
</tbody>
</table>

\(^a\) Catalyst labels are based on the composition of CuO, ZnO, ZrO\(_2\) (or CeO\(_2\)) and Al\(_2\)O\(_3\) by weight. The CuO and ZnO concentrations are kept constant at 15% (or 14%). The concentration of ZrO\(_2\) or CeO\(_2\) is given in the label and the balance is Al\(_2\)O\(_3\). The last part of the label indicates the preparation method, CI for co-impregnation, NP for co-impregnation on nanoparticle ZrO\(_2\) and SQ for sequential impregnation.

All catalysts in this study were prepared via some variation of wet impregnation, either concurrently or sequentially. The catalysts CuZnZrAl-10-CI and CuZnCeAl-10-CI were prepared by dissolving (in proper amounts) Zn(NO\(_3\))\(_2\)·6H\(_2\)O (Alfa Aesar), Cu(NO\(_3\))\(_2\)·6H\(_2\)O (Alfa Aesar), and ZrO(NO\(_3\))\(_2\)·6H\(_2\)O or Ce(NO\(_3\))\(_2\)·6H\(_2\)O in 50 ml of deionized water. The nanoparticle Al\(_2\)O\(_3\) (NanoScale, surface area ~650 m\(^2\)/g) was then dispersed in the solution, the excess water boiled off and the resulting paste dried at 105°C overnight. The dried sample was calcined at 300°C for 3 hours.
The catalyst CuZnZrAl-10-NP was prepared in a similar manner except that the zirconia was added as nanoparticle ZrO\textsubscript{2} powder (Nanostructured and Amorphous Materials) along with the nanoparticle Al\textsubscript{2}O\textsubscript{3} to the aqueous solution (50 ml) of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and Cu(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O (Alfa Aesar). The water was evaporated and the resultant mixture was then dried and calcined in the same manner described above.

The catalyst CuZnZr-70-NP was prepared as described above except that only ZrO\textsubscript{2} nanoparticles were dispersed in the aqueous solution of Cu and Zn nitrates and no Al\textsubscript{2}O\textsubscript{3} was used in this catalyst formulation. After impregnation of the ZrO\textsubscript{2} nanopowder the resulting catalyst was dried and calcined as described above.

Finally, the sequentially precipitated CuZnZrAl-10-SQ was prepared via two sequential impregnations. First, the ZrO(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O was dissolved in 50 ml water and then the Al\textsubscript{2}O\textsubscript{3} nanoparticles were dispersed in the solution. The sample was then boiled down to a paste and dried overnight at 105°C and calcined at 300°C for 3 hours. The calcined support was then ground to a fine powder. The Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and Cu(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O were then dissolved in 50 ml water and the impregnated ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} support was dispersed in the nitrate solution. The sample was again boiled down to a paste, dried and calcined in the same manner as the other samples. All catalysts were prepared in batches of 5 grams total weight after calcination. BET, N\textsubscript{2}O adsorption and temperature programmed reduction were performed on the calcined catalysts without further treatment.

The reference catalyst used in this study is the commercially available Süd-Chemie catalyst that is approximately 42% CuO, 47% ZnO and 11% Al\textsubscript{2}O\textsubscript{3} according to the manufacturer’s specifications. This is the same reference catalyst used in Chapter 2. Other related studies have used a similar reference catalyst [10,49].
3.2.2 Reactor and Gas Chromatograph Operation

Except where otherwise noted, for all catalyst experiments in this chapter the water/methanol ratio was constant at 1.4 volume / volume (~3.1 mol/mol), as was the case in Chapter 2. A water/methanol ratio of 0.6 volume/volume (1.4 mol/mol) was used in two temperature sweeps to demonstrate the insensitivity of the catalyst performance to the water/methanol ration in the feed. The chromatograph used in this study is the same Agilent 6890 series online gas chromatograph described previously. Repetition of data points to ensure reproducibility was done in the same manner described in Chapter 2. The major difference in the operation of the reactor and GC in this study is that no significant levels of CH$_2$O were detected at any temperature or any contact time. In all cases, reproducible results were obtained and there were no signs of catalyst deactivation due to aging with time on stream.

3.2.3 Water Gas Shift Equilibrium

In this chapter the calculated equilibrium data is presented by plotting the ratio $\Phi$ as defined in Equation 3-1. This is a similar procedure to what was outlined in Chapter 1.

$$\Phi = \frac{P_{CO_2} \ P_{H_2}}{K_{WGS} \ P_{CO} \ P_{H_2O}} \quad 3-1$$

In this equation $K_{WGS}$ is the temperature dependent equilibrium constant of the water gas shift reaction, calculated from the activation energy and pre-Arrhenius factor used by Peppley as was done in Chapter 2 [7]. This approach is used instead of the method used in Chapter 2 since in this study there were large fluctuations in the value of $P_{CO}$ that make plotting the pressure ratio shown in Equation 2-7 of Chapter 2 difficult.

Since water is not measured on the gas chromatograph, the water level in the effluent gas is estimated from the CO$_2$ level via the reforming reaction. Specifically, since there is a 1:1 molar
ratio of CO₂ produced to H₂O consumed, the moles of H₂O reacted are assumed to be equal to the (measured) moles of CO₂ produced. This number of moles of water is then subtracted from the (known) inlet concentration of H₂O. The remainder is assumed to be in the effluent. The assumption used here is that the amount of water reacted in the steam reforming reaction is much greater than any water involved in the water gas shift. This is reasonable given the disparity in the levels of CO₂ and CO in the effluent. Confidence levels are presented, and it is evident that even if the water level is off by 50%, the conclusions are not effected. According to the definition of Φ, a value of 1 represents the water-gas-shift reaction equilibrium. If Φ<1 the CO concentration is higher than what can be explained by the water-gas shift equilibrium and is Φ>1 the CO concentration is lower than the equilibrium CO water-gas-shift concentration.

3.3 Catalytic Activity Measurements

3.3.1 Methanol Conversion

Figures 3-1A through 3-1C show the methanol conversion as a function of temperature for all catalysts in Table 3-1. For comparison, the data obtained from the reference catalyst is also included in the figures. It is evident from Figure 3-1A that ZrO₂ is a much better promoter of the catalysts under these conditions compared with CeO₂. The CeO₂-containing catalyst (CuZnCeAl-10-CI) never attains a conversion comparable to the commercial catalyst. In contrast, above a temperature of 280°C the CuZnZrAl-10-CI catalyst exhibits a higher conversion than the reference catalyst. Increasing the ZrO₂ content from 10% to 36% increases the low temperature conversion, but this catalyst experiences deactivation above 265°C. To probe how sensitive the catalysts are to preparation method and ZrO₂ precursor, two additional 10% ZrO₂ catalysts were prepared (CuZnZrAl-10-SQ and CuZnZrAl-10-NP). Consequently, the nominal chemical composition of the CuZnZrAl-10-CI, CuZnZrAl-10-SQ and CuZnZrAl-10-NP
catalysts is the same. The differences are the order of Zr deposition (versus Cu and Zn) and the precursor (ZrO(NO₃)₂·6H₂O versus nanoparticle-ZrO₂), as explained in section 3.2.1. While the performance of the various CuZnZrAl-10 catalysts is similar up to 240°C, the preparation method and the ZrO₂ precursor evidently have a large influence on the catalytic activity above this temperature. The CuZnZrAl-10-NP catalyst exhibits the best performance of all catalysts in this series, and it is the only one to achieve ~80% conversion at the contact time used in the temperature sweep experiments. This conversion is significantly higher than the maximum of 62% obtained from the commercially available reforming catalyst. Only at the lowest temperature (225°C) does the commercial catalyst have a slightly higher conversion than our CuZnZrAl-10-NP catalyst. The CuZnZrAl-10-SQ catalyst exhibits the poorest performance of these three CuZnZrAl-10 catalysts with a maximum methanol conversion of 66%, although this is still higher than the maximum conversion of the commercial reference catalyst. The sequential catalyst is limited by deactivation above 285°C. The CuZnZrAl-10-CI and the CuZnZrAl-10-NP do not deactivate until temperatures above 300°C. A Cu-Zn catalyst supported on nano-particle ZrO₂ was also prepared to determine if presence of alumina is necessary to assure a high catalytic activity. The CuZnZr-70-CI catalyst exhibits the lowest maximum conversion of all catalysts in this study. Only at temperatures where the other catalysts experience significant deactivation, does the CuZnZr-70-NP catalyst have a higher conversion.

In order to probe the sensitivity of the system to the water/methanol ratio in the feed, two catalysts were also tested at a water/methanol feed ratio of 1.4 mol/mol. These results were then compared to the temperature sweep done at a water/methanol molar ratio of 3.1. This data is shown in Figure 3-1C. Evidently these catalysts are not sensitive to the water/methanol feed ratio in this range given there is no major difference in catalyst performance for either the CuZnZrAl-
10-NP or the CuZnZr-70-CI catalyst. This is the only experiment in this chapter which used the lower H₂O/CH₃OH feed ratio.

Figure 3-1. Methanol Conversion as a function of temperature A) for selected catalysts. CuZnZrAl-10-CI, CuZnZrAl-36-CI, CuZnZr-70-NP, CuZnCeAl-10-CI and Commercial Reference. Contact time for all curves is 0.15 kg cat*sec/mmol CH₃OH. B) for additional catalysts. CuZnZrAl-10-CI, CuZnZrAl-10-SQ, CuZnZr-70-NP, CuZnZrAl-10-NP and Commercial Reference. C) at two H₂O/CH₃OH molar feed ratios for two catalysts. CuZnZr-70-NP feed H₂O/CH₃OH=3.1, CuZnZrAl-10-NP feed H₂O/CH₃OH=3.1 and CuZnZr-70-NP feed H₂O/CH₃OH=1.4, CuZnZrAl-10-NP feed H₂O/CH₃OH=1.4.
Figure 3-1. Continued

Figure 3-2 displays the conversion as a function of contact time for selected catalysts, including the commercial reference. Only the most active catalysts with reasonably low CO conversions were subjected to the contact time activity measurements. The only exception to this is the CuZnCeAl-10-CI which was included for comparison. Again, the CuZnZrAl-10-NP catalyst exhibits the best performance of all the catalysts. The other catalysts required considerably longer contact times to reach 100% conversion. As with the conversion data shown in Figure 3-1, the CeO₂ containing catalyst exhibited the lowest activity. In the absence of catalyst deactivation, such as sintering, it is expected that all catalysts in the study will achieve 100% conversion given sufficient contact time.

However, as is well documented in the literature, longer contact times also increase the undesirable CO yields (see section 3.3.2) [4,9,10,28,60]. The CuZnZrAl-10-NP catalyst attains 100% conversion at shorter contact times than required for 100% conversion of the commercial catalyst. The shapes of the curves in Figure 3-2 are also worth noting. The CuZnZrAl-10-NP and CuZnZrAl-10-CI samples both exhibit the classic shape asymptotically approaching a
Figure 3-2. Conversion as a function of contact time for the 10% ZrO₂ catalysts, the 10% CeO₂ catalyst, and the commercial reference catalyst. CuZnZrAl-10-CI, CuZnZrAl-10-SQ, CuZnZrAl-10-NP, CuZnCeAl-10-CI and Commercial Reference. Temperature for all curves was held constant at 280°C.

conversion of 100% with increasing contact times. In contrast, the CuZnZrAl-10-SQ, CuZnCeAl-10-CI and the commercial reference catalysts display a rapid increase in conversion at intermediate contact times. This behavior is generally undesirable since the rapid increase in conversion is also followed by a significant increase in the CO concentration of the effluent gas (see Figure 3-4).

3.3.2 CO Selectivity

The CO selectivity as defined in Chapter 1 is shown in Figure 3-3 for all catalysts as a function of temperature. The CuZnZrAl-10-NP catalyst maintains the lowest CO selectivity of any catalyst in this study over the entire temperature range. This is remarkable considering that it also exhibits the highest conversions at these temperatures. Normally the CO yields increase rapidly with increasing temperature and increasing methanol conversion. Even at the maximum
conversion (305°C), the CuZnZrAl-10-NP catalyst exhibits a CO selectivity (3.6%) that is only slightly higher than the lowest value observed (2.9%) for this catalyst. This CO selectivity corresponds to a CO concentration of 0.6% (dry) in the reactor effluent. Of the other 10% ZrO₂ samples (CuZnZrAl-10-CI and CuZnZrAl-10-SQ), the sequentially impregnated catalyst exhibits a higher CO selectivity than the co-impregnated catalyst although the difference is not significant between 240° and 285°C. The CuZnCeAl-10-CI and CuZnZrAl-10-CI catalysts exhibit similar CO selectivities below 280°C. However, above 280°C there is a discontinuous increase in the CO selectivity for the CuZnCeAl-10-CI catalyst that is not evident in any of the other catalysts. The steep increase in the CO selectivity for this catalyst coincides with the loss of activity as seen in Figure 3-1A. Catalyst CuZnZrAl-36-CI exhibits the highest CO selectivity of the catalysts in the series. In fact, the CO selectivity of this catalyst is higher than the CO selectivities observed on the Cu-ZnO/nano-Al₂O₃ catalysts shown in Chapter 2. Consequently, using an impregnation method to prepare Cu/ZnO/ZrO₂/Al₂O₃ catalysts it is important to use ZrO₂ concentrations below, perhaps well below, 36%. The 70% ZrO₂ catalyst (CuZnZr-70-NP) exhibits a lower CO selectivity than the 36% ZrO₂ sample, but it is still higher than the CO selectivity for the alumina containing samples at temperatures below 250°C. The CO selectivity for this catalyst continues to decrease up to a temperature of 295°C. At this temperature only the 10% nano-ZrO₂ catalyst (CuZnZrAl-10-NP) has a lower CO selectivity. The methanol conversion of the CuZnZr-70-NP catalyst is only 45% at this temperature, which indicates that this catalyst is not a competitive methanol steam reforming catalyst for PEM fuel cell applications.
It is worth noting that the CO selectivity for all nanoparticle catalysts in this study either decreases or stays constant with increasing temperature below approximately 250°C. This is an important observation given that the only CO production routes, the reverse water gas shift and the methanol decomposition reaction, are both endothermic and thus CO production should be both kinetically and thermodynamically favored with increasing temperature. Consequently, the CO selectivity curves demonstrate that the methanol reforming reaction must be increasing at a faster rate than either the decomposition reaction or the reverse water gas shift reaction (or a combination of the two) for all catalysts. A similar phenomenon was observed previously during the nano-Al$_2$O$_3$ supported catalysts in Chapter 2. The temperature at which CO selectivity
begins to increase is not constant for all the catalysts, but appears to be near 250°C. The CuZnZrAl-10-NP catalyst is remarkable in that it does not exhibit a significant increase in CO selectivity until well above 300°C.

Figure 3-4 displays CO selectivity as a function of contact time for the most active catalysts, as well as the CuZnCeAl-10-CI and commercial reference catalyst. In this figure the CO selectivity of the CuZnZrAl-10-SQ catalyst is nearly double that of the other samples at and above contact times of 0.28 mmol/(g·sec). Since the conversion of CuZnZrAl-10-SQ catalyst at this contact time is only 59%, this catalyst is not appropriate for methanol steam reforming reactions where low CO concentrations are critical. The most interesting feature of this figure is the CO selectivity of the CuZnZrAl-10-NP. For this sample the CO production increases only slightly and then remains fairly constant with increasing contact time up to a value of 0.3 kg*sec/mmol. Consequently, the CuZnZrAl-10-NP catalyst is superior to the others in this study in that the conversion is increased significantly, while the CO selectivity remains almost constant.

An interesting hysteresis effect was also recorded in the contact time experiments. It was noted in Chapter 2 that catalysts exposed to temperatures higher than the maximum conversion temperature suffered deactivation and could not achieve previous (i.e. lower temperature) activity levels. A different hysteresis effect was recorded by varying the flow rate (contact time) for the CuZnZrAl-10-NP catalyst. The data for the CuZnZrAl-10-NP catalyst at different contact times is shown in Figure 3-5A and 3-5B. If the contact time sweep is started at longer contact times (lower flow rates)
Figure 3-4. CO selectivity as a function of contact time for the 10% ZrO$_2$ catalysts, the 10% CeO$_2$ catalyst, and the commercial reference catalyst.  

- ○ CuZnZrAl-10-CI, 
- ★ CuZnZrAl-10-SQ, 
- ■ CuZnZrAl-10-NP, 
- × CuZnCeAl-10-CI and 
- □ Commercial Reference.  Temperature for all curves was held constant at 280°C.

and the feed flow rate is increased, the CO selectivity curve does not have a zero intercept as described in Chapter 2 and shown in Figure 3-4. The zero intercept is observed for this catalyst if the contact time sweep is started at the highest flow rate (lowest contact time) and the flow rate is decreased (toward higher contact times). The effect of increasing the feed flow rate and then decreasing it again after exposure to high flow rates is shown in Figure 3-5. There is no apparent difference in CH$_3$OH conversion (Figure 3-5B), but the CO selectivity is affected (Figure 3-5A). Original CO selectivity levels cannot be repeated once the CuZnZrAl-10-NP catalyst has been exposed to the highest feed flow rates. The origin of this phenomenon is not clear, but likely has to do with the oxidation state of the Cu phase, which is covered in detail in the next chapter.
Figure 3-5. A. Conversion and B. CO selectivity as a function of contact time for CuZnZrAl-10-NP catalyst. □ increasing feed flow and ♦ decreasing feed flow. Temperature for all curves was held constant at 280°C.
3.4 Catalyst Characterization Results.

3.4.1 Surface Area Analysis

The BET surface area data, active copper surface area, copper dispersion, and turnover frequency (TOF) at approximately 250°C and 300°C are presented in Table 3-2 for all catalysts. Added to the table are also results for the commercial reference catalyst and the 35/35/30 catalyst from Chapter 2.

Table 3-2. Surface characteristics and activities of steam reforming catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area [m²]</th>
<th>Cu Surface Area [m²/g]</th>
<th>Cu Dispersion [%]</th>
<th>TOF*10³ [s⁻¹] 250°C</th>
<th>TOF*10³ [s⁻¹] 300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZnZrAl-10-CI</td>
<td>48.0</td>
<td>11.3</td>
<td>1.7</td>
<td>175</td>
<td>226</td>
</tr>
<tr>
<td>CuZnZrAl-10-NP</td>
<td>115.4</td>
<td>11.9</td>
<td>1.8</td>
<td>220</td>
<td>244</td>
</tr>
<tr>
<td>CuZnZrAl-10-SQ</td>
<td>119.6</td>
<td>13.8</td>
<td>2.1</td>
<td>134</td>
<td>122</td>
</tr>
<tr>
<td>CuZnZrAl-36-CI</td>
<td>93.4</td>
<td>13.7</td>
<td>2.1</td>
<td>197</td>
<td>177</td>
</tr>
<tr>
<td>CuZnCeAl-10-CI</td>
<td>39.5</td>
<td>14.7</td>
<td>2.3</td>
<td>91</td>
<td>74</td>
</tr>
<tr>
<td>CuZnZr-70-NP</td>
<td>19.0</td>
<td>3.4</td>
<td>0.53</td>
<td>216</td>
<td>342</td>
</tr>
<tr>
<td>CuZnAl-35/35/30-CI</td>
<td>46</td>
<td>5.3</td>
<td>0.8</td>
<td>89</td>
<td>132</td>
</tr>
<tr>
<td>Commercial</td>
<td>68</td>
<td>20.2</td>
<td>3.1</td>
<td>34</td>
<td>28</td>
</tr>
</tbody>
</table>

Evidently there is no correlation between the overall surface area and the Cu surface area of the catalysts, except that the catalyst with the lowest total surface area (CuZnZr-70-NP) also
does have the smallest Cu surface area. As expected, the lowest Cu surface area is observed on
the catalyst which does not contain any high surface area nanoparticle alumina. It is, however,
surprising that the different preparation methods and the varying ZrO$_2$ (or Al$_2$O$_3$) concentrations
do not result in catalysts with a larger variation in Cu surface areas. All ZrO$_2$- or CeO$_2$-
containing catalysts, except the CuZnZr-70-NP, have Cu surface areas in the range between 11
and 15 m$^2$/g. Despite the similar copper surface areas the catalytic activities of the catalysts are
considerably different. There is also no apparent correlation between the Cu surface area and the
catalytic activity on these catalysts. A very interesting observation is that the copper phase on
the nanoparticle ZrO$_2$-supported catalysts is significantly more active than the copper on the
CeO$_2$-promoted catalyst, the catalyst without CeO$_2$ or ZrO$_2$, as well as the catalysts prepared via
impregnation using the zirconium nitrate species. This is particularly evident on the CuZnZr-70-
NP catalyst, which has the lowest Cu surface area of the catalysts under investigation, but it has
the highest TOF observed. Consequently, the Cu on the surface of this catalyst is very active. It
is also evident from Table 3-2 that co-impregnation of the Cu, Zn and Zr precursors results in
more active catalysts than if the Zr precursor is added before the Cu and Zn precursors
(sequential impregnation). It is interesting to note that the catalyst with the highest Cu surface
area, the CuZnCeAl-10-CI catalyst, exhibits the lowest TOF.

The results reveal that the nanoparticle alumina does provide a high surface area on which
to deposit the active metal and promoters, which in turn is necessary to assure a reasonable Cu
surface area. However, addition of ZrO$_2$ (or CeO$_2$) further improves the Cu surface area, as is
evident when comparing the CuZnZrAl-10-series catalysts with the non-ZrO$_2$ containing
CuZnAl-35/35/30-CI catalyst. Perhaps even more importantly, addition of ZrO$_2$ evidently
results in a more active Cu species on the surface. This supports the notion of a “synergy” effect
between the copper phase and the zirconia support, which has been documented by other researchers [29,38].

3.4.2 Temperature Programmed Reduction Measurements

To further probe how the ZrO₂ influence the Cu on the surface, temperature programmed reduction experiments were performed on the prepared catalysts. The reduction profiles of all catalysts are presented in Figure 3-6.

![Temperature programmed reduction profiles for all catalysts in this study. Curves are labeled appropriately in the Figure. Dashed line has been added for visualization and shows a temperature of 300°C. Reduction was performed under 5% H₂ in N₂ at a temperature ramp of 5°C/min.](image)

The TPR data obtained from the commercial reference catalyst has also been added for comparison. It is evident that all ZrO₂- and CeO₂-containing catalysts are reduced at higher temperatures compared to the reference commercial catalyst. This is surprising, since addition of
ZrO₂ and CeO₂ usually results in catalysts that are easier to reduce than their ZrO₂-free analogues [14,18,29,44]. Furthermore, the study on impregnated and precipitated CuO, ZnO, ZrO₂ and Al₂O₃ catalysts done by Breen indicated that catalysts which reduce at lower temperatures were more active methanol steam reforming catalysts [60]. Other authors have indicated similar findings [83]. Evidently, the catalysts in this study do not follow this trend. In fact, the most active catalyst, CuZnZrAl-10-NP, exhibits the highest reduction temperature and a reduction profile consisting of two reduction peaks at 328° and 348°C. The reduction temperatures of the CuZnZrAl-10-SQ (320° and 338°C) and CuZnZrAl-10-CI (324°C) catalysts, which are among the more active catalysts, are also higher than the other catalysts with higher ZrO₂ content. Of the ZrO₂-containing catalysts, the CuZnZr-70-NP exhibits the lowest reduction temperature (273° and 300°C), which could be due to the lack of alumina. As noted previously, this catalyst also has the highest TOF of any sample in this study. Accordingly, the surface of this catalyst is highly active and this agrees with the trend in reduction temperatures noted by Breen [29]. However, the sample is apparently crippled by the low Cu surface area and hence is not an effective catalyst. The CuZnZrAl-36-CI catalyst (316°C) is only slightly more reducible than the CuZnZrAl-10-CI catalyst (324°C) even though it has a significantly higher ZrO₂ content.

It is evident from Figure 3-6 that the method of preparation, i.e. sequential versus co-impregnation, affects the reduction properties of the resulting catalysts. The CuZnZrAl-10-CI and CuZnZrAl-36-CI catalysts, in which the Cu, Zn and Zr precursors are impregnated onto the nano-Al₂O₃ at the same time, are the only ZrO₂-containing catalysts which exhibit a single reduction peak. All the other ZrO₂-containing catalysts exhibit two distinct reduction peaks. While it is possible that the two reduction peaks are due to a step-wise reduction of CuO via
Cu$_2$O to Cu metal [81], another explanation is that the two peaks are due to different types of Cu on the surface [14]. These two copper species could be a highly dispersed copper phase together with larger copper particles [18,29]. In addition, copper supported on monoclinic ZrO$_2$ has been shown to give two reduction peaks due to copper interactions with two different types of oxygen on the ZrO$_2$ surface [84]. It is not easy to explain why the CuZnZrAl-10-NP and CuZnZrAl-10-SQ catalysts would result in a two-step reduction of CuO, while the CuO on the CuZnZrAl-10-CI catalyst would reduce to Cu metal in one step. Therefore, it may be more likely that the two reduction peaks are due to the presence of two different Cu species on the surface. The ZrO$_2$ nanoparticles, according to the manufacturer, consist of 95% or more of the monoclinic phase. If this phase indeed results in two different copper-oxygen interactions at the surface, then it is expected that the two reduction peaks would be more distinct on the CuZnZr-70-NP compared with the CuZnZrAl-10-NP catalyst, which is observed. However, this does not rule out the presence of widely varying Cu particle sizes on the surface, i.e. highly dispersed Cu and larger Cu particles. Evidently, the copper phases on the CuZnZrAl-10-SQ and CuZnZrAl-10-NP catalysts exhibit similar reduction behavior, since they both display two distinct reduction peaks.

In contrast, co-deposition of Cu, Zn and Zr apparently does not result in the same Cu-ZrO$_2$ interactions as deposition of Cu and Zn onto a nanoparticle-ZrO$_2$/nanoparticle-Al$_2$O$_3$ mixture, since the CuZnZrAl-10-CI catalyst only exhibit a single reduction peak. The same is true for the CuZnZrAl-36-CI catalyst, although this catalyst has a shoulder at higher temperature which is probably due to the higher ZrO$_2$ content.

Of the catalysts with a 10% dopant level, the CuZnCeAl-10-CI exhibits the lowest reduction temperature (326°C, with a shoulder at 308°C) and reduction is complete at a lower temperature than any of the 10-36% ZrO$_2$-containing catalysts. Despite the lower reduction
temperature and the higher Cu surface area, the CuZnCeAl-10-CI has a lower catalytic activity than any of the ZrO$_2$-containing catalysts. Therefore, under these conditions there is no correlation between the methanol conversion or TOF and the reduction temperature of the catalyst for this series of catalysts. In agreement with our results there are recent studies which indicate that the reducibility of the copper species does not play the decisive role in determining catalytic performance, and in fact in some cases the catalysts which are more difficult to reduce tend to be more active [59].

3.4.3 X-ray Diffraction Analysis

Figure 3-7A shows the XRD spectra collected from all catalysts after calcination. The characteristic peaks of CuO are evident on all samples, as expected. None of the impregnated zirconia samples exhibit a crystalline ZrO$_2$ phase. The monoclinic ZrO$_2$ phase of the nanoparticle zirconia is evident on catalysts where the ZrO$_2$ nanoparticles are used in the catalyst preparation (NP catalysts). It is interesting that even for the case of the CuZnZrAl-36-CI sample no crystalline ZrO$_2$ phase is present. In fact, the catalyst with 36% ZrO$_2$ exhibits the poorest crystallinity of the catalysts in this investigation, with only the CuO phase and a poorly crystalline ZnAl$_2$O$_4$ spinel phase evident from the spectra. The CuZnZr-70-NP sample is highly crystalline with all three phases (CuO, ZnO, ZrO$_2$) evident in the XRD spectra. There is a spinel ZnAl$_2$O$_4$ phase present on the CuZnZrAl-10-CI and CuZnCeAl-10-CI, and CuZnZrAl-36-CI catalysts. This is the same spinel phase documented in Chapter 2. This phase does not form during the sequential preparation method, when the ZrO$_2$ is deposited first, and it also appears to be hindered by the presence of the nanoparticle ZrO$_2$. 

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Figure 3-7. XRD spectra obtained for all A. fresh and B. spent catalysts. a) CuZnZr-70-NP, b) CuZnZrAl-36-CI, c) CuZnZrAl-10-CI, d) CuZnZrAl-10-NP, e) CuZnZrAl-10-SQ and f) CuZnCeAl-10-CI. ◇ Cubic CeO$_2$, ▼ ZnAl$_2$O$_4$, ★ CuO, ● Cu, □ ZnO, and △ Monoclinic ZrO$_2$.

Particle size information presented in Table 3-3 was calculated using the (1 1 1) peak position and the full width at half maximum of CuO, ZrO$_2$, CeO$_2$ (when present) and ZnAl$_2$O$_4$. 

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Figure 3-7B shows the spectra from the spent catalysts after the temperature sweep experiments shown in Figure 3-1. The large well defined peak at 43° is the (1 1 1) peak of Cu metal which is evident in all samples. This peak was used to calculate the Cu metal particle size of the spent catalysts. The CeO₂, ZrO₂ and ZnAl₂O₄ phases are not significantly altered by exposure to reaction conditions. In contrast, there is a significant increase in the Cu particle size after exposure to reaction conditions for all catalysts except the CuZnZrAl-10-CI and CuZnZrAl-36-CI, compared to the particle size of the original CuO after calcination. This increase in Cu particle size is evidence of significant sintering of the catalysts. This is the most likely explanation for the deactivation evident in Figure 3-1.

Table 3-3. Particle sizes of the different compounds on the various CuO/ZnO/ZrO₂/Al₂O₃ catalysts in the current work. The particle sizes have been determined from the XRD data using the Scherrer equation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Species</th>
<th>Cu</th>
<th>CuO</th>
<th>ZnO</th>
<th>ZnAl₂O₄</th>
<th>ZrO₂</th>
<th>CeO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZnZrAl-10-CI Fresh</td>
<td></td>
<td>--</td>
<td>21.2</td>
<td>--</td>
<td>5.4</td>
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<tr>
<td>CuZnZrAl-10-CI Spent</td>
<td></td>
<td>15.5</td>
<td>--</td>
<td>--</td>
<td>6.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CuZnZrAl-10-SQ Fresh</td>
<td></td>
<td>--</td>
<td>20.0</td>
<td>25.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CuZnZrAl-10-SQ Spent</td>
<td></td>
<td>30.0</td>
<td>--</td>
<td>28.0</td>
<td>--</td>
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<td>--</td>
</tr>
<tr>
<td>CuZnZrAl-10-NP Fresh</td>
<td></td>
<td>--</td>
<td>22.2</td>
<td>21.3</td>
<td>--</td>
<td>20.0</td>
<td>--</td>
</tr>
<tr>
<td>CuZnZrAl-10-NP Spent</td>
<td></td>
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<td>--</td>
<td>38.9</td>
<td>--</td>
<td>20.3</td>
<td>--</td>
</tr>
<tr>
<td>CuZnZr-70-NP Fresh</td>
<td></td>
<td>--</td>
<td>13.1</td>
<td>--</td>
<td>--</td>
<td>19.1</td>
<td>--</td>
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Table 3-3. Continued

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZnZr-70-NP Spent</td>
<td>30.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>19.0</td>
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<tr>
<td>CuZnZrAl-36-CI Fresh</td>
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<td>21.6</td>
<td>6.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CuZnZrAl-36-CI Spent</td>
<td>13.5</td>
<td>--</td>
<td>5.2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CuZnCeAl-10-CI Fresh</td>
<td>--</td>
<td>17.0</td>
<td>--</td>
<td>5.8</td>
<td>--</td>
</tr>
<tr>
<td>CuZnCeAl-10-CI Spent</td>
<td>30.5</td>
<td>--</td>
<td>--</td>
<td>5.9</td>
<td>--</td>
</tr>
</tbody>
</table>

3.5 Breaking the Water Gas Shift Equilibrium

Figure 3-8 shows the Φ ratio, as defined in equation 3-1, as a function of conversion for three catalysts. As can be seen in the figure, Φ<1 for both the CuZnZrAl-10-SQ and CuZnZrAl-36-CI catalysts, which means that the CO concentrations are higher than the water-gas-shift equilibrium CO concentration. Only the CuZnZrAl-10-NP catalyst gives values of is Φ larger than 1.0 at methanol conversions of 65% and above (which corresponds to a temperature range of 300°C to 345°C). At higher temperatures, methanol conversion decreases (see Figure 3-1) and the Φ ratio also decreases as the CO levels increase with increasing temperature. Since the CO concentration is higher than the water-gas-shift equilibrium concentration, this means that the source of the CO must be from another reaction, i.e. the methanol decomposition. This is in agreement with the observation by Peppley et al. [7,8]. Evidently, the CuZnZrAl-10-NP catalyst appears to suppress the decomposition reaction at relatively high methanol conversions. This is interesting, since the contribution of CO from the methanol decomposition reaction is usually greater at higher temperatures and higher methanol conversions. The fact that the CO concentrations in the reactor effluent are below that of the water-gas-shift equilibrium at
methanol conversions of 65-80% for the CuZnZrAl-10-NP reveals that this is a very promising methanol steam reforming catalyst for PEM fuel cell applications.

![Figure 3-8](chart)

**Figure 3-8.** Dimensionless water gas shift equilibrium constant, $\Phi$, as a function of temperature for three nanoparticle catalysts. $\Delta$ CuZnZrAl-36-Cl, $\star$ CuZnZrAl-10-SQ and $\blacksquare$ CuZnZrAl-10-NP. Contact time for all curves is 0.15 kg cat·sec/mmol CH$_3$OH which corresponds to 300mg catalyst and a total liquid inlet flow rate of 0.8 ml/hr. Dashed line reveals the equilibrium value ($\Phi = 1$).

Addition of the nanoparticle ZrO$_2$ to the system may induce a certain morphology of the copper phase on the surface which could suppress CO formation via the methanol decomposition reaction. A favorable surface morphology has been cited by other researchers in the fabrication of highly active methanol reforming catalysts [13]. However, the ZrO$_2$ may also stabilize a Cu$^+$ species on the surface [27], which could potentially suppress CO formation. This is supported by the observation that CO is adsorbed more strongly on Cu$_2$O compared with Cu metal [11], which means that CO desorption would not be as facile on a Cu$_2$O covered surface.

Furthermore, there would also be oxygen present for oxidation of the CO to CO$_2$, which is
important since the CO production has been shown to increase with increasing extent of reduction of the catalyst [20]. Evidently, presence of nanoparticle ZrO$_2$ also results in a highly active surface. This increased activity is not related to a decrease in reduction temperature or an increase in the Cu surface area of the catalyst. It has been shown by Bell that in the methanol synthesis reaction the system is highly sensitive to the zirconia phase [85,86]. For instance, methanol synthesis catalysts supported on monoclinic ZrO$_2$ are more active than those supported on tetragonal ZrO$_2$ [85,86]. It has further been demonstrated that during calcination of impregnated zirconia catalysts, the ZrO$_2$ first forms as an amorphous phase, and then the metastable tetragonal phase forms below 550°C [39,42]. Monoclinic ZrO$_2$ forms only above 550°C, which is much higher than the calcinations used in this work. In the present case, however, the ZrO$_2$ nanoparticles consist of mainly a monoclinic ZrO$_2$ phase. Therefore, the CuZnZrAl-10-NP and the CuZnZr-70-NP catalysts, which exhibit the highest turnover frequencies in this study, are also the only two catalysts that contain a monoclinic ZrO$_2$ phase, as seen in the XRD spectra. The differences in the electronic characteristics of these materials, which are likely responsible for the differences in catalytic behavior, will be the subject of the following chapter.

### 3.6 Conclusions

Addition of ZrO$_2$ to Cu-ZnO catalysts supported on nanoparticle alumina results in highly active methanol reforming catalysts. Under similar conditions, our ZrO$_2$-promoted catalysts achieve higher methanol conversions and lower CO selectivities in the methanol steam reforming reaction compared to the commercial catalyst. This is an improvement over the data presented in Chapter 2. The catalysts are sensitive to both preparation method and ZrO$_2$ precursor. Co-impregnation of Cu, Zn and Zr onto the nanoparticle alumina results in a more active catalyst.
compared to a catalyst that is prepared by adding Zr before the Cu and Zn using the sequential impregnation method. The best performing catalyst is the CuZnZrAl-10-NP, in which the ZrO₂ is added in the form of nanoparticles. This catalyst outperforms all the other catalysts, including the commercial reference, since it attains the highest methanol conversion and the lowest CO selectivity over a wide range of the conditions tested. Only the CuZnZr-70-NP catalyst exhibits a higher TOF than the CuZnZrAl-10-NP catalyst. However, since the CuZnZr-70-NP catalyst does not contain any high surface area alumina, this catalyst is limited by its low Cu surface area.

There is no correlation between the Cu surface area and the catalytic activity (methanol conversion and turnover frequency) for the ZrO₂- and CeO₂-promoted catalysts in this study. Under the conditions used in the study, CeO₂ is a much less efficient promoter compared with ZrO₂. It is evident from the high turn over frequencies of the CuZnZr-70-NP and CuZnZrAl-10-NP that the use of nanoparticle ZrO₂ results in a very active Cu phase on the surface. Furthermore, there is no correlation between the reducibility and the catalytic activity under the conditions used. This is surprising since data from the literature usually indicate that the more active catalysts contain copper oxide phases that are easy to reduce. In contrast, our best performing catalyst, CuZnZrAl-10-NP, also exhibits the highest reduction temperature.

Another interesting result is that the CO selectivities over our nanoparticle-supported catalysts decrease with temperature below 250-300°C. Since both the CO forming reactions are exothermic and the rates thus increase with increasing temperatures, this indicates that the steam reforming reaction (equation 1-1) increases faster than the reverse water-gas-shift (equation 1-2) and the methanol decomposition (equation 1-3) reactions. Despite this, the CO levels for most of our catalysts are above the water-gas-shift equilibrium concentration, which indicate that the CO
decomposition reaction must be considered. Only the CuZnZrAl-10-NP catalyst results in CO levels well below the water-gas-shift CO concentration at temperatures in the range 275°-325°C.

In summary, the results from this study clearly demonstrate that there are advantages in the use of nanoparticle precursor materials. The use of ZrO₂ nanoparticles results in highly active copper phases. Under the conditions used in this study, the reaction system is evidently sensitive to structural or electronic differences between the different catalysts since there is not a simple correlation between the Cu surface area and the catalytic activity. Furthermore, the ZrO₂-containing catalysts suppress CO formation via the methanol decomposition and reverse water-gas-shift reactions. The combined effects result in unique, promising catalysts for the methanol steam reforming in fuel cell applications.

The task remaining is to determine what chemical or electronic characteristic is responsible for the increase in catalytic activity observed for the nanoparticle ZrO₂ catalyst. A more intensive investigation into the electronic characteristics of the catalysts is the subject of Chapter 4.

3.7 Acknowledgements

This work was supported by NASA Glenn Research Center, Grant NAG 3-2930, monitored by Mr. Tim Smith.

The authors would also like to thank Oseas Ayerdi for help with catalyst preparations and data processing of the GC measurements.
4.1 Introduction and Literature Review

As was mentioned in Chapter 3, a comprehensive study of Al₂O₃ and ZrO₂ supported reforming catalysts performed by Breen and Ross found that the most active reforming catalysts contained both Al₂O₃ and ZrO₂ and that the catalysts are very sensitive to the fabrication techniques used [29]. For example, Breen et al. [29] found that catalysts made by sequential precipitation (copper, then zinc) on a mixed ZrO₂/Al₂O₃ support are more active in the reforming reaction than coprecipitated (copper and zinc together) catalysts. They also postulated that the role of the Al₂O₃ is to “protect the amorphous nature of ZrO₂” in the catalyst and that catalytic activity decreases significantly if the ZrO₂ crystallizes [29]. This is in agreement with an earlier study of CH₃OH synthesis over ZrO₂ supported catalysts [87]. In a recent study by Wang et al. [42], the catalytic activity of Cu/ZrO₂ catalysts increases with the crystallization of a monoclinic-enriched zirconia in the surface region. Likewise, there have been several studies on methanol synthesis by Bell et al. [85,86] which demonstrate that monoclinic ZrO₂ is considerably more active than tertiary ZrO₂ toward methanol synthesis. The problem with ZrO₂ from impregnated or precipitated precursors is that the metastable tertiary ZrO₂ phase appears to form first and that the monoclinic phase does not form below 550°C [39,87]. The result is that the Cu particles are subject to severe sintering due to the elevated temperatures needed to form monoclinic ZrO₂ in the bulk of the catalyst [86,87]. This results in a decrease in both Cu surface area and also in catalytic activity in both the methanol synthesis [86] and steam reforming reactions [87].

The purpose of this work is to demonstrate that these difficulties in forming monoclinic ZrO₂ can be avoided if the catalyst is fabricated using a physical mixture of nanoparticle
monoclinic zirconia and nanoparticle \( \gamma \)-alumina as the catalyst support. The copper and zinc phases can then be impregnated onto this mixed oxide support as is typically done. In this way the high calcination temperatures, with concomitant Cu sintering, can be avoided resulting in a more active Cu/ZnO/ZrO\(_2\)/Al\(_2\)O\(_3\) methanol reforming catalyst. Extensive XPS studies will also be performed in an attempt to elucidate the cause for the superior performance of the CuZnZrAl-10-NP catalysts as shown in the previous chapter.

4.2 Experimental Methods

Most of the experimental procedures used in this chapter have already been covered in detail in the preceding chapters. The catalysts studied in this chapter are the same as those studied in Chapter 3, and therefore the catalyst preparation procedure, TPR, N\(_2\)O titration, and reactor experiments are covered in Chapter 3. The naming used in this chapter has been simplified since all catalysts have the formula CuZnZrAl-10, and only the preparation method is different. Therefore, the ZrO\(_2\) concentration is dropped from the label since it is constant in this chapter. Thus, CuZnZrAl-10-NP becomes CuZnZrAl-NP. Some additional reactor data is shown here to further explore the differences in performance between three catalysts of the same nominal composition. XRD data shown here is fundamentally the same as was shown in Chapter 3 except that only there three CuZnZrAl-10 catalysts are investigated in this chapter. The XPS data is unique to this chapter. For all XPS measurements, the catalyst powders were pressed into aluminum cups prior to insertion into the ultra-high vacuum (UHV) chamber (base pressure \(1 \times 10^{-10}\) Torr). The XPS data were collected using a double pass cylindrical mirror analyzer (PHI model 25-270AR) with incident radiation from a Mg K\(\alpha\) X-ray source (PHI 04-151). Spectra were taken in the retarding mode with a pass energy of 50 eV for survey spectra and 25 eV for
high resolution spectra. Data were collected using a computer interface and then digitally smoothed [88]. Charge shift corrections were made by assuming a C 1s signal of 284.6 eV [89].

4.3 Results and Discussion

4.3.1 Catalytic Activity and CO Selectivity

The conversion of methanol over the CuZnZrAl-10-NP catalyst with increasing temperature is shown in Figure 4-1 for a constant feed rate and water/methanol ratio.

![Figure 4-1](image_url)

Figure 4-1. CH$_3$OH conversion and corresponding CO$_2$, H$_2$ and CO production rates for the CuZnZrAl-NP catalyst. –– CH$_3$OH conversion, –– CO$_2$ production, - - - H$_2$ production and - - - CO production in sccm. The water/methanol ratio was ~3/1 and the total inlet liquid flow rate was 0.8 ml/hr over 340 mg catalyst.

The system does not achieve thermodynamic equilibrium at this feed rate so higher conversions are possible at longer contact times [35,76]. The actual production rates of H$_2$, CO and CO$_2$ are also displayed. Over the entire temperature range, H$_2$ and CO$_2$ are produced in approximately a 3:1 ratio, as expected for steam reforming of methanol. The decrease in
methanol conversion at high temperatures reflects the thermal deactivation of the catalyst at elevated temperatures as discussed in previous studies [29, 76].

The moles of H₂ produced per surface Cu atom per time, expressed as turnover frequency (TOF), and CO production as a function of temperature for all three catalysts are shown in Figure 4-2 (same reaction conditions as in Figure 4-1) and the gas effluent compositions at different temperatures are given in Table 4-1.

Figure 4-2. H₂ (solid lines) and CO (dashed lines) production rates for all catalysts. –∇– CuZnZrAl NP, –☆– CuZnZrAl CI, and –◆– CuZnZrAl SQ. All reaction conditions were the same as those in Figure 4-1.

Below 240°C, there is no significant difference in the activity of the three catalysts. Between 240°C and 270°C the CuZnZrAl-NP and CuZnZrAl-Cl catalysts perform similarly, but above 270°C the CuZnZrAl-NP catalyst achieves higher H₂ production levels than either of the impregnated ZrO₂ catalysts.
Table 4-1. Reactor effluent composition for all catalysts at selected temperatures.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZnZrAl-CI</td>
<td>305</td>
<td>78.6</td>
<td>1.27</td>
<td>20.2</td>
</tr>
<tr>
<td>CuZnZrAl-SQ</td>
<td>305</td>
<td>77.2</td>
<td>1.27</td>
<td>21.5</td>
</tr>
<tr>
<td>CuZnZrAl-NP</td>
<td>305</td>
<td>78.6</td>
<td>0.69</td>
<td>20.7</td>
</tr>
<tr>
<td>CuZnZrAl-CI</td>
<td>240</td>
<td>74.6</td>
<td>1.32</td>
<td>24.1</td>
</tr>
<tr>
<td>CuZnZrAl-SQ</td>
<td>235</td>
<td>75.3</td>
<td>1.08</td>
<td>23.7</td>
</tr>
<tr>
<td>CuZnZrAl-NP</td>
<td>235</td>
<td>71.7</td>
<td>0.84</td>
<td>27.4</td>
</tr>
</tbody>
</table>

At 305°C the CuZnZrAl-NP reaches a H₂ production rate that is 15% higher than that of the CuZnZrAl-CI catalyst and over 30% higher than that of the CuZnZrAl-SQ catalyst, demonstrating the benefit of the nanoparticle ZrO₂ precursor in the reforming reaction. For all catalysts the CO production increases as a function of temperature. This is often attributed to an increase in the reaction rate of the reverse water gas shift and/or the methanol decomposition reaction with increasing temperature [29,49,87,76,80]. The CuZnZrAl-NP catalyst exhibits the lowest CO production rate over the temperature range examined.

4.3.2 X-Ray Diffraction Analysis

XRD spectra obtained from the fresh and used catalysts are shown in Figure 4-3. This is a more detailed view of the XRD data presented in Chapter 3. There are several interesting differences in the XRD spectra obtained from the three catalysts that will be covered in greater detail here than in the previous chapter. There is no crystalline ZrO₂ phase present in either the
CuZnZrAl-SQ or CuZnZrAl-CI catalysts, in agreement with available literature data for impregnated and precipitated ZrO\textsubscript{2} catalysts calcined below 550°C [86,87]. The CuZnZrAl-NP catalyst displays a crystalline monoclinic ZrO\textsubscript{2} phase. This result is expected since the nanoparticle ZrO\textsubscript{2} precursor is in the monoclinic phase, as stated above. This was independently verified using XRD on the untreated ZrO\textsubscript{2} nanoparticles (not shown). Another difference is the poorly crystalline ZnAl\textsubscript{2}O\textsubscript{4} spinel phase present on the CuZnZrAl-CI which was documented in Chapter 3.

The figure clearly shows there is no change in the monoclinic ZrO\textsubscript{2} phase as for the CuZnZrAl-NP catalyst. Similarly, no crystalline ZrO\textsubscript{2} phase is formed during reaction for the other two catalysts. The particle sizes of the crystalline components in the catalysts were calculated using the Scherrer equation and were presented in Chapter 3. It was shown in Table 3 that Cu particle sizes confirm the trend in Cu surface area observed from the N\textsubscript{2}O decomposition measurements; i.e. that the CuZnZrAl-SQ catalyst has the smallest Cu particles (largest Cu surface area) and the CuZnZrAl-CI catalyst has the largest Cu particles (smallest Cu surface area), although the difference between the Cu particles on the CuZnZrAl-CI and CuZnZrAl-NP is not significant. The ZnAl\textsubscript{2}O\textsubscript{4} spinel phase is not significantly altered during reduction and reaction. An unexpected result is that the sintering of the Cu phase is more severe on the most active catalyst (CuZnZrAl-NP) compared to the other catalysts. These results further support the conclusion that there is not a simple correlation between the catalytic activity and the Cu surface area, which has been noted throughout this dissertation. Also, the coimpregnation catalyst preparation technique results in a catalyst more resistant to Cu sintering compared to the sequential method. Furthermore, the catalyst preparation does not appear to alter the particle
Figure 4-3. XRD spectra obtained from A) fresh catalysts and B) spent catalysts, a) CuZnZrAl-NP, b) CuZnZrAl-Cl and b) CuZnZrAl-SQ. • monoclinic ZrO₂, ★ CuO, ▼ ZnAl₂O₄, ★ Cu
sizes of the nanoparticle ZrO₂, although there is a slight increase in ZrO₂ particle size during the reaction (used CuZnZrAl-NP). However, sintering of the ZrO₂ particles is less severe than the Cu particle agglomeration.

4.3.3 X-Ray Photoelectron Spectroscopy Analysis

4.3.3.1 Peak area ratios

A labeled survey spectrum obtained from the fresh CuZnZrAl-CI catalyst is shown in Figure 4-4. The survey spectra obtained from all the fresh and used catalysts are similar except for differences in the relative peak sizes so only one survey spectrum is shown.

![Figure 4-4](image)

Figure 4-4. Labeled XPS survey spectra for CuZnZrAl-CI catalyst.

Peak area ratios obtained from these spectra are given in Table 4-2. These peak area ratios are determined by two factors: (1) the relative amounts of the elements in the outermost 6 nm and (2) the spatial arrangement of the elements in this region (the matrix effect). Since these catalysts all have the same support and similar compositions, the differences observed between the catalysts in Table 4-2 are mostly due to the matrix effect.
Table 4-2. Peak area ratios for all catalysts calculated from the XPS data.

<table>
<thead>
<tr>
<th>Peak Ratio</th>
<th>SQ Fresh</th>
<th>SQ Spent</th>
<th>CI Fresh</th>
<th>CI Spent</th>
<th>NP Fresh</th>
<th>NP Spent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s / Al 2p</td>
<td>0.77</td>
<td>0.78</td>
<td>0.59</td>
<td>0.55</td>
<td>0.72</td>
<td>0.66</td>
</tr>
<tr>
<td>O 1s / Al 2p</td>
<td>2.83</td>
<td>1.83</td>
<td>1.61</td>
<td>2.05</td>
<td>2.94</td>
<td>2.37</td>
</tr>
<tr>
<td>Zr 3d / Al 2p</td>
<td>0.51</td>
<td>0.39</td>
<td>0.07</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu 2p / Al 2p</td>
<td>0.09</td>
<td>0.05</td>
<td>0.08</td>
<td>0.04</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Zn 2p / Al 2p</td>
<td>0.17</td>
<td>0.12</td>
<td>0.09</td>
<td>0.08</td>
<td>0.09</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Use of the homogeneous assumption to obtain compositions of supported catalysts leads to large errors so peak area ratios are used in this study.

The differences between the three types of fresh catalysts are quite large. The fresh CuZnZrAl-SQ catalyst has much larger Zr/Al, Cu/Al and Zn/Al peak area ratios than the other two types of catalysts. The fresh ChZnZrAl-CI catalyst has a smaller O/Al peak area ratio than the other two fresh catalysts. All three fresh catalysts have similar C/Al peak area ratios.

Significant changes occur in these peak area ratios during the reaction. The Zr/Al peak area ratio of the CuZnZrAl-SQ catalyst decreases by about 25% while those of the other two types of catalysts do not change significantly. The fresh CuZnZrAl-CI and CuZnZrAl-SQ catalysts have similar Cu/Al peak area ratios which decrease by about 50% during reaction. Contrary to this the fresh CuZnZrAl-NP has a low Cu/Al peak area ratio of 0.48 which more than doubles to 1.14 during reaction, but this is still lower than the corresponding values of the other two catalysts. The Zn/Al peak area ratios decrease significantly (20-35%) for all these catalysts. The O/Al peak area ratio of the fresh CuZnZrAl-CI is much lower than that of the other two
catalysts. However, during reaction the O/Al peak area ratio increases for the CuZnZrAl-CI catalyst and decreases for the other two catalysts. After reaction the O/Al peak area ratios are similar for the CuZnZrAl-CI and CuZnZrAl-SQ catalysts but markedly higher for the CuZnZrAl-NP catalyst. The C/Al ratios are similar for all of the catalysts and do not change very much during reaction.

4.3.3.2 Fresh catalysts

Zr 3d XPS spectra obtained from the calcined catalysts and the nanoparticle ZrO$_2$ support are shown in Figure 4-5.

![Figure 4-5A](image)

Figure 4-5. Zr 3d XPS spectra obtained from A) fresh catalysts and B) spent catalysts. Nanoparticle ZrO$_2$ is included as a reference. Curves are appropriately labeled in the figure.
The Zr 3d$_{5/2}$ peak obtained from the CuZnZrAl-CI catalyst is centered at a binding energy of 181.5 eV, and that obtained from the CuZnZrAl-SQ catalyst is centered at a BE of 181.4 eV. This is lower than the Zr 3d$_{5/2}$ binding energy for the nanoparticle ZrO$_2$ at 181.8 eV. The presence of a more reduced Zr species has been associated with a high population of oxygen vacancies in the ZrO$_2$ lattice [40,87], and Zr species with high electron densities have been observed previously for both Cu on ZrO$_2$ methanol reforming catalysts and also on Fe-promoted ZrO$_2$ catalysts [90,91]. The low binding energies of the Zr 3d$_{5/2}$ peak suggest the possibility of strong CuO-ZrO$_2$ interactions at the surface of these catalysts [90]. Compared to the Zr 3d peaks obtained from the nanoparticle ZrO$_2$, the Zr 3d peaks obtained from the CuZnZrAl-CI and CuZnZrAl-SQ catalysts are broader due to contributions from additional states and/or differing
amounts of charge transfer. Also a significant shoulder at 181.9 eV is apparent on the CuZnZrAl-CI and CuZnZrAl-SQ spectra, which is due to the unperturbed ZrO₂ state. In contrast, the Zr 3d₅/₂ obtained from the CuZnZrAl-NP catalyst is shifted to 181.0 eV, indicating an even stronger interaction between the CuO and ZrO₂ at the surface of this catalyst; i.e. a higher contribution from the electron-rich Zr 3d state [90]. The peak shapes of the Zr 3d peaks obtained from the the CuZnZrAl-NP catalyst and the nanoparticle ZrO₂ are similar, indicating one predominant Zr species. For the CuZnZrAl-NP catalyst the dominant species is the electron-rich Zr species with a 3d₅/₂ binding energy of 181.0 eV and there is only a minor contribution from the unperturbed ZrO₂ state at 181.9 eV.

The Cu 2p peaks obtained from the calcined and spent catalysts are shown in Figure 4-6.

Figure 4-6. Cu 2p XPS spectra obtained from A) fresh and B) spent catalysts. a) CuZnZrAl-NP, b) CuZnZrAl-CI c) CuZnZrAl-SQ
Figure 4-6. Continued

The Cu 2p$_{3/2}$ feature is located near 933.6 eV, and the Cu 2p$_{1/2}$ feature is located near 953.3 eV for all catalysts in Figure 4-6A. These binding energies and the intense satellite bands located at approximately 10 eV higher than the photoelectron lines are typical of Cu$^{2+}$ [39,90]. This is also typical for Cu/ZnO/ZrO$_2$/Al$_2$O$_3$ reforming catalysts [39,90]. The Cu 2p peaks obtained from the CuZnZrAl-CI and CuZnZrAl-SQ are similar. Both display the same peak position, and both exhibit a small low binding energy shoulder. The peak position of the Cu 2p$_{3/2}$ main line is the same for the CuZnZrAl-NP catalyst, but the low binding energy shoulder is more pronounced than on the other two catalysts, resulting in a highly asymmetric Cu 2p$_{3/2}$ peak for the CuZnZrAl-NP catalyst. The low binding energy shoulder of the Cu 2p$_{3/2}$ electron is located at 932.4 eV, compared to the main peak at 933.6 eV. A state at a low binding energy of 932 eV
has been observed by Wang et al. [42], and was attributed to copper oxide located near oxygen vacancies on the surface of the zirconia. The oxygen vacancies in the matrix give the copper species a higher electron density similar to the Zr species. This reveals a very close Cu-ZrO₂ interaction. The larger contribution from the state at low binding energy obtained from the CuZnZrAl-NP catalyst further suggests that the Cu-ZrO₂ interactions in this catalyst are more developed than in the other two catalysts.

The O1s spectra of all fresh and used catalysts and the nanoparticle ZrO₂ precursor are shown in Figure 4-7.

![Figure 4-7](image)

Figure 4-7. O 1s XPS spectra obtained from fresh (solid lines) and spent (dashed lines) catalysts. Curves are labeled appropriately in the figure.

The O1s spectra for the catalysts are not significantly affected by exposure to reaction conditions. Therefore the spectra from fresh and spent catalysts are combined into a single figure. The minimal difference between the fresh and spent O1s spectra indicates that the spectra
are dominated by the contribution of the O present in Al2O3, which is not reduced during the reaction. There is a high BE shoulder present on the O1s spectra of the nanoparticle ZrO2 precursor located at 532.3 eV. This is indicative of hydroxyl groups present at the surface.

### 4.3.3.3 Spent catalysts

After reaction the ZrO2 peaks obtained from all catalysts are shifted to slightly higher binding energy (Figure 4-5B). A higher Zr 3d5/2 binding energy due to the presence of Zr(OH)4 after reduction and exposure to the reaction conditions have been observed previously [16]. Although the Zr 3d5/2 binding energies obtained from the used catalysts are not as high as those obtained from Zr(OH)4 [16], the presence of hydroxyl groups in the ZrO2 precursor indicates that there is likely a contribution from a Zr(OH)x species present on the catalyst surfaces after reaction. Hydroxyl groups near oxygen vacancies could potentially result in binding energies similar to ZrO2. The increase in binding energy suggests that the electron densities on the Zr species after reaction are slightly lower than before reduction and exposure to the reaction conditions, but they are still higher than that of the pure nanoparticle ZrO2. This suggests that there are oxygen vacancies on the surface after reaction, but comparing the catalysts before and after reaction is complicated by the potential presence of hydroxyl groups on the surface.

Reduction of the Cu2+ to Cu1+ or Cu0 is evident in the Cu 2p peaks obtained from the used catalysts (Figure 4-6B). The peaks are narrower and the Cu 2p3/2 main line is located at 931.6 eV for all catalysts after reaction, compared to the 933.6 eV before reaction. In all cases the satellite structures, indicative of Cu2+, are no longer present. The binding energy is lower than expected for Cu or Cu2O (932.4-932.6 eV), which again may indicate that the Cu is interacting with the oxygen vacancies on the ZrO2 support, although there may not be as many oxygen vacancies as on the fresh catalysts. In addition to the feature at 931.6 eV, all catalysts also exhibit shoulders of varying intensity at 933.6 eV. The CuZnZrAl-SQ catalyst exhibits the smallest contribution
The analysis of the Zr 3d\textsubscript{5/2} XPS peaks is complicated by the presence of oxygen vacancies and also hydroxyl groups on the ZrO\textsubscript{2} surface. Apparently, the crystalline phase of ZrO\textsubscript{2} influences the catalytic reaction. There is a decrease in Zr 3d\textsubscript{5/2} binding energy with increasing calcination temperature for Cu/ZrO\textsubscript{2} catalysts in the literature which coincides with the formation of a monoclinic ZrO\textsubscript{2} phase [39,42]. The catalytic activity also increases up to a certain temperature, above which the activity declines again [39,42]. This is consistent with Cu-based ZrO\textsubscript{2}-containing methanol synthesis catalysts, in which a monoclinic ZrO\textsubscript{2} support results in catalysts with significantly higher activities than catalysts supported on tetragonal ZrO\textsubscript{2} [85,86]. These facts are consistent with a complex interaction between the ZrO\textsubscript{2} and the Cu at the catalyst surface.

Despite this complexity, there are strong metal-support interactions on these catalysts. These interactions appear to result in electron-rich Cu and Zr species on both fresh and used catalysts, as well as oxygen transfer on the used catalysts. The more oxidized Cu species observed on the used catalysts may have a higher affinity for CO, and can “promote the activity
for methanol synthesis” [39]. This partially oxidized Cu surface species may have a higher affinity for the oxidation of CO via the water gas shift or, conversely, is less active in the reduction of CO₂ via the reverse water gas shift. The CuZnZrAl-NP catalyst, which has the lowest CO production rate, has the largest Cu oxidation feature in the Cu 2p spectra of the used catalysts. Similarly, the CuZnZrAl-SQ has the highest CO production rate and the Cu 2p spectra of the used catalyst show little or no evidence of a partially oxidized Cu species. The CuZnZrAl-CI is intermediate in both CO production and intensity of the Cu higher binding energy shoulder. A similar argument can be made that the partially oxidized Cu sites have a stronger affinity towards methanol in the reforming reaction. This may explain why the CO production levels and selectivity are consistently lower for the CuZnZrAl-NP catalyst compared to the other two catalysts; i.e. the oxidized surface Cu species is both more active in the reforming reaction and at the same time inhibits CO₂ reduction via the reverse water gas shift. The data presented here suggests that strong metal-support (i.e. Cu-ZrO₂) interactions are important for a high catalytic activity in the methanol steam reforming reaction and a high selectivity to CO₂.

4.4 Conclusions

This study has shown that it is possible to form highly active methanol reforming catalysts using nanoparticle ZrO₂ supports. The use of nanoparticle ZrO₂ supports is preferable to the use of a more traditional ZrO₂ phase impregnated from ZrO(NO₃)₂·6H₂O. The nanoparticle ZrO₂ catalyst is more active in the reforming reaction and also exhibits lower CO production levels, which is consistent with a suppression of the reverse water gas shift. The nanoparticle ZrO₂ precursor is monoclinic, allowing a monoclinic ZrO₂ phase to be introduced into the catalyst matrix without the use of high calcination temperatures, which are necessary when zirconia is impregnated from a nitrate precursor. The less active tetragonal ZrO₂ phase is avoided by using
the monoclinic ZrO$_2$ nanoparticles. The impregnated catalysts calcined at 300°C result in an amorphous ZrO$_2$ phase which is not apparent with XRD. The higher activity of the monoclinic ZrO$_2$ catalyst is in agreement with the available literature in both methanol synthesis and methanol reforming studies. The advantage of the monoclinic ZrO$_2$ phase appears to be that it has a relatively higher population of oxygen vacancies. This results in a partially oxidized Cu surface species which is more active in the methanol reforming reaction than copper without the oxidation features.
CHAPTER 5
DESIGN AND CONTROL OVER CuO PARTICLE SIZE AND Cu SURFACE AREA IN Cu/ZrO₂ METHANOL REFORMING CATALYSTS FROM NANOPARTICLE AND MICROEMULSION PRECURSORS.

5.1 Introduction and Literature Review

As noted, traditional methanol steam reforming catalysts often consist of Cu and ZnO and sometimes a small amount of Al₂O₃ [6,35]. Chapters 3 and 4 focused on the use of reducible metal oxides, such as ZrO₂ and CeO₂ as alternatives or additions to Al₂O₃. It was shown that ZrO₂ addition to Cu-based alumina-supported catalysts increased methanol conversion and reduced CO yields. This is consistent with the literature [14,18,27,56]. It was further demonstrated that there is a distinct advantage to using nanoparticle ZrO₂ compared to more traditional impregnated ZrO₂. There is strong evidence of an electronic interaction (charge transfer) between Cu and Zr in the Cu and nanoparticle ZrO₂ reforming catalysts [39,42,90]. To further complicate the picture, Bell, et al. [86] showed that the ZrO₂ crystal phase present in the catalyst is of critical importance. Wu et al. [39] further demonstrated that there is an advantage to increasing the calcination temperature of Cu/ZrO₂ catalysts. It was concluded that the increase in calcination temperature to 550°C or above encourages the crystallization of a monoclinic ZrO₂ phase [39]. This agrees well with the results of Bell. However it was also demonstrated that there are potential problems associated with calcination temperatures above 550°C, including a severe loss of Cu surface area due to sintering of the Cu phase [42]. The role of monoclinic ZrO₂ in quaternary CuO/ZnO/ZrO₂/Al₂O₃ systems was demonstrated in Chapter 3 and further explained in Chapter 4. These results demonstrated that potential problems with increased calcination temperatures could be avoided entirely if monoclinic nanoparticle ZrO₂ was used as the ZrO₂ precursor in the catalyst.
In addition to the advantages of the use of monoclinic ZrO₂ in methanol reforming, a recent study by Ritzkopf, et al. demonstrated that there is also an advantage to using Cu/ZrO₂ methanol reforming catalysts that are prepared via a reverse (i.e. water in oil) microemulsion technique. Ritzkopf showed that this microemulsion catalyst had a dramatically lower CO selectivity at similar methanol conversions when compared to a commercial catalyst [44]. It was mentioned in Chapter 1 that Agrell showed that a similar microemulsion technique also gave very promising results for Cu/ZnO [45] and Pd/ZnO [46] catalysts.

With the results from the Bell, Agrell and Ritzkopf studies, in addition to our previous results, the authors were interested in determining if there was a further advantage in the use of nanoparticle precursors in conjunction with the microemulsion fabrication techniques mentioned above. This study incorporates these recent advances in methanol reforming catalysts and the use of nanoparticle catalyst materials.

5.2 Experimental Methods

As in the previous chapters, the catalyst preparation methods used herein are unique to this chapter and are covered in detail here. TPR, N₂O titrations, XRD and BET surface area analysis were performed as described in Chapter 1.

5.2.1 Catalyst Preparation

The concentrations of CuO and ZrO₂ were held constant at 15% and 85%, respectively, for all catalysts in this study except the commercial reference catalyst. The 15% CuO catalysts were used to facilitate comparison with the catalysts in the Ritzkopf study (4-16% Cu) mentioned in the introduction. The microemulsion catalysts were fabricated by adding an aqueous solution of Cu(NO₃)₂·6H₂O (Alpha Aesar) of varying Cu molarity to an organic solution of Tween 80 (Fisher) in toluene (Acros organics). The components were added such that the concentrations of
each component of the emulsion were held constant at 10% water, 15% surfactant and 75% toluene by weight for all samples. After dissolving the Tween 80 in toluene, the aqueous phase was prepared by dissolving the Cu(NO$_3$)$_2$·6H$_2$O precursor in H$_2$O to the desired concentration of metal (see Table 5.1). After the Cu(NO$_3$)$_2$·6H$_2$O was completely dissolved, the appropriate mass of ZrO$_2$ nanoparticles (Nanostructured and Amorphous Materials) was dispersed into the aqueous solution. The aqueous phase was then added drop-wise to the organic solution containing the surfactant under intense stirring.

The molarity of the aqueous phase was altered to determine the effect of the Cu(NO$_3$)$_2$·6H$_2$O concentration in the emulsion on the catalyst performance. Three different molarities were used in this study. Cu45Zr samples was made by adding 2.8 grams of Cu(NO$_3$)$_2$·6H$_2$O to 21 ml H$_2$O for a molarity of 0.45 M Cu. The molarity of the Cu22Zr samples was altered by doubling the amount of H$_2$O to 42 ml while keeping mass of Cu(NO$_3$)$_2$·6H$_2$O constant at 2.8 grams, for a Cu molarity of 0.22 M. The toluene and surfactant volumes were scaled up (or down, as appropriate) to keep the relative concentrations of toluene, surfactant, and aqueous phase the same in the emulsion. A similar procedure was followed for the Cu73Zr sample by decreasing the amount of water used to make the emulsion while again holding the Cu(NO$_3$)$_2$·6H$_2$O mass constant.

After the emulsion had stabilized, Cu(NO$_3$)$_2$·6H$_2$O is reduced in solution to Cu metal by addition of 50 % excess hydrazine in the form of hydrated N$_2$H$_2$ (85% N$_2$H$_2$ to 15% H$_2$O weight/weight, Fisher). This is a similar procedure to what was done in the Pd/ZnO microemulsion catalyst study done by Agrell, et al. [46]. After the reduction was complete, the resultant mixture was centrifuged at 3000 rpm for one hour. The resultant solids were recovered and sonicated in CH$_3$OH for one hour. This step was needed to break up the micelles and
remove any residual surfactant from the solids. After sonication, the washed solids were again centrifuged at 3000 rpm for one hour to separate the solids from the alcohol solution. Finally, the solids were dried overnight at 105°C. The catalysts were then calcined at 300°C, 500°C, or 700°C for 3 hours. Any Cu in the sample is oxidized to CuO during the calcination. In this way three different Cu molarities were each calcined at three different temperatures for a total of 9 catalysts used in this study. In all cases the catalysts were prepared in 5 gram batches of calcined CuO/ZrO₂ catalyst. Table 5-1 summarizes the differences in the catalyst samples used in this study.

Table 5-1. Catalyst Preparation Details

<table>
<thead>
<tr>
<th>Name</th>
<th>Cu Molarity (mol/L)</th>
<th>Calcination Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu22ZrA</td>
<td>0.22</td>
<td>300</td>
</tr>
<tr>
<td>Cu22ZrB</td>
<td>0.22</td>
<td>500</td>
</tr>
<tr>
<td>Cu22ZrC</td>
<td>0.22</td>
<td>700</td>
</tr>
<tr>
<td>Cu45ZrA</td>
<td>0.45</td>
<td>300</td>
</tr>
<tr>
<td>Cu45ZrB</td>
<td>0.45</td>
<td>500</td>
</tr>
<tr>
<td>Cu45ZrC</td>
<td>0.45</td>
<td>700</td>
</tr>
<tr>
<td>Cu73ZrA</td>
<td>0.73</td>
<td>300</td>
</tr>
<tr>
<td>Cu73ZrB</td>
<td>0.73</td>
<td>500</td>
</tr>
<tr>
<td>Cu73ZrC</td>
<td>0.73</td>
<td>700</td>
</tr>
</tbody>
</table>

The reference catalyst used in this study is the same commercially available Süd-Chemie catalyst used throughout this dissertation.

5.2.2 Reactor Experiments

The only difference in reactor operation in this chapter compared to previous chapters is that the H₂O/CH₃OH ratio in the feed was decreased to 1.4 mol/mol. The reference catalyst was also tested at this decreased feed ratio. No CH₄, CH₂O, CH₃OCH₃, or any other carbon
containing by-product were ever detected in this chapter, as in Chapters 3 and 4. Catalyst samples were activated in situ in 10% H₂ in Ar (45 sccm total flow rate) at 300°C for 3 hours before being exposed to the reactant mixture. The catalyst behavior was verified by repeated experiments in each case using fresh catalysts. In all cases catalyst deactivation due to time on stream for relevant time lengths (~40 hours) was not found to affect the analysis or conclusions in this study.

5.3 Catalytic Activity Measurements.

5.3.1 Methanol Conversion

Figure 5-1 shows methanol conversion as a function of temperature for the three different Cu molarity preparations used in this study and the reference material tested under the same conditions. All microemulsion catalysts in Figure 1 were calcined at 300°C. It is evident in the figure that the Cu45ZrA catalyst exhibits the highest conversion of the prepared catalysts below 320°C and that the Cu22ZrA catalyst reaches the highest activity of the three microemulsion catalysts and the commercial reference.

The conversion maximum of the Cu22ZrA is shifted to a higher temperature compared to the other two microemulsion samples, but the catalyst retains 100% conversion of methanol over the temperature range of 320°C to 350°C. The Cu45ZrA catalyst exhibits a steady increase up to a maximum activity at 300°C above which the catalytic activity declines steadily. The catalyst prepared from the highest Cu molarity microemulsion used in this study, the Cu73ZrA, obviously does not achieve nearly the activity levels of the catalysts prepared from a lower Cu concentration in the microemulsion precursor. Reasons for this decrease in activity will be
Figure 5-1. Methanol conversion as a function of temperature for catalysts fabricated from different microemulsion precursors. — Cu73ZrA, —Cu45ZrA, —Cu22ZrA, —Commercial Reference. H₂O/CH₃OH ratio 1.4mol/mol and total liquid inlet flow 0.8 ml/hr. Contact time for all curves is 0.1 kg cat*sec/mmol CH₃OH.

explored later in this study. The dramatic decrease in activity in the Cu73ZrA catalyst was also reflected in the Cu73ZrB and Cu73ZrC catalysts. Therefore, additional figures with the Cu73Zr samples are omitted, although turn over frequency data is shown in section 5.4.3. Figure 5-2 shows methanol conversion for three different calcination temperatures for the 0.45 M Cu microemulsion catalysts. It is evident in the figure that the Cu45ZrA achieves the highest conversion of the three calcinations temperatures. It is also evident that the calcination at 700°C severely damages the catalytic activity, and the Cu45ZrC is the only sample that does not out perform the reference catalyst. Again, this trend was consistent for all “C” catalysts. It is also evident that there is not a large difference in performance of the Cu45ZrA and Cu45ZrB catalysts except for the spike in activity for Cu45ZrA at approximately 300°C. Since the Cu22ZrA catalyst had the highest activity of the catalysts shown in Figure 5-1, a comparison of the conversion versus temperature curves for all three Cu22Zr catalysts are shown in Figure 5-3.
Figure 5-2. Methanol Conversion as a function of temperature for catalysts of different calcination temperatures.  - Cu45ZrA, - Cu45ZrB, *- Cu45ZrC. Reactor conditions as in Figure 5-1.

Cu45ZrB catalyst is also shown to ease comparison between the two catalysts from different precursors both calcined at 500°C. For the decreased Cu molarity preparation method, it is evident that the calcination temperature of 500°C is actually preferred. The conversion curve is shifted to both higher conversions and lower temperatures for the Cu45ZrB sample. In fact, the Cu22ZrB attains the highest conversion at the lowest temperature of any catalyst in this study, reaching 100% conversion at 275°C and remaining at that conversion until 315°C. Likewise, the Cu73ZrB catalyst achieved higher conversion than the Cu73ZrA catalysts (not shown). In both cases the higher calcination temperature did not deactivate the catalyst but apparently has some beneficial consequence. It is evident that the 500°C calcination does not have the same beneficial effect for the 0.45 M Cu microemulsion precursor catalysts given that the activity of Cu45ZrA is higher than Cu45ZrB.
Figure 5-3. Methanol conversion for selected catalysts. **Cu45ZrB**, **Cu22ZrB**, **Cu22ZrA**. Reaction conditions as in Figure 5-1.

5.3.2 CO Selectivity

As mentioned in the introduction, the other main parameter of interest is CO selectivity. The CO selectivity over the three catalysts from different Cu molarity microemulsions and all calcinated at 300°C is shown in Figure 5-4.

Despite relatively large differences in methanol conversion shown in Figure 1, the catalysts all have similar CO selectivity levels below 320°C. The Cu45ZrA does show a slightly lower CO selectivity compared to the other two microemulsion samples, and has a lower CO selectivity than the reference catalyst at all temperatures above 220°C. However, it is the Cu22ZrA which maintains the lowest CO selectivity over the high end of the temperature range. Cu73ZrA is consistently, if only slightly, higher in CO selectivity than the other two microemulsion catalysts. This data represents the lowest CO selectivity curves in any chapter of this dissertation.
Figure 5-4. CO selectivity for catalysts fabricated from different microemulsion precursors. — Cu73ZrA, — Cu45ZrA, — Cu22ZrA, — Commercial Reference. Reactor conditions as in Figure 5-1.

Figure 5-5. CO selectivity as a function of temperature for catalysts of different calcination temperatures. — Cu45ZrA, — Cu45ZrB, — Cu45ZrC. Reactor conditions as in Figure 5-1.
Figure 5-5 compares the effect of calcination temperature on CO selectivity by showing the results from the Cu45ZrA, Cu45ZrB and Cu45ZrC catalysts. Again, there is only a small difference in CO selectivity between the three different calcination temperatures in that Cu45ZrC deviates from the other two catalysts and has a notably higher CO selectivity above 280°C. Surprisingly, Figure 6 shows that there is dramatic change in performance when the catalyst from the lower Cu concentration in the microemulsion preparation is calcined at 500°C. Catalyst Cu22ZrB has a much lower CO selectivity than the Cu22ZrA catalyst at the lower end of the temperature range, although this trend then reverses above 270°C. Consequently, there is a large variation in CO selectivity between the two Cu22Zr A and B catalysts, while the CO selectivities are similar for the Cu45ZrA and Cu45ZrB catalysts as shown in Figure 5. The commercial reference material has a consistently higher CO selectivity than any of the microemulsion samples above 260°C.

![Figure 5-6](image)

Figure 5-6. CO Selectivity for selected catalysts. — Cu45ZrB, — Cu22ZrB, — Cu22ZrA, — Commercial Reference. Reaction conditions as in Figure 5-1.
5.4 Catalyst Characterization Results

5.4.1 Temperature Programmed Reduction

TPR was used to provide some insight into the reducibility of the copper species on the various catalysts. Figure 7a, 7b and 7c show TPR spectra collected from different catalysts used in this study. Figure 7a shows the effect of the Cu molarity in the microemulsion precursor on the catalyst TPR profile. As is shown in the figure, decreasing the Cu molarity shifts the TPR profiles to lower temperatures. Since it has been noted in a related study that more active methanol reforming catalysts tend to have lower reduction temperatures [29], this trend is consistent with our data, i.e. Cu22ZrA is both more active and has a lower reduction temperature than Cu45ZrA (at least at reaction temperatures of 320°C and above). It is also noted that decreasing the Cu molarity forms smaller CuO crystals in the catalysts (See Section 3.4).

Intuitively, it is expected that smaller Cu particles would be easier to reduce, unless there are strong metal-support interactions that inhibit reduction. Evidently, any metal-support interactions in the microemulsion catalysts do not prevent reduction, and the catalysts follow the trend of smaller CuO particle sizes having a lower reduction temperature (Figure 5-7A and Section 5.3.4). It has been noted in a related study of the reduction of unsupported CuO nanoparticles that decreasing CuO particle size does not necessarily facilitate reduction of CuO to Cu [65] although this trend is not observed in the present study. The trend of increasing H2 peak consumption temperature with increasing calcinations temperature is also observed for the Cu22Zr and Cu73Zr catalysts (not shown).

As is shown in Figure 5-7B, higher calcinations temperatures shift the maximum H2 consumption towards higher reduction temperatures. If these catalysts follow the trend observed in the literature [29], then catalyst Cu45ZrA should have the lowest reduction temperature and
Figure 5-7. A) TPR profiles for Cu45Zr catalysts calcined at different temperatures. a. Cu45ZrA, b. Cu45ZrB, c. Cu45ZrC. B) TPR profiles for catalysts from different microemulsion precursors. a. Cu73ZrA, b. Cu45ZrA, c. Cu22ZrA. C) TPR profiles for Cu22Zr catalysts calcined at different temperatures. a. Cu22ZrA, b. Cu22ZrB, c. Cu22ZrC. TPR is performed with 100mg catalyst with 50 sccm of 5% H₂ in N₂ with a temperature ramp of 5°C/min. The dashed line marks the maximum H₂ consumption temperature for the bottom curve.
Figure 5-7. Continued

Cu45ZrC the highest, which is indeed observed. H₂ consumption for Cu45ZrA catalyst peaks at roughly 280°C, while that of Cu45ZrB peaks at 290°C and Cu45ZrC peaks at 305°C. Higher calcinations temperatures apparently form a CuO phase on the catalyst that is more resistant to reduction than CuO formed at lower temperatures. This could also be a particle size effect, i.e. the smaller particles at the lower calcination temperatures are easier to reduce than larger particles at higher calcination temperatures.

The trend of higher reduction temperatures due to higher calcinations temperatures is again evident for the Cu22Zr catalysts in Figure 5-7C. The only difference between the TPR profiles in of the Cu45Zr catalysts (Figure 5-7B) and those of the Cu22Zr catalysts (Figure 5-7C) is that the profiles of the Cu22Zr catalysts appear slightly narrower. This is likely because the smaller CuO particles in the Cu22Zr catalysts reduce more readily. Otherwise the trends in reduction temperature are very similar.
5.4.2 X-ray Diffraction Analysis

XRD spectra were collected for all catalysts both before and after exposure to reaction conditions. This data provides insight into the crystalline phases apparent in the sample and also to the particle sizes of each phase. Figure 5-8a shows the XRD spectra for the Cu45Zr catalysts after calcination from 2θ between 25° to 47.5°. The spectra shown in Figure 5-8b are for the same catalysts after exposure to reaction conditions over the same 2θ range.

Additional XRD data was collected for the other catalysts in the study to compute the particle sizes of the Cu and Zr phases. Through use of the Scherrer equation as described previously, particle sizes for the CuO and ZrO₂ phases can be easily computed. This information is summarized in Table 5-2.

As can be clearly seen in the table, the ZrO₂ particle size is nearly constant at 20nm. This is consistent with the particle size indicated by the manufacturer of the raw ZrO₂ nanoparticles and indicates that the nanoparticles are not significantly affected by the catalyst preparation and calcination processes. The CuO particle size, on the other hand, depends on both the Cu molarity in the microemulsion and also on the calcination temperature of the catalyst. CuO particle size steadily increases as a function of Cu concentration in the microemulsion for samples calcined at 300°C: CuO particle sizes are 12.1 nm for the catalyst prepared from the 0.22 M Cu aqueous phase precursor, 13.1 nm for the 0.45 M Cu precursor, and 13.6 nm for the 0.73 M Cu precursor. This trend is not evident at calcinations of 500°C or 700°C, with CuO particle size constant at just under 15 nm for 500°C calcination and 18 nm-19 nm for 700°C calcination regardless of the Cu molarity of the precursor. Increasing the calcination temperature of the samples also tends to increase the CuO particle size.
Figure 5-8. XRD spectra collected from a) Fresh Catalysts. b). Spent Catalysts. A. Cu45ZrA, B. Cu45ZrB, C. Cu45ZrC ■ monoclinic ZrO$_2$, ○ CuO, ★ Cu metal.
Table 5-2. Particle sizes for CuO/ZrO₂ catalysts.

<table>
<thead>
<tr>
<th>Catalyst Name</th>
<th>Cu Molarity in Aq phase</th>
<th>Calcination Temp</th>
<th>CuO Particle Size</th>
<th>Cu particle size</th>
<th>ZrO₂ particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu22ZrA</td>
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<td>14.8</td>
<td>31.2</td>
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</tr>
<tr>
<td>Cu22ZrC</td>
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<td>30.7</td>
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<td>28.0</td>
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<td>500</td>
<td>14.8</td>
<td>32.9</td>
<td>20.6</td>
</tr>
<tr>
<td>Cu73ZrC</td>
<td>0.73</td>
<td>700</td>
<td>19.1</td>
<td>30.2</td>
<td>19.1</td>
</tr>
</tbody>
</table>

This is seen in catalysts from all of the three Cu concentration precursors used. Increase in CuO size with increasing temperature is consistent with a sintering of CuO at higher temperatures. Interestingly, this trend is not consistent for the spent samples. In the case of the Cu45Zr samples, the trend actually reverses. Samples calcined at higher temperatures (B and C catalysts) have lower Cu particle sizes than the A samples. The fresh Cu45ZrC catalyst goes from a CuO particle size of 19.3 nm to a Cu particle size in the spent catalyst of 18.1 nm, a change of -7%. The fresh Cu45ZrA catalyst, on the other hand, has a CuO particle size of 13.1 nm but the spent catalyst has a Cu particle size of 22.0 nm, a change of +40%. Evidently the higher calcination temperatures, which inhibit CuO reduction to Cu also inhibit Cu particle growth through sintering. This trend is consistent in all samples: the Cu73ZrA particle size increases by 231% while that of Cu73ZrC increases by 58%. Another interesting feature of Table 5-2 is that despite similar CuO particle sizes for all three “B” catalysts, the resultant Cu particle size of the Cu45ZrB is drastically different from the other two samples. The catalyst with the intermediate Cu molarity in the precursor evidently undergoes a very different reduction
mechanism than the other two samples. It is also evident from Table 5-2 that altering the Cu molarity of the aqueous phase provides some degree of control over the CuO particle size in these catalysts.

### 5.4.3 Surface Area Analysis

The BET surface area data, active copper surface area and copper dispersion, are presented for all catalysts in Table 5-3. Additionally, Turnover Frequency (TOF) data at approximately 250°C and 300°C are presented in Table 5-3 for all catalysts.

#### Table 5-3. Surface Characteristics of Cu/ZrO₂ catalysts.

<table>
<thead>
<tr>
<th>Name</th>
<th>BET surface area (m²/g)</th>
<th>Cu surface area (m²/g)</th>
<th>Cu dispersion (%)</th>
<th>TOF(^a) 250°C (sec(^{-1}))</th>
<th>TOF 300°C (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu22ZrA</td>
<td>28.7</td>
<td>16.7</td>
<td>2.5</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu22ZrB</td>
<td>25.1</td>
<td>10.4</td>
<td>1.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Cu22ZrC</td>
<td>19.2</td>
<td>1.2</td>
<td>0.18</td>
<td>49.2</td>
<td>46.1</td>
</tr>
<tr>
<td>Cu45ZrA</td>
<td>26.2</td>
<td>11.6</td>
<td>1.8</td>
<td>0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu45ZrB</td>
<td>24.5</td>
<td>4.0</td>
<td>0.61</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu45ZrC</td>
<td>21.3</td>
<td>0.4</td>
<td>0.05</td>
<td>29.8</td>
<td>19.6</td>
</tr>
<tr>
<td>Cu73ZrA</td>
<td>22.1</td>
<td>10.2</td>
<td>1.6</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu73ZrB</td>
<td>15.7</td>
<td>9.9</td>
<td>1.8</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Cu73ZrC</td>
<td>17.6</td>
<td>5.9</td>
<td>0.90</td>
<td>7.8</td>
<td>8.7</td>
</tr>
<tr>
<td>Reference</td>
<td>68.0</td>
<td>20.2</td>
<td>3.1</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\(^a\) Turnover Frequency is defined as the molecules of H₂ produced per surface Cu atom per second.

The information contained in Table 5-3 shows that the Cu surface area is dramatically affected by both calcination temperature as well as the Cu concentration used in the microemulsion precursor. A lower Cu concentration in the aqueous phase of the microemulsion clearly results in higher Cu surface area. This correlates well with the CuO particle sizes from Section 5.3.4. It is also evident that the increase in calcination temperature adversely affects the
Cu surface area. The decrease in Cu surface area with increasing calcination temperature evident for the Cu45Zr catalysts in Table 5-3 is interesting given the decrease of the Cu particle size at the same calcination temperatures evident in Table 5-2 (smaller crystalline Cu particles but also smaller Cu surface area at higher calcinations temperatures). These results indicate the presence of a poorly crystalline or amorphous Cu phase on the catalysts after reaction that is not detected with XRD. This observation is further supported by the fact that the CuO particle size does correlate well with the Cu surface area data shown in Table 5-3 (smaller CuO particle sizes result in larger Cu surface areas after reduction of the CuO phase, as expected). The growth of an amorphous Cu phase for Cu/ZrO2 catalysts during reaction has been proposed previously [42]. This related study by Wang, et al. [42] proposed a dominant morphology change of the Cu phase at elevated calcinations temperatures, and that there is a spreading effect which increases the Cu surface area despite a growth in Cu particle size which occurred simultaneously. That study attributed the effect to the formation of a monoclinic ZrO2 phase at calcinations above 500°C. This is not a likely explanation in the present work given that the ZrO2 precursor used in the catalyst fabrication is monoclinic ZrO2 nanoparticles and there is no evidence that the ZrO2 is altered during the course of the reaction. However, with the monoclinic phase already present, the higher temperatures may increase metal-support interactions. In any case, the slight difference in the Cu particle size shown between the spent Cu45ZrA and Cu45ZrB samples cannot account for the more than 50% change in the Cu surface area between the same two samples. There must be a Cu phase which forms over the course of the reaction which is not visible on the XRD spectra and accounts for the differences in Cu surface area. Likewise, the ~2% change in Cu particle size between Cu22ZrB (31.2 nm) to Cu22ZrC (30.7 nm) catalysts is difficult to correlate with the 850% decrease in Cu surface area between the same two catalysts.
after reaction. Therefore in all cases there is not a simple correlation between Cu particle sizes determined via XRD and Cu surface area determined via N$_2$O titration. This difficulty has been noted in a closely related study [42].

The BET surface areas, on the other hand, follow the expected trend of decreasing surface area with increasing calcination temperature. This observation is more easily explained, as the growth of CuO particles seen in Table 5-2 likely results both a decrease in CuO surface area as well as clogging of pores in the ZrO$_2$ and thereby decreasing the total catalyst surface area as well.

The turnover frequency (TOF) data clearly indicates that the most active Cu species in the study are on the Cu22ZrC and Cu45ZrC. However, it is worth noting that all of the microemulsion catalysts fabricated for this study have a TOF higher (generally by more than an order of magnitude) than the commercial reference catalyst. TOF is also generally higher than has been attained in the preceding chapters. More active surfaces can clearly be made by using nanoparticles and the microemulsion fabrication technique. The peak in activity for the Cu45ZrA catalyst shown in Figure 5-1 is also clearly evident in the jump in TOF between 250°C and 300°C. Perhaps the most interesting TOF data is that of the Cu22ZrC and Cu45ZrC catalysts. The Cu surface area of these catalysts is very small compared to the “A” and “B” versions but what Cu remains at the surface is extremely active in the reforming reaction. The same trend is evident to a lesser extent in the Cu73Zr catalysts. A similar phenomenon of increasing TOF with a corresponding loss of Cu surface area has been documented by Günter, et al. [59]. The TOF numbers are an order of magnitude higher than the next most active catalyst, and a full three orders of magnitude more active than the reference catalyst. However, as shown in Figure 5-2, the methanol conversion over the Cu45ZrC catalyst peaks at a value 20% lower than conversion
of the Cu45ZrA and Cu45ZrB catalysts. A similar finding is evident in the Cu22Zr catalysts (not shown). This data indicates that a reasonable Cu surface area is necessary for catalytic activity, but the Cu surface area alone does not determine the activity of a catalyst. This is consistent with the results from Chapters 2 and 3. There is apparently a strong interaction between the Cu and Zr phases which is most evident at high calcination temperatures. This phenomenon has been noted by other researchers [38] who stated that “the powerful synergy between copper and zirconia” must be taken into account when determining catalyst activity. This synergy is not simply due to a phase change from tetragonal to monoclinic ZrO$_2$ as has been proposed in the past [38,42] since the ZrO$_2$ in this study is monoclinic ZrO$_2$ in all catalysts.

5.4 Water Gas Shift Equilibrium

Figure 5-9 shows the $\Phi$ ratio shown in previous chapters plotted on a semi-log plot as a function of temperature for the Cu22ZrA, Cu45ZrA, Cu73ZrA, and Cu22ZrB catalysts. There are dramatic differences in performance between the different catalysts. The Cu73ZrA shows CO levels that are similar to those seen in the catalysts used in Chapters 2 and 3. The CO levels are above the WGS equilibrium level ($\Phi < 1.0$) at all temperatures. This indicates further that this catalyst holds little promise in PEM applications. The Cu22ZrA and Cu22ZrB on the other hand show CO levels that are much lower ($\Phi >> 1.0$) than what can be explained by WGS equilibrium. Additionally, the system is the furthest from WGS equilibrium that has been documented in any part of this study. This demonstrates the superior performance of these catalysts.
5.5 Conclusions

This study has demonstrated that manipulation of the catalyst preparation procedure using microemulsion catalyst precursors affords some degree of control over both the CuO particle size and the Cu surface area of the resulting catalysts. Catalysts fabricated using this microemulsion technique exhibit an amorphous Cu phase which develops over the course of the reaction, leading to Cu surface area measurements which do not correlate well with the XRD particle size data. Conversions attained using the microemulsion fabrication technique are higher than what can be attained using a commonly available commercial reference. Additionally, CO selectivity levels are dramatically below those achieved using the same commercial reference. This leads to the conclusion that the combination of using nanoparticle ZrO₂ and a microemulsion catalyst preparation technique results in superior catalyst performance over commercially available alternatives. There is apparently some advantage to using a calcination temperature of 500°C in these CuO/ZrO₂ systems, since catalysts calcined at 500°C demonstrate...
either similar, if not superior, methanol conversion but lower CO selectivity over the same
temperature range. This increase in catalytic activity coincides with a decrease in Cu surface
area of the catalysts, which indicates that Cu surface area alone is not responsible for catalytic
activity. The change in catalytic activity at 500°C calcination is not due to a phase change in the
ZrO$_2$ support since the ZrO$_2$ is monoclinic in all cases. Calcinations of 700°C result in extremely
reactive Cu surfaces, although these catalysts are apparently crippled by the sintering of the CuO
phase during calcination.

The results of this study further demonstrate that the microemulsion preparation
technique is preferable to the simpler impregnation and precipitation techniques used in Chapters
2 and 3. It is also apparent that there is little need for tertiary or quaternary systems and that the
binary Cu/ZrO$_2$ catalysts are promising in the methanol reforming reaction if the microemulsion
preparation procedure is used.

5.6 Acknowledgement

Special Thanks is owed to Miss Corene Cano and Miss Sara DiBiase for their help in the
preparation of the microemulsion catalysts used in this chapter.
CHAPTER 6
SUMMARY AND CONCLUSIONS

This study covered several different methanol reforming catalyst formulations, multiple preparation techniques, and many characterization procedures. Several conclusions can be made drawn from the four complete catalyst studies in this work. Chapter 2 clearly demonstrated that there was an advantage to using nanoparticle Al₂O₃. The most revealing piece of data from this study was that the Turnover Frequency (TOF) of the nanoparticle containing catalysts was dramatically higher than that of the commercial reference material. Another observation that was made became a reoccurring theme through the different studies contained herein. Namely, even thought the 5/5/90 CuO/ZnO-Al₂O₃ catalyst had a Cu surface area approaching 60 m²/g, it still did not surpass the catalytic activity of the other samples, which had much lower Cu surface areas. This demonstrated that simply having a high Cu surface area is not sufficient to make a highly active reforming catalyst. This observation was confirmed repeatedly in the later studies. Chapter 2 also demonstrated that Al₂O₃ supports do ultimately retard catalyst activity and if they are to be used in methanol reforming catalysts they must be used either in relatively low concentrations or in conjunction with an alternative oxide support. This lead naturally to the study done involving ZrO₂ and CeO₂ documented in Chapter 3.

The work done with CeO₂ and ZrO₂ supports quickly demonstrated that ZrO₂ is the preferable promoter. The CeO₂ containing catalyst showed little promise. The most important observation in Chapter 3 is that there is certainly an advantage to using nanoparticle ZrO₂ in quaternary CuO/ZnO/ZrO₂/Al₂O₃ catalyst, but that using simple impregnation of ZrO₂ nanoparticles is insufficient for making highly active reforming catalysts. This was evidenced by the relatively low activity of the CuZnZr-70-NP catalyst where nanoparticle ZrO₂ was used as the support. Hence the need for the nanoparticle Al₂O₃ to ensure a sufficient catalyst surface area
in these systems. At the end of the study of the ZrO$_2$ containing catalysts in Chapter 3 it was unclear whether the high activity of the 10% nanoparticle ZrO$_2$ catalyst was due to the presence of the nanoparticles or the fact that this was the only catalyst to contain a monoclinic ZrO$_2$ phase. Further information on the electronic structure of the CuO/ZnO/ZrO$_2$/Al$_2$O$_3$ catalyst was needed.

Detailed XPS studies of the three 10% ZrO$_2$ containing catalysts were subsequently performed. This study was shown in Chapter 4. XPS data showed very clearly that there is a strong charge transfer between the Cu and ZrO$_2$ species that is most pronounced in the 10% nanoparticle ZrO$_2$ catalyst. This charge transfer interaction results in an electron deficient Cu species (and electron rich ZrO$_2$) species which is responsible for the increase in catalytic activity. The partially oxidized Cu species also appears useful in the suppression of the reverse water gas shift reaction: the partially oxidized Cu species tends to promote the oxidation of CO to CO$_2$.

The next step was to attempt to exploit the Cu-Zr interaction without the need of Al$_2$O$_3$ supports. In order to exploit the synergy documented in Chapter 4 while avoiding the problems with impregnation of ZrO$_2$ supports seen in Chapter 3, new catalyst preparation techniques had to be employed. The microemulsion preparation procedure is inherently more difficult than the relatively simple impregnation and precipitation procedures used in the earlier studies. However, as seen in Chapter 5 the resultant catalysts are dramatically superior to the other tertiary and quaternary systems. The catalytic activity was further promoted through an increased calcination temperature. This was true despite the fact that the Cu surface area decreased with the increasing calcination temperatures. It was further shown that a degree of control over the CuO particle size could be gained by manipulating the characteristics of the microemulsion precursor.

The superior performance of the binary Cu/ZrO$_2$ catalysts is especially evident in Figure 5-9. The water gas shift equilibrium plot shows very clearly that the Cu$_{22}$ZrA, Cu$_{22}$ZrB and
Cu45ZrA catalysts are able to effectively suppress the reverse water gas shift reaction to an extent not seen in the previous studies. Certainly, the decrease in the excess of H2O used in the feed in this study contributes to the shifting of the equilibrium of the system. However, in any case the CO selectivity curves seen in Figure 5 of Chapter 5 are superior to any of the CO selectivity data seen in earlier studies.

Given the promising results seen in Chapter 5, it is logical that future studies of this work would seek to continue to exploit the Cu-Zr interaction seen in Chapters 4 and 5. Specifically, detailed XPS studies of the catalysts used in Chapter 5 have at the time of this publication not been performed. It would be useful to examine the electronic structure of the binary Cu/ZrO2 systems to determine if the charge transfer seen in the quaternary systems is further enhanced through the microemulsion preparation. Additionally, very recent results in the literature suggest that there may well be a benefit to using yttria stabilized zirconia (YSZ) supports in methanol reforming. At the time of this publication no work has been done involving either nanoparticle YSZ or YSZ catalyst prepared using the microemulsion procedure detailed in Chapter 5.

In summary, the key to fabricating highly active Cu and Cu-ZnO based methanol reforming catalysts appears to be not simply making high surface area nanomaterials but rather using nanomaterials to promote strong interactions between the catalyst components which results in highly active catalyst surfaces. Charge transfer relationships between the active phase and support seem to be the most important of these interactions, which results in catalyst activity levels not previously attainable using more traditional catalyst materials and preparation methods.
REFERENCES


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BIOGRAPHICAL SKETCH

Sam Jones was born in Columbus, Ohio in 1981. His family moved to Waco, Texas, in 1985; Austin, Texas, in 1988, and finally to Tampa, Florida, in 1994. Sam attended high school in Tampa and got his first job working on a fishing boat near his home. He graduated second in a class of 560 graduating seniors with a perfect 4.0. He was admitted to Rice University in Houston, Texas, in August 2000. He finished his bachelor’s degree in chemical engineering with a focus in environmental engineering in May 2004 and graduated cum laude. During his time at Rice, Sam worked as a teaching assistant for the Organic Chemistry Department as well as the Communications Department.

Sam entered the University of Florida Department of Chemical Engineering Ph.D. program in August 2004. He joined Dr. Helena Weaver’s research group and, along with Luke Neal, was one of her first two students. His research focused on development of methanol reforming catalysts for on-board hydrogen production in passenger vehicles. Other research interests include reaction engineering, surface chemistry, and fuel cells. Sam served as the social chair for the Graduate Association of Chemical Engineers (GRACE) from 2005-2006 and as GRACE president from 2006-2007. In 2007 he completed a semester as a research assistant at the National Aeronautics and Space Administration (NASA) where he received a New Product Development award for his work in polymeric “smart coatings.” After graduation, he plans to join Intel Corporation in Portland, Oregon, as a process engineer.