#### **RESEARCH RESULTS**

## I. Cu/ZrO<sub>2</sub> CATALYSTS FOR ALCOHOL SYNTHESIS

#### Introduction

Since Natta's review in 1955 on the catalytic synthesis of methanol from synthesis gas over both copper-containing and copper-free catalysts [Natta, 1955], much research has focused on the conventional Cu/ZnO-based catalysts for methanol production from synthesis gas (H<sub>2</sub>/CO/CO<sub>2</sub>) [Solymosi, 1968; Kung, 1980; Klier, 1982; Bart and Sneeden, 1987; Herman, 1991; Hindermann et al., 1993; Fox, 1993]. Efforts have been made to understand the nature of the catalytically active sites, as well as the mechanism of methanol and higher alcohol formation [Herman et al., 1979; Mehta et al., 1979; Klier et al., 1982; Takahama et al., 1983; Bridgewater et al., 1983; Friedrich et al., 1983; Fleisch and Mieville, 1984; Klier et al., 1988; Nunan et al., 1988; Nunan et al., 1989a; Nunan et al., 1989b; Klier et al., 1993]. It was found that methanol yields could be greatly enhanced by the addition of small amounts of CO<sub>2</sub> and H<sub>2</sub>O to the synthesis gas feed [Klier, 1982; Vedage et al., 1984a; Vedage et al., 1984b]. Doping Cu/ZnO catalysts with cesium has also been reported to increase the productivities of methanol and higher alcohols, especially isobutanol [Nunan et al., 1988; Nunan et al., 1986; Bybell et al., 1986; Klier et al., 1984].

Recently, zirconia-supported copper catalysts have been shown to be active for methanol synthesis [Denise and Sneeden, 1986; Amenomiya, 1987; Denise et al., 1989; Gasser and Baiker, 1989; Koeppel et al., 1991 and 1992; Schild et al., 1990]. Although it is known that methanol can be synthesized from  $CO/H_2$  or  $CO_2/H_2$ , few studies on the relative effectiveness of  $CO/CO_2$  in the feed mixture have been reported for the Cu/ZrO <sub>2</sub> catalysts [Denise and Sneeden, 1986; Bartley and Burch, 1988; Denise et al., 1989]. Denise et al. [1989] studied the effect on methanol productivity upon gradual replacement of  $CO_2$  by CO and of CO by  $CO_2$  over  $Cu/ZrO_2$  catalysts at different pressures. At atmospheric pressure, the methanol productivity profile was reported to be similar to that obtained over the Cu/ZnO catalysts, although the magnitude of enhancement and optimum concentration were different. However, methanol yields were slightly different when binary CO/H<sub>2</sub> synthesis gas was utilized compared to the use of a CO<sub>2</sub>/H<sub>2</sub> feed gas at atmospheric pressure. The  $CO/H_2$  mixture yielded more methanol than the  $CO_2/H_2$ However, the same research group reported that CO<sub>2</sub>/H<sub>2</sub> produced more mixture. methanol than CO/H2 when higher reaction pressure (1 MPa) was used [Denise and Sneeden, 1986]. It is apparent that the relative effectiveness of  $CO/H_2$  or  $CO_2/H_2$  in methanol synthesis varies with reaction conditions. Bartley and Burch [1988] have also indicated that reaction conditions have a strong influence on the role of  $CO_2$  in the feed.

One of the major goals of this study was to clarify the influence of  $CO_2$  on the activity of  $Cu/ZrO_2$  catalysts. Since carbon dioxide and water are complementary *via* the water gas shift reaction, a water injection experiment was designed to demonstrate the similarities or differences of  $H_2O$  compared to  $CO_2$  in the catalytic system. To our knowledge, this type of experiment had not previously been performed. With Cu/ZnO-based catalysts, cesium doping has been shown to promote the synthesis of methanol and higher alcohols, while suppressing dimethylether production by neutralizing acid sites on the Cu/ZnO catalysts, especially those on alumina- or chromia-supported catalysts [Amenomiya, 1987; Nunan et al., 1989a]. Cesium doping of the Cu/ZrO<sub>2</sub> catalysts.

# Experimental

## **Catalyst Preparation**

The 10/90 mol% and 30/70 mol% Cu/ZrO<sub>2</sub> and pure ZrO<sub>2</sub> catalysts used in this study were prepared by the coprecipitation method described previously for the Cu/ZnO catalysts [Herman et al., 1979; Himelfarb et al., 1985]. This procedure consisted of the initial precipitation of hydroxycarbonate precursors from nitrate solutions of copper and zirconium at a constant pH of 7 using a sodium carbonate solution. The resulting slurry was washed with warm water, filtered, and then dried at room temperature overnight. The dried precursors were crushed, sieved to 20-35 mesh, and then treated by stepwise calcination to form the final catalysts. Calcination was carried out in air to final temperatures of 623, 673, and 773K, which were held for 3 hr. Cesium doping of the 10/90 mol% Cu/ZrO<sub>2</sub> catalyst was achieved by addition of the calcined catalyst to a N<sub>2</sub>purged solution of cesium formate, followed by evaporation to dryness under flowing N<sub>2</sub>. The doped catalyst was then re-calcined in air at 623K for 3 hr. The compositions of the three catalysts studied (10/90, 30/70, and 3% Cs-10/90) were verified by chemical analysis.

## **Catalyst Characterization**

With a Micromeritics Gemini 2360 instrument, the BET technique was employed to measure the specific surface areas of catalysts before and after catalytic testing. The samples were heated at 523K for 2 hr before measurement, with nitrogen used as the adsorbent at 77K (-196°C). Surface areas were computed by built-in software dedicated to the system.

X-Ray powder diffraction (XRD) patterns of the catalysts were obtained using a Philips APD1700 automated powder diffractometer. Cu  $K_{\alpha}$  radiation ( $\lambda = 0.154$  nm) was used as the X-ray source, and the instrument was operated at 45 kV and 30 mA. Patterns were obtained for  $2\theta = 5^{\circ}$  to  $85^{\circ}$  at a rate of 1.0 deg/min with an angle increment of 0.020°.

Transmission electron microscopy (TEM) was carried out with a Philips 400T electron microscope operated at 120 kV. To prepare a sample for microscopy, a few milligrams of finely powdered catalyst were dispersed in ethanol. One drop of this solution was then placed on a carbon-coated 200 mesh copper grid, and evaporation left the fine catalyst powder adhering to the grid surface. All the TEM observations were time independent, indicating the electron beam had insignificant effect on the specimens.

The X-ray photoelectron spectra (XPS) were taken with a Scienta ESCA-300 spectrometer with a monochromatic Al  $K_{\alpha}$  (1486.7 eV) X-ray source. XPS samples were prepared by pelletizing the finely powdered catalyst. The sample was then inserted into the specimen chamber that was maintained at 10<sup>-9</sup> Torr or lower. Step sizes of 1.0 eV for survey scans and 0.1 eV for restricted scans were used. The instrument was operated such that the Fermi level width was 0.4 eV for silver. The surface charging problem caused by the liberation of photoelectrons was minimized by flooding the sample surface with a beam of low energy electrons (5-10 eV). The XPS data were recorded by a microcomputer and analyzed using ESCA-300 software. For all the spectra, Shirley background was subtracted, and a Voigt function was used to analyze the various peaks.

## **Kinetic Catalytic Testing**

Catalyst testing was carried out in a tubular fixed-bed downflow stainless steel reactor. The setup of this reactor system has been described previously [Herman et al., 1979]. Since iron carbonyl (Fe(CO)<sub>5</sub> formed through contact of CO with Fe-containing surfaces) is known to deactivate Cu/ZnO-based catalysts [Bodgan et al., 1988], steps were taken to minimize its formation. The reactor was lined internally with copper, and the axial thermocouple was fitted inside a copper well before it was placed inside the reactor. In addition, a charcoal trap was placed in the CO inlet line between the CO cylinder and the reactor system. In the case of the water injection experiments, H<sub>2</sub>O was passed through a preheater maintained at 403-423K before entering the reactor.

In each of the kinetic tests, 2.0 g of the selected catalyst were diluted with 5 ml of 0.5 mm Pyrex beads and loaded into the middle portion of the reactor. The remaining portions of the reactor were packed with 3-4 mm Pyrex beads. In addition, a blank reactor containing only Pyrex beads was tested, as well as a Cu-free  $ZrO_2$  sample, in order to establish any baseline catalytic activity. Both H<sub>2</sub> and CO gas streams were regulated by mass flow controllers (Linde, Model 5851-B2E1A). For the experiments with CO<sub>2</sub> addition, 30/70 vol% CO/H<sub>2</sub> and 30/70 vol% CO<sub>2</sub>/H<sub>2</sub> cylinders were used for easy composition adjustment. In the water injection experiments, distilled water was delivered by a Gilson Model 302 high-pressure liquid pump. As noted above, liquid water was vaporized in a preheater section of the reactor, where it was mixed with the inlet gas flow. All lines after the reactor were heated to prevent condensation of products. Adjustment and maintenance of system pressure were achieved by a Grove Model SD-91XW back pressure regulator. After the back pressure regulator, a liquid nitrogen- cooled trap was available for product condensation and collection.

Kinetic testing experiments were carried out at a system pressure of 7.6 MPa, with gas hourly space velocity (GHSV) of either 5500 or 6120 l/kg cat/hr. The H<sub>2</sub>/CO ratio was varied from 0.45 to 2.33, whereas the reaction temperature was within the range of 523 to 603K. Under each set of conditions, steady-state activity was attained within 4 hr, and conditions were then maintained for 24-48 hr before they were changed to other conditions. For the CO<sub>2</sub> injection experiments, CO<sub>2</sub> was varied from 0 to 30% of the total inlet flow by replacement of CO such that CO + CO<sub>2</sub> was always equal to 30% of the total flow. In the water injection experiments, the water liquid flow rate was varied in the range of 0-6 ml/min, where the 6.0 ml/min liquid flow rate corresponds to approximately 7.5 ml/min of vapor. Catalyst pretreatment consisted of reduction in 2% H<sub>2</sub>/N<sub>2</sub> at 523K and atmospheric pressure. The reduction process was monitored by water production as detected by gas chromatography (GC). Reduction was considered complete when the intensity of the peak for water became insignificant on the chromatogram.

Reaction products were monitored and analyzed by an on-line dedicated Hewlett-Packard Model 5890 gas chromatograph coupled to a Hewlett-Packard 3396 integrator and a personal computer for data collection and manipulation with ChromPerfect (Justice Innovations) software. The reactor exit stream was sampled every 20-60 min *via* an automated in-line heated Valco sampling valve. Both capillary PoraPLOT Q (Chrompack) and packed Porapak Q (Supelco) columns were used to separate the products that were then detected by TCD or FID. Peak identification was verified by liquid product collection followed by GC/MS analysis. Space time yields (STY) of the products were calculated by carbon balance. The total productivity closely matched data obtained from liquid collection.

### Results

#### **Catalyst Characterization**

**BET** Surface Areas. The BET surface areas of 10/90 and 30/70 Cu/ZrO<sub>2</sub> catalysts calcined at various temperatures are given in Table 1. The surface area of the 10/90 catalyst varied from 63 m<sup>2</sup>/g when calcined at 773K to 148 m<sup>2</sup>/g when calcined at 623K. Likewise, the surface area of the 30/70 catalyst ranged from 25 m<sup>2</sup>/g at 773K to 78 m<sup>2</sup>/g at 623K. Samples calcined at 623K were chosen for further study because they exhibited the highest surface areas. After kinetic testing, the 10/90 catalyst surface area decreased by approximately 50%, changing from 148 to 72 m<sup>2</sup>/g. As shown in Table 1, cesium doping had no significant effect on the surface area of the 10/90 catalysts that were used for after kinetic testing.

# Table 1. BET surface areas for the $Cu/ZrO_2 = 10/90$ and 30/70 mol% catalysts.

Cu/ZrO <sub>2</sub> Catalyst	Calcination Temp. (K)	BET Surface Area (m <sup>2</sup> /g)
10/90	773	63
10/90	673	112
10/90	623	148
10/90	623, after testing	72
3% Cs/10/90	623, after testing	73
30/70	773	25
30/70	673	73
30/70	623	78
30/70	623, after testing	55

In all cases, the calcination temperature indicated was maintained for 3 hr.

*X-Ray Diffraction Analysis.* Figure 1 shows the X-ray diffraction patterns obtained from the  $Cu/ZrO_2 = 10/90$  catalyst calcined at three different temperatures. The patterns from samples calcined at 623 and 673K did not exhibit any sharp peaks, indicating the absence of crystallinity. However, the sample calcined at 773K showed crystalline structure indicated by prominent peaks in the XRD pattern. This pattern was identified as that of either the tetragonal or cubic phase of zirconia. No signature for crystalline copper oxide was observed. The XRD pattern of the tested sample, which had been calcined at 623K before catalytic testing was initiated, also indicated the presence of crystalline zirconia. Even after kinetic testing (to be described), there was no XRD evidence for the presence of crystalline copper oxide.

The Cu/ZrO<sub>2</sub> = 30/70 catalyst samples calcined at the above-mentioned three temperatures gave XRD patterns similar to those observed with the Cu/ZrO<sub>2</sub> = 10/90 samples. The XRD patterns of all of the catalysts calcined at low temperatures (623 and 673K) demonstrated the amorphous character of the samples. Crystalline zirconia was observed in the samples calcined at high temperature (773K), as well as in the tested catalyst.



**Relative Intensity (Counts)** 

 $2\Theta$  (degrees)

Figure 1. X-Ray diffraction patterns for the  $Cu/ZrO_2 = 10/90$  catalyst samples calcined at the three different temperatures of (a) 623K, (b) 673K, and (c) 773K and (d) after catalytic testing.

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The patterns were obtained by scanning from  $5-85^{\circ}$  at a rate of 1 deg/min.

**Transmission Electron Microscopy Study**. Both of the tested Cu/ZrO<sub>2</sub> catalysts were examined by transmission electron microscopy (TEM), and a micrograph obtained from the 10/90 Cu/ZrO<sub>2</sub> tested catalyst is shown in Figure 2. The corresponding selected area diffraction (SAD) pattern is given in Figure 3. It is evident from the micrograph that two phases of different contrast are present. Copper, which is more electronically dense than zirconia, appears as a dark region in the electron micrograph. The zirconia matrix gives rise to relatively lighter regions in the micrograph. Lattice spacings obtained from the SAD pattern correspond to reference data for copper [ASTM card # 4-836, JCPDS-ICDD (1995)]. The appearance of less intense concentric rings is due to the formation of copper particles. It was found from measurements of the dimensions of dark spots in the electron micrographs that the metallic copper particle size was  $\approx$ 4.0 nm for the 10/90 sample and  $\approx$ 5.5 nm for the 30/70 sample.

**X-Ray Photoelectron Spectroscopy.** Figure 4 shows the X-ray photoelectron spectroscopy (XPS) survey scan over the 0 to 1350 eV range for the 3 mol% Cs-doped  $Cu/ZrO_2 = 10/90$  catalyst after testing for catalytic activity. Narrow range XPS spectra of regions of particular interest are presented in Figure 5. The Zr  $3d_{5/2}$  peak (182.5 eV) was used as a reference since ZrO<sub>2</sub> is believed to be a better spectral reference than the C *Is* line in this system. The Cu 2p spectrum is shown in Figure 5a. The major peak at 932.8 eV is the Cu 2p signal, whereas the smaller peak on the lower binding energy side is believed to arise from a Cs Auger line. Figure 5b shows the spectrum for Zr 3d. The two well-separated peaks correspond to the Zr  $3d_{5/2}$  and Zr  $3d_{3/2}$  lines, respectively, with a 2.38 eV separation. Figure 5c is the spectrum for the Cs 3d core level. The location of the peak at 724.8 eV signifies the presence of Cs<sup>+</sup> species. The O *Is* spectrum obtained from the tested catalyst is shown in Figure 5d, and the shoulder on the well-resolved O *Is* peak indicates that two different states of oxygen are present in the catalyst.

The surface composition of the sample was estimated using standard analysis procedures by normalizing the peak areas with Scofield cross sections of the individual elements. The surface composition of the catalyst (in terms of metal ratio) was found to be Cs/Cu/Zr = 11/16/73 mol%. The higher cesium concentration on the catalyst surface indicates that the alkali metal was located on the surface of the catalyst and was uniformly dispersed.



Figure 2. Transmission electron micrograph from the  $Cu/ZrO_2 = 10/90$  tested catalyst.







Figure 4. XPS survey scan of the tested 3% Cs - 10/90 Cu/ZrO<sub>2</sub> catalyst.

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Figure 5. XPS spectra of the 3% Cs - 10/90 Cu/ZrO<sub>2</sub> tested catalyst in the (a) Cu 2p region, (b) Zr3d region, (c) Cs 3d region, and (d) O 1s region.

## **Kinetic CatalyticTests**

Kinetic testing was first carried out in a blank reactor run in which the reactor was packed only with Pyrex beads. This run was carried out at a temperature of 523K and with a synthesis gas of  $H_2/CO = 2.33$  with GHSV = 6120 l/kg cat/hr. Pure ZrO<sub>2</sub> was also tested under these same reaction conditions. In neither case was any significant product formation observed.

*Effect of CO*<sub>2</sub> *in the Synthesis Gas.* The effect of CO<sub>2</sub> on the activity of the Cu/ZrO<sub>2</sub> = 10/90 catalyst was investigated at a reaction temperature of 523K. In this experiment, the CO reactant was replaced stepwise by CO<sub>2</sub> so that the sum of CO + CO<sub>2</sub> was constant at 30 mol% of the reactant mixture, with H<sub>2</sub> = 70 mol%. Figure 6a shows that as the CO <sub>2</sub> concentration was increased, the methanol STY progressively increased. Methanol STY initially exhibited a sharp increase up to a CO<sub>2</sub> concentration of approximately 5%. Beyond this concentration, a more gradual increase of methanol STY was observed. After stepwise variation of CO<sub>2</sub> concentration from 0% (30% CO) to 30% (0% CO), the system was returned to the initial conditions (0% CO<sub>2</sub>, with H<sub>2</sub>/CO = 70/30 mol%) in order to check for catalyst deactivation. Methanol STY for the second testing sequence was found to be only slightly lower than those observed in the first test, and the trend indicated by the three second test CO<sub>2</sub> concentrations (7.5, 22.5, and 26.5%) corresponded closely to that of the first test.

Dimethyl ether (DME) was also observed as a product over this catalyst, and the DME STY as a function of CO<sub>2</sub> concentration is depicted in Figure 6b. In all cases, the productivity of DME was appreciably less then that of methanol. Upon increasing the CO<sub>2</sub> content of the synthesis gas mixture from 0 to 5% mol%, corresponding to H<sub>2</sub>/CO/CO<sub>2</sub> = 70/25/5, a dramatic decrease in the productivity of dimethyl ether was observed. The DME STY then became rather constant at  $\approx 1$  g/kg cat/hr after that point. Productivities for dimethyl ether obtained in the second test were in very good agreement with those observed in the first testing sequence.



Figure 6. Effect of CO<sub>2</sub> addition on production of (a) methanol and (b) dimethyl ether over the Cu/ZrO<sub>2</sub> = 10/90 catalyst with  $H_2/(CO + CO_2) = 2.33$  at 7.6 MPa and 523K with GHSV = 6120 l/kg cat/hr.

*Effect of Reaction Temperature.* The CO hydrogenation reactions were carried out at temperatures of 523, 548, 563, 583, and 603K with  $H_2/CO = 0.45$  and GHSV = 5500 l/kg cat/hr for both the Cu/ZrO<sub>2</sub> = 10/90 and 30/70 catalysts; the results are shown in Figure 7. For the 10/90 catalyst, the methanol STY remained nearly unchanged, while there was a small maximum in productivity of methanol around 563K for the 30/70 catalyst. In contrast, the reaction temperature had a strong positive effect on dimethyl ether STY for both samples. Dimethyl ether productivity increased approximately 20-fold when the temperature was raised from 523 to 603K.





*Effect of H<sub>2</sub>/CO Ratio.* Results of the investigation of the influence of H<sub>2</sub>/CO ratio on the product productivities are shown in Figure 8. The H<sub>2</sub>/CO ratio was varied from 0.45 to 2.33 at a reaction temperature of 583K, with a GHSV of 5500 l/kg cat/hr. For the Cu/ZrO<sub>2</sub> = 10/90 sample, the methanol STY changed from approximately 23 g/kg cat/hr at H<sub>2</sub>/CO = 0.45 to approximately 30 g/kg cat/hr when the H<sub>2</sub>/CO molar ratio was increased to 2.33. The corresponding values for methanol synthesis over the 30/70 catalyst were approximately 24 and 38 g/kg cat/hr, respectively. Thus, methanol synthesis productivity increased as the H<sub>2</sub>/CO molar ratio was increased. An opposite trend was observed for dimethyl ether synthesis, with STY decreasing from approximately 60 to 44 g/kg cat/hr for both catalysts as the H<sub>2</sub>/CO synthesis gas ratio was increased.



Figure 8. Effect of  $H_2/CO$  ratio on methanol and dimethyl ether synthesis over the  $Cu/ZrO_2 = 10/90$  and 30/70 catalysts at 7.6 MPa, 583K, and GHSV = 5500 l/kg cat/hr.

Effect of Water Injection into the Synthesis Gas. Since a significant effect on the catalytic behavior of the Cu/ZrO<sub>2</sub> catalyst was observed upon adding CO<sub>2</sub> to the synthesis gas, the effect of the presence of water in the reactant mixture was examined. The experiment was carried out at 523K with  $H_2/CO = 2.33$  and GHSV = 6210 l/kg cat/hr. Water injection rates of 0.5, 1.0, 2.0, 3.0, 5.0, and 6.0 ml/min were utilized, where the highest liquid flow rate of 6.0 ml/min corresponded to a synthesis gas composition of  $H_2/CO/H_2O = 67/29/4$  mol%. Again, the products observed were methanol and dimethyl ether. As expected,  $CO_2$  was also produced as a result of the water gas shift reaction. Methanol productivity showed a gradual decrease from 25 g/kg cat/hr when no water was injected (H<sub>2</sub>/CO/H<sub>2</sub>O = 70/30/0) to 4 g/kg cat/hr when water was injected at 6.0 ml/min  $(H_2/CO/H_2O = 67/29/4)$ , as indicated in Figure 9. Likewise, dimethyl ether productivity also decreased upon water injection, and the dimethyl ether STY was nearly zero for the higher water injection rates. In contrast, the formation of CO<sub>2</sub> via the water gas shift reaction showed a continuous increase with the amount of water injected, wherein the CO<sub>2</sub> STY increased from 8 g/kg cat/hr with no water injected to 131 g/kg cat/hr at the highest water injection rate of 6.0 ml/min. It is noted that although the experimental procedures were different, the CO<sub>2</sub> generated by the water gas shift reaction did not promote methanol synthesis, as was the case when the CO reactant was progressively replaced by  $CO_2$ .



Figure 9. Effect of  $H_2O$  injection on the productivity of methanol, dimethyl ether, and carbon dioxide over the 10/90 Cu/ZrO<sub>2</sub> catalyst with an initial synthesis gas composition of  $H_2/CO = 2.33$  at 7.6 MPa and 523K with GHSV = 6120 l/kg cat/hr.

*Effect of Cesium Doping of the Cu/ZrO*<sub>2</sub> = 10/90 Catalyst. Since cesium doping is known to enhance the productivity of methanol over Cu/ZnO catalysts [Klier et al., 1984; Nunan et al., 1986; Bybell et al., 1986; Nunan et al., 1988], this effect was investigated over the Cu/ZrO<sub>2</sub> = 10/90 catalyst by doping the catalyst with 3 mol% Cs. Data obtained from both the doped and undoped 10/90 Cu/ZrO<sub>2</sub> catalysts as a function of reaction temperature are presented in Figure 10. As can be seen, cesium doping greatly promoted the productivity of methanol. Promotional effects were observed at each of the five temperatures studied, with a maximum at 583K, in contrast to the undoped catalyst that exhibited a nearly constant methanol productivity. As can be seen in Figure 10, cesium doping significantly diminished the productivity of dimethyl ether. The trend in dimethyl ether productivity observed over the two catalysts with temperature was similar, but the doped catalyst showed consistently lower productivity of the ether.



Figure 10. Effect of reaction temperature on the production of methanol and dimethyl ether over the 3 mol% Cs-doped 10/90 and Cs-free 10/90 Cu/ZrO<sub>2</sub> catalysts from  $H_2/CO = 0.45$  synthesis gas at 7.6 MPa and with GHSV = 5500 l/kg cat/hr.

The influence of the H<sub>2</sub>/CO molar ratio on the productivity obtained over the Cs-doped Cu/ZrO<sub>2</sub> = 10/90 catalyst was also investigated. The STYs of the two major products as a function of the H<sub>2</sub>/CO reactant ratio for doped and undoped samples are given in Figure 11. These kinetic tests were performed at a reaction temperature of 583K with GHSV = 5500 l/kg cat/hr. The trends in STY of methanol and dimethyl ether synthesis as the H<sub>2</sub>/CO ratio was varied were similar for the two catalysts. As indicated in the Figure 11, cesium doping greatly enhanced methanol productivity and decreased the productivity of dimethyl ether. The maximum methanol productivity was observed with H<sub>2</sub>/CO in the range of 0.75-1.0.



Figure 11. Effect of H<sub>2</sub>/CO ratio on the space time yields of methanol and dimethyl ether over the 3% Cs-10/90 and Cs-free 10/90 Cu/ZrO<sub>2</sub> catalysts at 7.6 MPa and 583K, with the reactant flow rate of GHSV = 5500 l/kg cat/hr.

## Discussion

This study has shown the influence of several experimental parameters and pre-treatment methods on the structure and activity of zirconia-supported copper catalysts. BET surface areas showed a strong dependence on calcination temperature. Samples calcined at higher temperatures showed a marked decrease in surface area. This loss of surface area is related to the development of more crystalline phases, as observed from XRD patterns. The XRD data suggest the presence of either tetragonal or cubic zirconia. Based on the literature [Schild et al., 1991], the tetragonal phase is more likely. Contrary to reports by Koeppel et al. [1992] and Nitta et al. [1993], copper was not observed to be crystalline, even after catalytic testing. Data from the TEM study demonstrated that the metallic copper particles were small, and the absence of lines in the XRD patterns indicated that the copper particles were X-ray amorphous and poorly crystalline.

Since copper surface area is reported to be an important parameter for determining catalyst activity [Chinchen et al., 1984; Hoppener et al., 1986; Bowker et al., 1988; Burch et al., 1990], efforts have been made toward its quantification [Bulko et al., 1979; Bartley et al., 1988]. N<sub>2</sub>O has been widely used as a titrant to measure copper surface area [Denise et al., 1987; Bartley and Burch, 1988; Kanoun et al., 1992]. However, Bartley and Burch [1988] reported drawbacks associated with this technique. In this study, copper particle size was estimated from TEM micrographs, as described previously [Mehta et al., 1979], and the TEM data were used in conjunction with surface composition as determined by XPS to calculate copper surface areas, with the assumption that copper particles were hemi-spherical. For the 10/90 catalyst, the copper surface area was estimated to be 83 m<sup>2</sup>/g Cu, which is in agreement with data reported elsewhere [Kanoun et al., 1992]. XPS analysis of the catalyst also indicated surface enrichment of copper. The surface ratio was found to be 18/82 Cu/Zr, compared to the bulk ratio of approximately 10/90 Cu/Zr. This phenomenon of copper surface segregation has been reported elsewhere [Gasser and Baiker, 1989].

The present study has shown the promotional effect of  $CO_2$  toward the production of methanol over the  $Cu/ZrO_2 = 10/90$  mol% catalyst. This effect was most pronounced at concentrations of  $CO_2$  below 5%. This research group has previously shown the promotional effect of  $CO_2$  on methanol synthesis over Cu/ZnO catalysts [Vedage et al., 1984a and 1984b]. Over a very active Cu/ZnO = 30/70 catalyst, a maximum promotion effect was seen at a  $CO_2$  concentration of 2% (H<sub>2</sub>/CO/CO<sub>2</sub> = 70/28/2). Similar results have been reported by Denise et al. [1989] over  $Cu/ZnO/Al_2O_3$  catalysts. However, in the case of the  $Cu/ZrO_2$  catalysts, the present findings are not in agreement with the results obtained at a pressure of 0.1 MPa by Denise et al. [1989]. In contrast to our continuous increase in methanol productivity with  $CO_2$  concentration, as shown in Figure 6a, a small maximum in methanol productivity was observed by Denise et al. [1989] at a  $CO_2$  concentration of approximately 3%, with methanol productivity fairly constant at other concentrations. Denise and Sneeden [1986] have reported higher methanol productivity

with CO<sub>2</sub> than with CO at atmospheric pressure (0.1 MPa), but higher productivity with CO than CO<sub>2</sub> at 1 MPa. Under this higher pressure, a lower methanol productivity was reported for a mixture of CO/CO<sub>2</sub> than for CO or CO<sub>2</sub> alone. Bartley and Burch [1988] concur that the CO<sub>2</sub> effect on methanol productivity over Cu/ZrO<sub>2</sub> catalysts is not well-defined. The current study, on the other hand, does indicate that the presence of CO<sub>2</sub> enhances catalyst activity toward methanol production. This might support the reports by other researchers [Schild et al., 1990b; Koeppel et al., 1992] that methanol is formed directly from the hydrogenation of CO<sub>2</sub> over Cu/ZrO<sub>2</sub> catalysts, although the reaction pressures in those investigations were different from that utilized in the present study.

The results of the water injection experiment show a continuous decrease in the productivity of methanol with water addition. In view of the promotion effect of CO<sub>2</sub>, it is interesting that water does not have a similar effect. Carbon dioxide formed from water via the water gas shift reaction is expected to behave, with respect to methanol production, in a manner similar to  $CO_2$  introduced as part of the reactant mixture.  $CO_2$ formed when H<sub>2</sub>O was injected at 6.0 ml/min corresponded to ~2 ml/min in the exit stream (see data in Figure 9). Since carbon conversion was low, this can be approximated as a reactant feed of  $H_2/CO/CO_2 = 70/29/1$  mol%. However, the expected behavior in methanol productivity was not observed. A reactant feed mixture of  $H_2/CO/CO_2 =$ 70/29/1 would be expected to produce ~30 g/kg cat/hr of methanol (see Figure 6a). In contrast, with H<sub>2</sub>O injected at the rate of 6.0 ml/min, only 4 g/kg cat/hr of methanol were produced. This may be explained by properties of the zirconia surface. The zirconia surface is reported to retain hydroxyl groups even at high temperatures (~873K) [Johansson; 1995]. The amount of water injected during these experiments was significantly greater than that generated by the reaction system. It is therefore speculated that the injected water interacted with the catalyst surface and generated hydroxyl groups that covered a significant portion of the surface. Consequently, active sites for the hydrogenation reaction were blocked by hydroxyl species, and thereby rendered inactive. Due to the strong interaction of hydroxyl groups with the surface, it is expected that these species remained on the surface even after water injection was terminated.

Another possible contribution to the observed lower catalyst activity in the water injection experiment might be the formation of iron carbonyl, which is known to cause catalyst deactivation [Bogdan et al., 1988]. During the water injection, the injection port was heated to approximately 393-423K, which may have been high enough to induce iron carbonyl formation. After kinetic testing, chemical analysis indicated the presence of 80 ppm (wt %) iron in the catalyst sample. This concentration of iron might be sufficient to deactivate the catalyst, but this factor was not examined further.

Doping with heavy alkali is known to enhance the activity of Cu/ZnO catalysts [Klier et al., 1984; Nunan et al., 1986; Bybell et al., 1986; Nunan et al., 1988; Herman, 1991]. The present study has demonstrated the large enhancement of methanol productivity of

Cu/ZrO<sub>2</sub> catalysts by cesium doping. The greatest enhancement in methanol productivity was achieved at a reaction temperature of 583K, where 78 g/kg cat/hr were produced as compared to 22 g/kg cat/hr for the undoped catalyst under the same conditions. Cesium doping is also known to increase the yields of *higher alcohols* and oxygenates over Cu/ZnO catalysts, especially under H<sub>2</sub>-deficient reaction conditions [Nunan et al., 1986; Bybell et al., 1986; Nunan et al., 1988]. In the present study, no detectable amounts of such products were observed for these catalysts. Therefore, under the reaction conditions that were employed in this study, no promotional effect of cesium doping on higher alcohols and oxygenates over the Cu/ZrO<sub>2</sub> catalyst was observed.

A good understanding of the mechanism of methanol synthesis provides insight into the cesium doping effect. This mechanism is believed to proceed *via* a surface formate species [Nunan et al., 1988]. It is proposed that the basicity induced by the cesium cation activates the process by which this surface species is formed. In the analogous  $Cu/ZrO_2$  system, cesium is likely to perform a similar function in the scheme of methanol synthesis. The large decrease in dimethyl ether formation over the cesium-doped catalyst is reasonable since acidic sites are required for its formation.

In the current work, yields of dimethyl ether over the three catalysts studied showed a strong dependence on reaction temperature; that is, dimethyl ether productivity increased dramatically with temperature. However, reaction temperature did not exhibit such a strong influence on methanol yield. In fact, over the undoped catalysts, methanol productivity remained fairly constant. Over the cesium-doped catalyst, an increase of  $\approx 60\%$  in methanol productivity was observed as the reaction temperature was increased from 523 to 583K. However, as the temperature was increased further, methanol productivity dropped significantly. Low methanol productivity at high temperatures can be explained by thermodynamic considerations, since methanol production is favored at low temperatures [Nunan et al., 1986]. In addition, at high temperatures, dimethyl ether yield is increased at the expense of methanol.

It was reported that copper surface area had an influence on the activity of  $Cu/ZrO_2$  catalysts [Chinchen et al., 1984; Hoppener et al., 1986; Bowker et al., 1988; Burch et al., 1990]. Based on copper particle sizes from TEM data, the copper surface area per gram of copper from the 30/70 sample was found to be approximately 40% higher than that of the 10/90 sample. A comparison of the results for the Cu/ZrO<sub>2</sub> = 10/90 and 30/70 catalysts (see Figures 7 and 8) tends to indicate that there is no clear-cut relationship between copper surface area and catalyst activity.

The  $H_2/CO$  ratio did not have a strong influence on methanol or dimethyl ether productivity. Methanol productivity initially showed a gradual increment, after which no significant variation occurred (Figures 8 and 11). Based on stoichiometric considerations, an appropriate  $H_2/CO$  ratio is needed for optimal conversion of reactants to methanol.

Below that ratio, methanol production is expected to decrease as the  $H_2/CO$  ratio is decreased further, while above that ratio a plateau of constant productivity is attained. It is expected that at a ratio beyond that explored in the current study, methanol production will decrease, again based on stoichiometry.

The current investigation demonstrated that the Cu/ZrO<sub>2</sub> catalyst is active for CO hydrogenation. The copper particle size in the Cu/ZrO<sub>2</sub> system was comparable to that in Cu/ZnO [Bulko et al., 1979]. However, the catalytic performance over these two catalysts is drastically different. Methanol yield of 250 g/kg cat/hr was obtained for the 30/70 Cu/ZnO catalyst at 523K [Nunan et al., 1986]. Under the same conditions, the 30/70 Cu/ZrO<sub>2</sub> catalyst produced about 23 g/kg cat/hr of methanol. For a 10/90 Cu/ZnO catalyst with a synthesis gas mixture of H<sub>2</sub>/CO/CO<sub>2</sub> = 70/24/6 at 7.6 MPa and a reaction temperature of 523K, the methanol STY was found to be 20 g/kg cat/hr [Herman et al., 1979]. In comparison, the yield of methanol over the 10/90 Cu/ZrO<sub>2</sub> catalyst was found to be 39 g/kg cat/hr (see Figure 6a). The significant differences between these two catalysts cannot be simply explained by copper particle size. It is clear then, that the interaction of copper with the support plays a major role in governing the catalytic activity of these systems.

## Conclusions

This study has confirmed that zirconia-based copper catalysts, that is,  $Cu/ZrO_2 = 10/90$  and 30/70 mol%, are active for methanol synthesis from H<sub>2</sub>/CO at 7.6 MPa, as well as for dimethyl ether production, where these products are very selectively formed. The addition of  $CO_2$  to the synthesis gas enhanced methanol yield. However, H<sub>2</sub>O injection suppressed methanol production and deactivated the catalyst. Similar to Cu/ZnO catalysts, cesium doping increased methanol productivity while decreasing dimethyl ether formation. Although the surfaces of tested catalysts were found to be enriched with copper, comparison of the 10/90 and 30/70 samples indicated that the relationship between copper surface area and catalyst activity is not well-defined. The Cu/ZrO<sub>2</sub> catalysts for the synthesis of alcohols from synthesis gas.