OXYGENATES *via* SYNTHESIS GAS

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EXECUTIVE SUMMARY

Methanol synthesis from H_2/CO has been carried out at 7.6 MPa over zirconia- supported copper catalysts. Catalysts with nominal compositions of 10/90 mol% and 30/70 mol% Cu/ZrO_2 were used in this study. Additionally, a 3 mol% cesium-doped 10/90 catalyst was prepared to study the effect of doping with heavy alkali, and this promoter greatly increased the methanol productivity. The effects of CO_2 addition, water injection, reaction temperature, and H_2/CO ratio have been investigated. Both CO_2 addition to the synthesis gas and cesium doping of the catalyst promoted methanol synthesis, while inhibiting the synthesis of dimethyl ether. Injection of water, however, was found to slightly suppress methanol and dimethyl ether formation while being converted to CO_2 *via* the water gas shift reaction over these catalysts. There was no clear correlation between copper surface area and catalyst activity. Surface analysis of the tested samples revealed that copper tended to migrate and enrich the catalyst surface.

The concept of employing a double-bed reactor with a pronounced temperature gradient to enhance higher alcohol synthesis was explored, and it was found that utilization of a Cs-promoted $Cu/ZnO/Cr_2O_3$ catalyst as a first lower temperature bed and a Cs-promoted ZnO/Cr_2O_3 catalyst as a second high-temperature bed significantly promoted the productivity of 2-methyl-1-propanol (isobutanol) from H_2/CO synthesis gas mixtures. While the conversion of CO to C_{2+} oxygenates over the double-bed configuration was comparable to that observed over the single Cu-based catalyst, major changes in the product distribution occurred by the coupling to the zinc chromite catalyst; that is, the productivity of the C_1-C_3 alcohols decreased dramatically, and 2-methyl branched alcohols were selectively formed. The desirable methanol/2-methyl oxygenate molar ratios close to 1 were obtained in the present double-bed system that provides the feedstock for the synthesis of high octane and high cetane ethers, where the isobutanol productivity was as high as 139 g/kg cat/hr.

Higher alcohol synthesis has been investigated over a $Cs/Cu/ZnO/Cr_2O_3$ catalyst at temperatures higher (up to 703K) than those previously utilized, and no sintering of the catalyst was observed during the short-term testing. However, the higher reaction temperatures led to lower CO conversion levels and lower yield of alcohols, especially of methanol, because of equilibrium limitations. With the double catalyst bed configuration, the effect of pressure in the range of 7.6-12.4 MPa on catalyst activity and selectivity was studied. The upper bed was composed of the copper-based catalyst at 598K, and the lower bed consisted of a copper-free $Cs\text{-}ZnO/Cr_2O_3$ catalyst at a high temperature of 678K. High pressure was found to increase CO conversion to oxygenated products, although the increase in isobutanol productivity did not keep pace with that of methanol. It was also shown that the $Cs/Cu/ZnO/Cr_2O_3$ catalyst could be utilized to advantage as the second-bed catalyst at 613-643K instead of the previously used copper-free $Cs\text{-}ZnO/Cr_2O_3$ catalyst at higher temperature. With double $Cs/Cu/ZnO/Cr_2O_3$ catalysts, high space time yields of up to 202 g/kg cat/hr, with high selectivity to isobutanol, were achieved.

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RESEARCH RESULTS

I. Cu/ZrO_2 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 ($H_2/CO/CO_2$) [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_2 and H_2O 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_2 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_2 synthesis gas was utilized compared to the use of a CO_2/H_2 feed gas at atmospheric pressure. The CO/H_2 mixture yielded more methanol than the CO_2/H_2 mixture. However, the same research group reported that CO_2/H_2 produced more methanol than CO/H_2 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_2 catalysts was also investigated to probe the promotional effect of alkali dopants on these catalysts.

Experimental

Catalyst Preparation

The 10/90 mol% and 30/70 mol% Cu/ZrO_2 and pure ZrO_2 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_2 catalyst was achieved by addition of the calcined catalyst to a N_2-purged solution of cesium formate, followed by evaporation to dryness under flowing N_2. 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_α 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° 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_α (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^{-9} 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 ($Fe(CO)_5$ 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_2O 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_2 and CO gas streams were regulated by mass flow controllers (Linde, Model 5851-B2E1A). For the experiments with CO_2 addition, 30/70 vol% CO/H_2 and 30/70 vol% CO_2/H_2 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_2/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_2 injection experiments, CO_2 was varied from 0 to 30% of the total inlet flow by replacement of CO such that CO + CO_2 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_2/N_2 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_2 catalysts calcined at various temperatures are given in Table 1. The surface area of the 10/90 catalyst varied from 63 m^2/g when calcined at 773K to 148 m^2/g when calcined at 623K. Likewise, the surface area of the 30/70 catalyst ranged from 25 m^2/g at 773K to 78 m^2/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^2/g, while the surface area for the 30/70 catalyst decreased by about 30%, from 78 to 55 m^2/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.
In all cases, the calcination temperature indicated was maintained for 3 hr.

Cu/ZrO_2 Catalyst	Calcination Temp. (K)	BET Surface Area (m^2/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

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 or copper oxide.

The Cu/ZrO_2 = 30/70 catalyst samples calcined at the above-mentioned three temperatures gave XRD patterns similar to those observed with the Cu/ZrO_2 = 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.

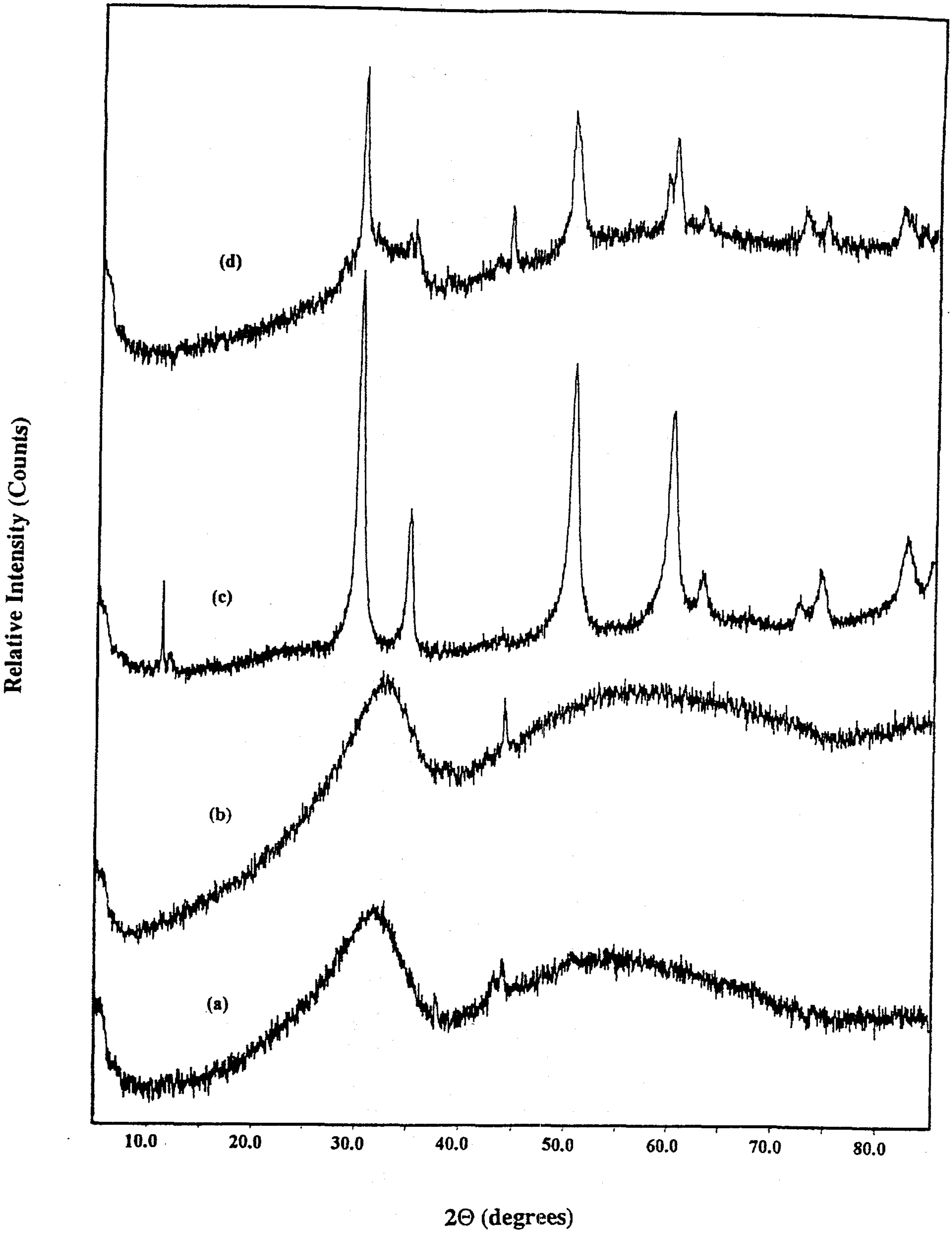

Figure 1. X-Ray diffraction patterns for the Cu/ZrO$_2$ = 10/90 catalyst samples calcined at the three different temperatures of (a) 623K, (b) 673K, and (c) 773K and (d) after catalytic testing.

The patterns were obtained by scanning from 5-85° at a rate of 1 deg/min.

Transmission Electron Microscopy Study. Both of the tested Cu/ZrO_2 catalysts were examined by transmission electron microscopy (TEM), and a micrograph obtained from the 10/90 Cu/ZrO_2 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 ≈4.0 nm for the 10/90 sample and ≈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_2 is believed to be a better spectral reference than the C *1s* 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^+ species. The O *1s* spectrum obtained from the tested catalyst is shown in Figure 5d, and the shoulder on the well-resolved O *1s* 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.

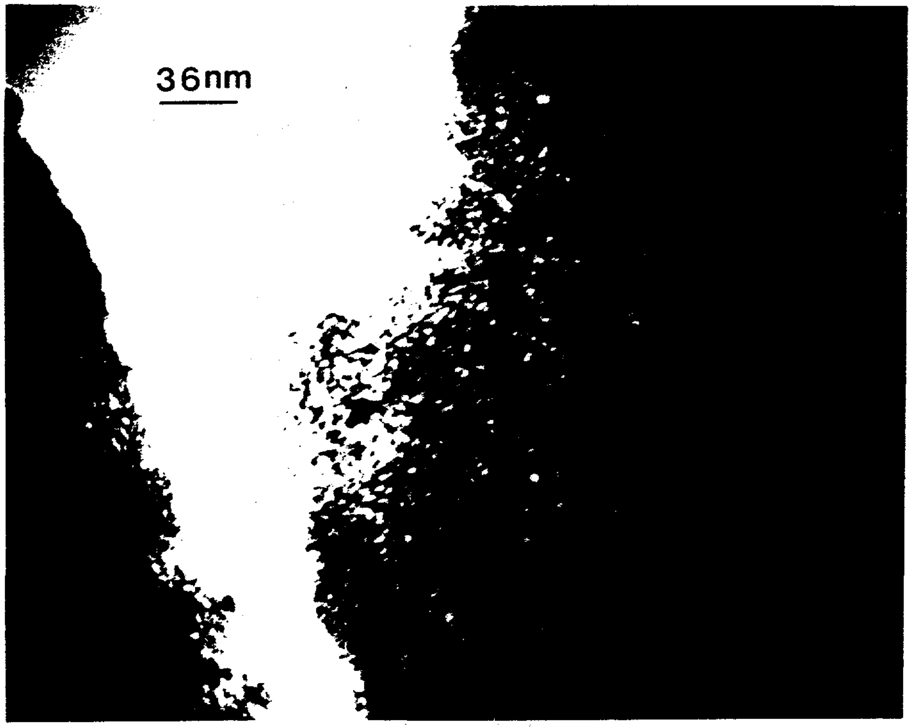

Figure 2. Transmission electron micrograph from the Cu/ZrO_2 = 10/90 tested catalyst.

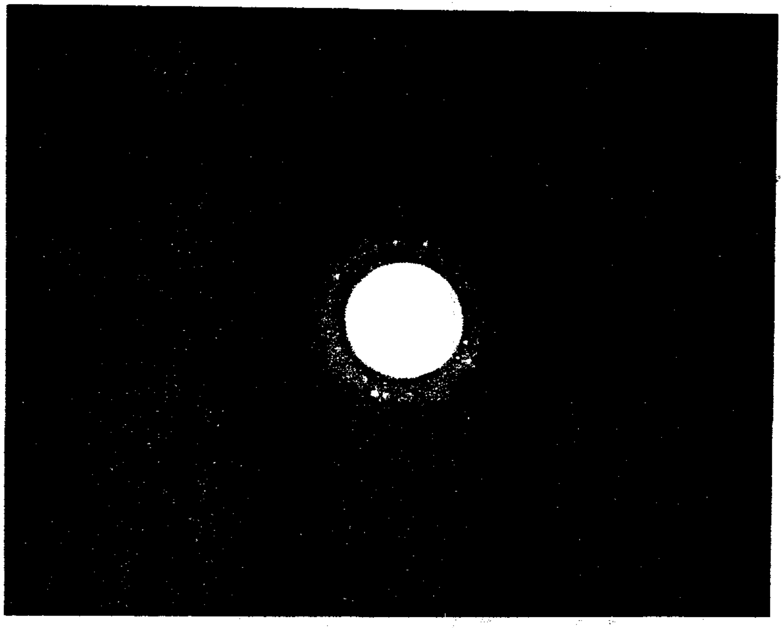

Figure 3. Selected area diffraction pattern of the Cu/ZrO_2 = 10/90 tested catalyst.

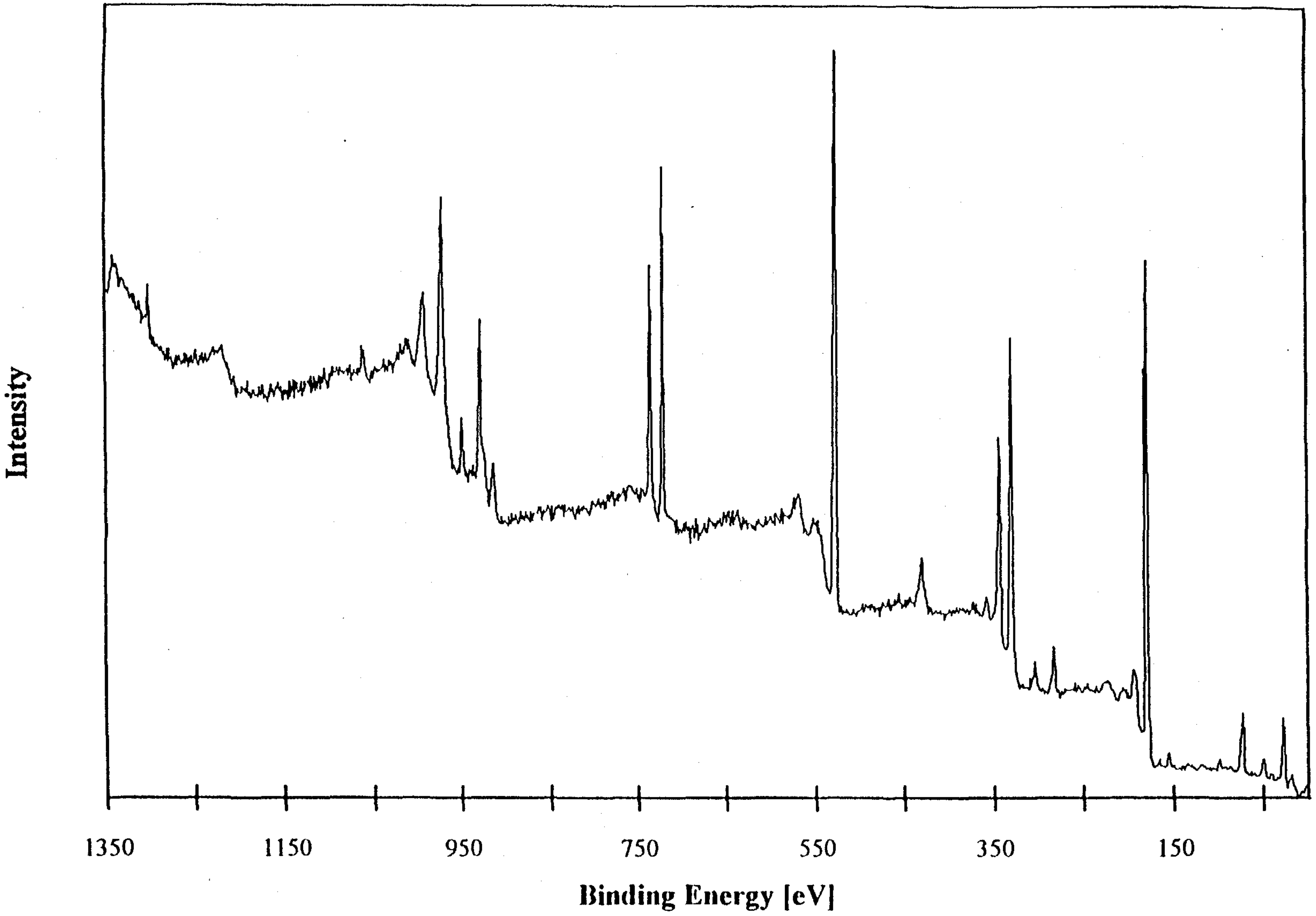

Figure 4. XPS survey scan of the tested 3% Cs - 10/90 Cu/ZrO_2 catalyst.

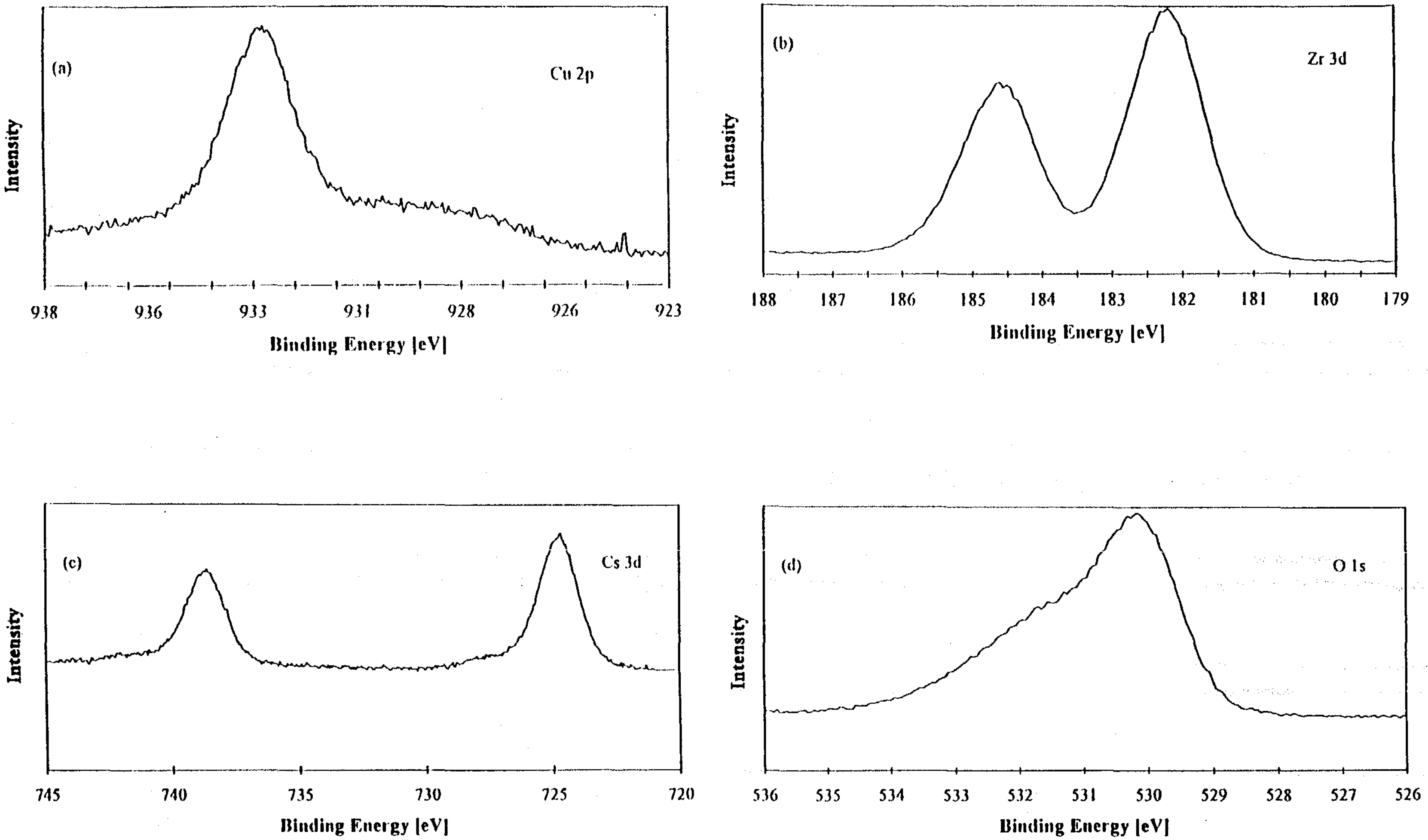

Figure 5. XPS spectra of the 3% Cs - 10/90 Cu/ZrO$_2$ tested catalyst in the (a) Cu *2p* region, (b) Zr*3d* region, (c) Cs *3d* region, and (d) O *1s* region.

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_2 was also tested under these same reaction conditions. In neither case was any significant product formation observed.

Effect of CO_2 in the Synthesis Gas. The effect of CO_2 on the activity of the Cu/ZrO_2 = 10/90 catalyst was investigated at a reaction temperature of 523K. In this experiment, the CO reactant was replaced stepwise by CO_2 so that the sum of CO + CO_2 was constant at 30 mol% of the reactant mixture, with H_2 = 70 mol%. Figure 6a shows that as the CO_2 concentration was increased, the methanol STY progressively increased. Methanol STY initially exhibited a sharp increase up to a CO_2 concentration of approximately 5%. Beyond this concentration, a more gradual increase of methanol STY was observed. After stepwise variation of CO_2 concentration from 0% (30% CO) to 30% (0% CO), the system was returned to the initial conditions (0% CO_2, with H_2/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_2 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_2 concentration is depicted in Figure 6b. In all cases, the productivity of DME was appreciably less then that of methanol. Upon increasing the CO_2 content of the synthesis gas mixture from 0 to 5% mol%, corresponding to $H_2/CO/CO_2$ = 70/25/5, a dramatic decrease in the productivity of dimethyl ether was observed. The DME STY then became rather constant at ≈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.

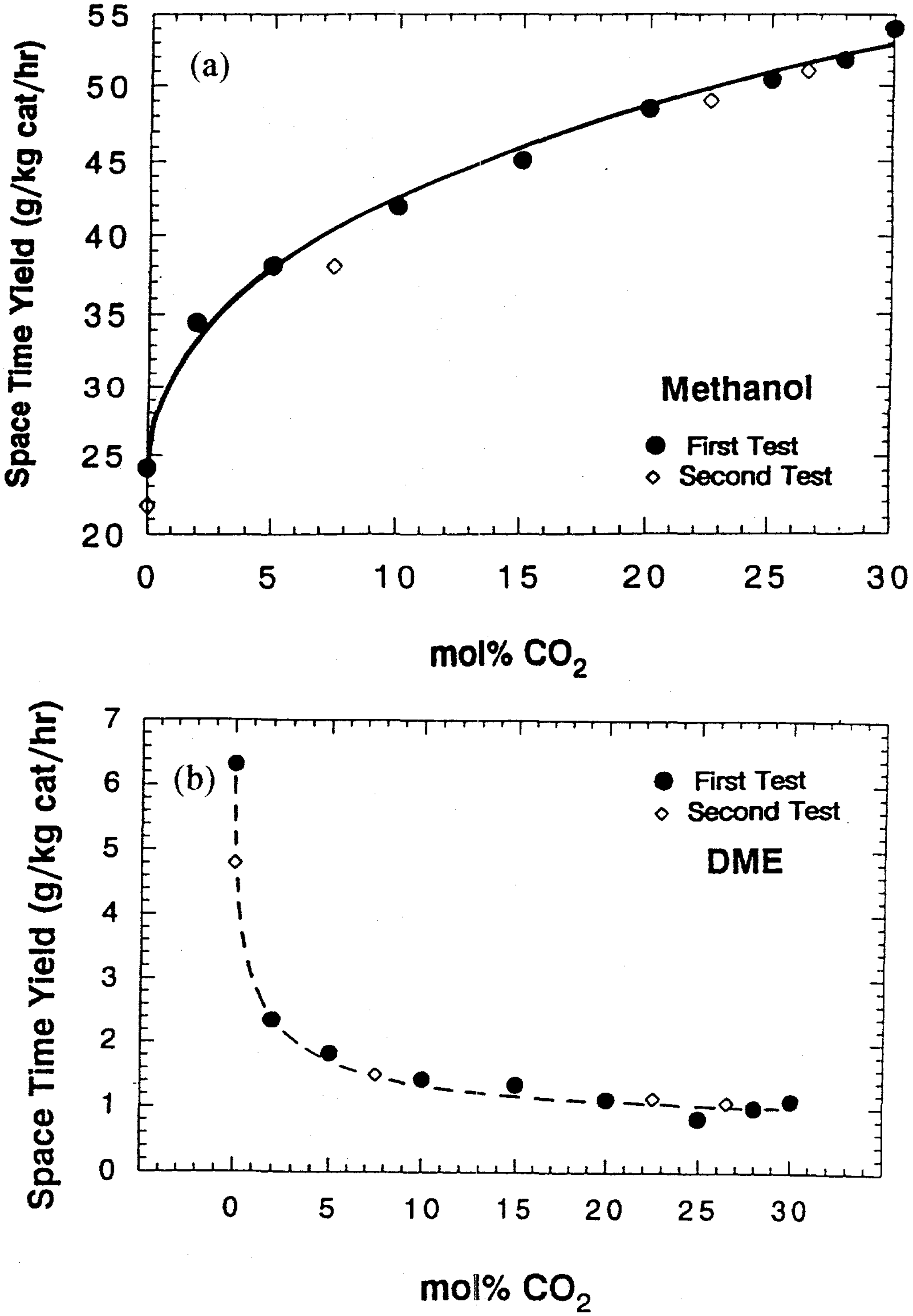

Figure 6. Effect of CO_2 addition on production of (a) methanol and (b) dimethyl ether over the Cu/ZrO_2 = 10/90 catalyst with $H_2/(CO + CO_2)$ = 2.33 at 7.6 MPa and 523K with GHSV = 6120 l/kg cat/hr.

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_2 = 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.

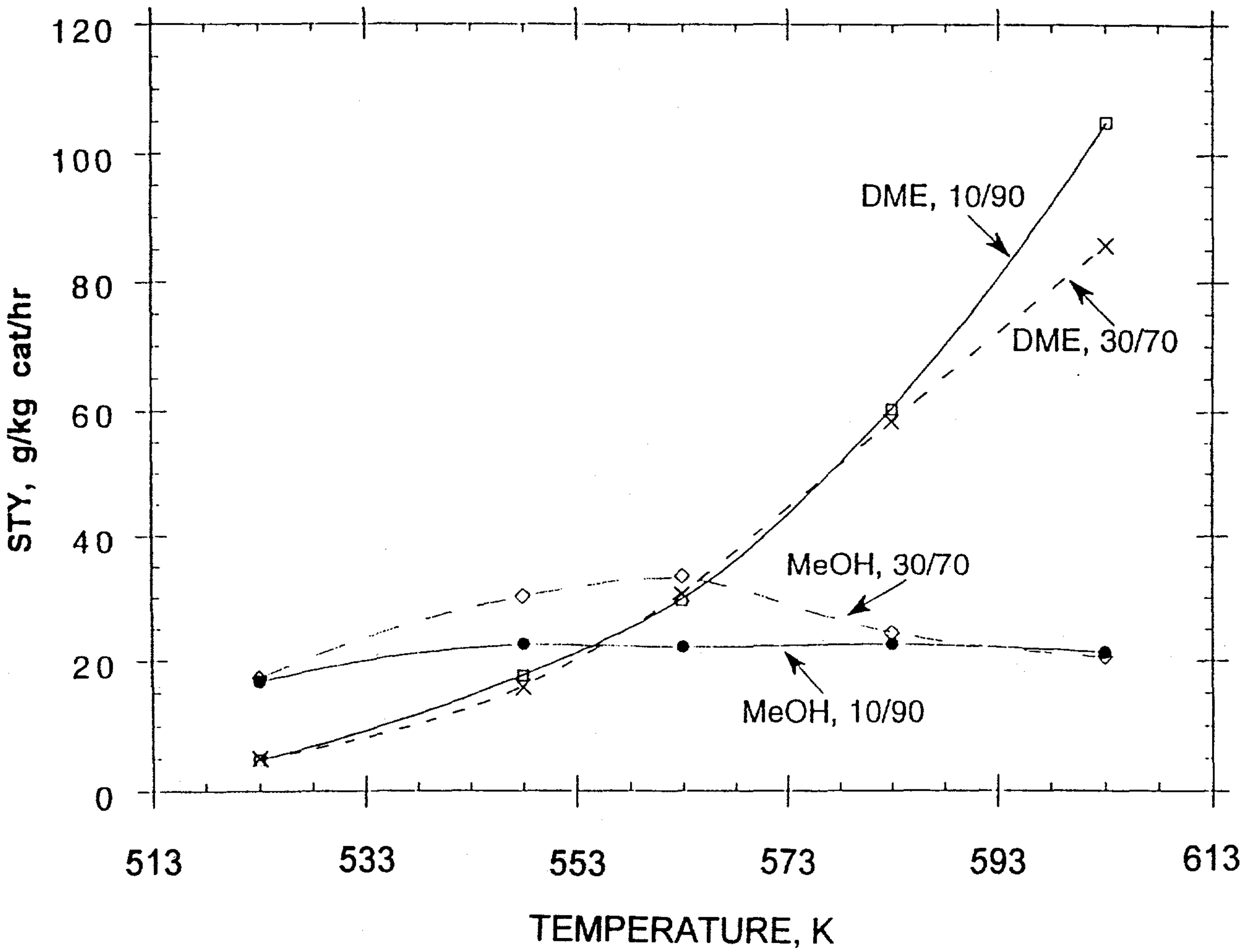

Figure 7. Effect of reaction temperature on the production of methanol and dimethyl ether over the Cu/ZrO_2 = 10/90 and 30/70 catalysts using $H_2/CO = 0.45$ synthesis gas at 7.6 MPa with GHSV = 5500 l/kg cat/hr.

Effect of H_2/CO Ratio. Results of the investigation of the influence of H_2/CO ratio on the product productivities are shown in Figure 8. The H_2/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_2 = 10/90 sample, the methanol STY changed from approximately 23 g/kg cat/hr at H_2/CO = 0.45 to approximately 30 g/kg cat/hr when the H_2/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_2/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_2/CO synthesis gas ratio was increased.

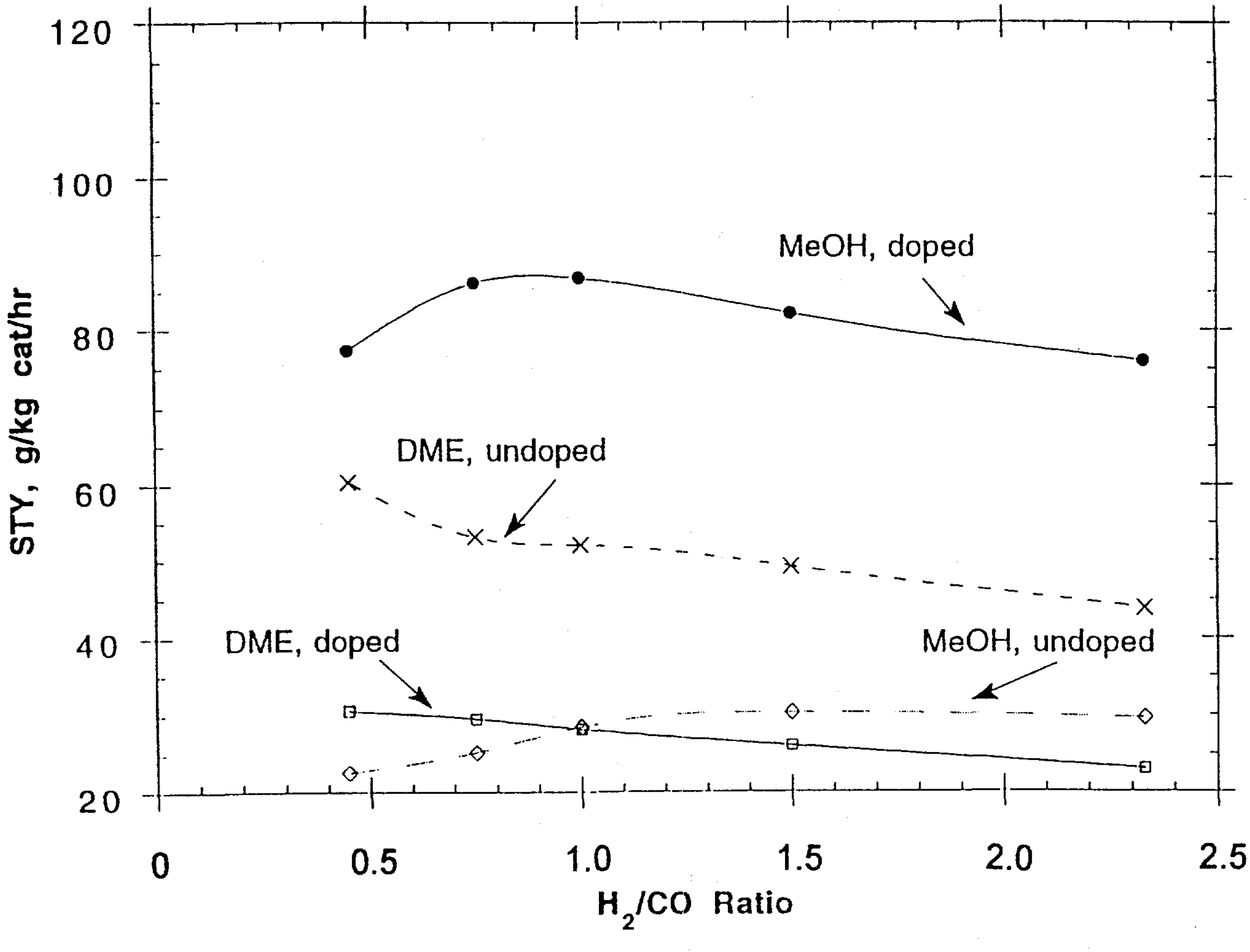

Figure 8. Effect of H_2/CO ratio on methanol and dimethyl ether synthesis over the Cu/ZrO_2 = 10/90 and 30/70 catalysts at 7.6 MPa, 583K, and GHSV = 5500 l/kg cat/hr.

Effect of Water Injection into the Synthesis Gas. Since a significant effect on the catalytic behavior of the Cu/ZrO_2 catalyst was observed upon adding CO_2 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 ($H_2/CO/H_2O = 70/30/0$) 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_2 *via* the water gas shift reaction showed a continuous increase with the amount of water injected, wherein the CO_2 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_2 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.

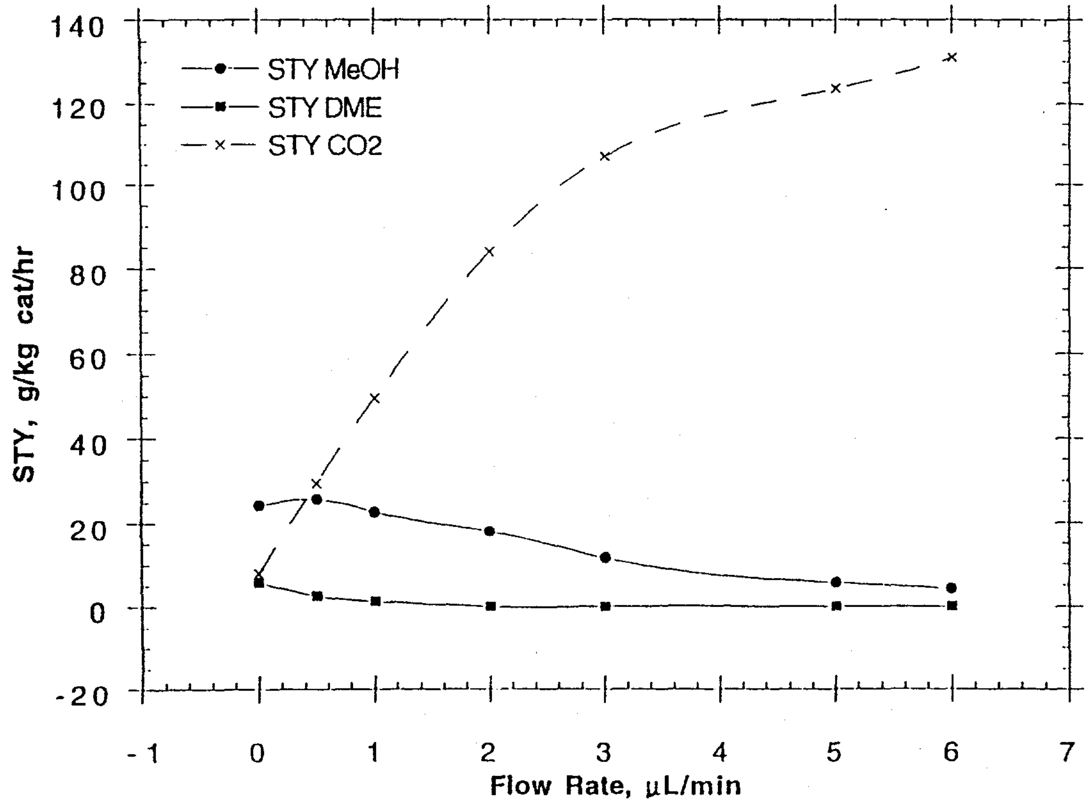

Figure 9. Effect of H_2O injection on the productivity of methanol, dimethyl ether, and carbon dioxide over the 10/90 Cu/ZrO_2 catalyst with an initial synthesis gas composition of $H_2/CO = 2.33$ at 7.6 MPa and 523K with GHSV = 6120 l/kg cat/hr.

Effect of Cesium Doping of the Cu/ZrO$_2$ = 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$_2$ = 10/90 catalyst by doping the catalyst with 3 mol% Cs. Data obtained from both the doped and undoped 10/90 Cu/ZrO$_2$ 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.

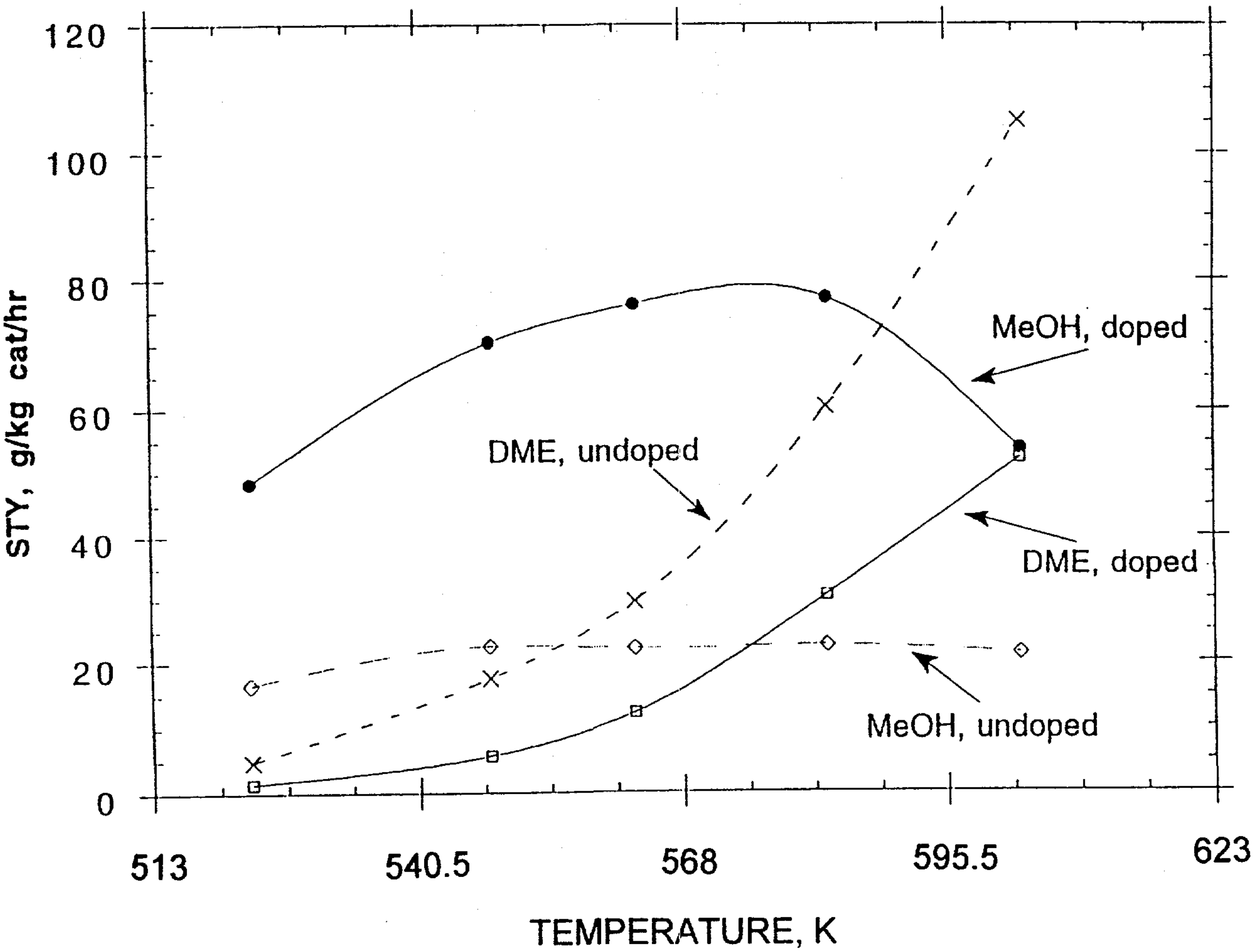

Figure 10. Effect of reaction temperature on the production of methanol and dimethyl ether over the 3 mol% Cs-doped 10/90 and Cs-free 10/90 Cu/ZrO$_2$ catalysts from H$_2$/CO = 0.45 synthesis gas at 7.6 MPa and with GHSV = 5500 l/kg cat/hr.

The influence of the H_2/CO molar ratio on the productivity obtained over the Cs-doped Cu/ZrO_2 = 10/90 catalyst was also investigated. The STYs of the two major products as a function of the H_2/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_2/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_2/CO in the range of 0.75-1.0.

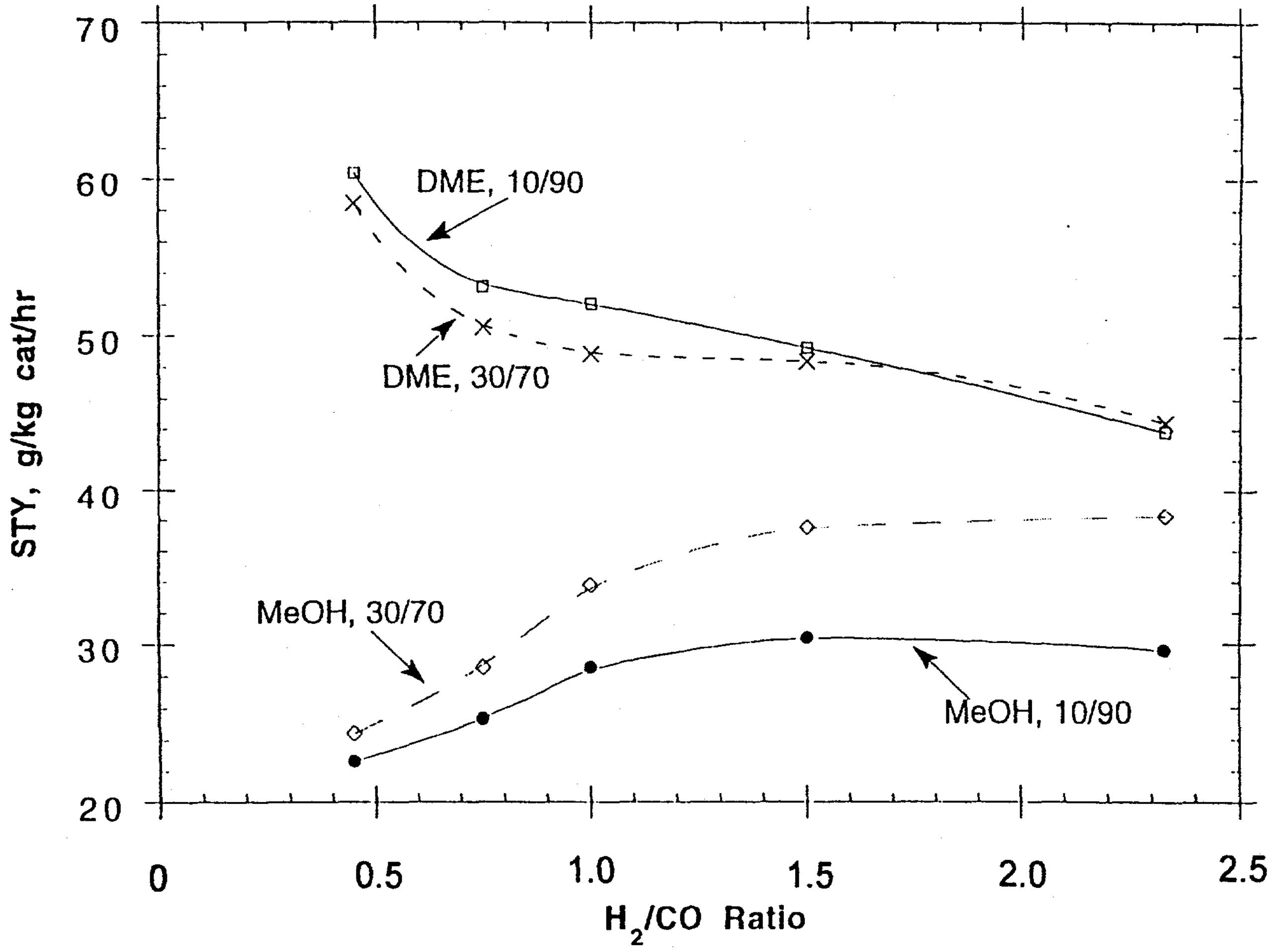

Figure 11. Effect of H_2/CO ratio on the space time yields of methanol and dimethyl ether over the 3% Cs-10/90 and Cs-free 10/90 Cu/ZrO_2 catalysts at 7.6 MPa and 583K, with the reactant flow rate of GHSV = 5500 l/kg cat/hr.

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_2O 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^2/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% ($H_2/CO/CO_2$ = 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_2 than with CO at atmospheric pressure (0.1 MPa), but higher productivity with CO than CO_2 at 1 MPa. Under this higher pressure, a lower methanol productivity was reported for a mixture of CO/CO_2 than for CO or CO_2 alone. Bartley and Burch [1988] concur that the CO_2 effect on methanol productivity over Cu/ZrO_2 catalysts is not well-defined. The current study, on the other hand, does indicate that the presence of CO_2 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_2 over Cu/ZrO_2 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_2, 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_2O 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_2O 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_2 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_2-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_2 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 ≈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_2 = 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_2 catalyst is active for CO hydrogenation. The copper particle size in the Cu/ZrO_2 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_2 catalyst produced about 23 g/kg cat/hr of methanol. For a 10/90 Cu/ZnO catalyst with a synthesis gas mixture of $H_2/CO/CO_2 = 70/24/6$ 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_2 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_2/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_2O 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_2 catalysts are quite selective for methanol synthesis, but they are less active than the Cu/ZnO catalysts for the synthesis of alcohols from synthesis gas.

II. $Cs/Cu/ZnO/Cr_2O_3$ AND $Cs/ZnO/Cr_2O_3$ CATALYSTS AS SINGLE BEDS AND IN A DOUBLE-BED CONFIGURATION FOR HIGHER ALCOHOL SYNTHESIS

Introduction

The current interest in higher alcohol synthesis (HAS) from H_2/CO synthesis gas mixtures is the potential application of this process to the production of high-value gasoline octane enhancers [Brown, 1993; Zhou, 1994]. The coupling of methanol and 2-methyl branched alcohols, directly produced by catalytic hydrogenation of CO, has in fact been proposed in the literature for the synthesis of ethers like MTBE (methyl tertiary-butyl ether) and TAME (methyl tertiary-amyl ether) *via* a 1- or 2-step process [Nunan et al., 1985; Keim and Falter, 1989; Klier et al., 1993; Sanfilippo, 1993]. Therefore, a high productivity to 2-methyl oxygenates up to a 1 to 1 molar ratio with methanol represents the target.

Over the traditional HAS catalysts, including the low-temperature Cu-based catalysts [Nunan et al., 1989a-c; Hindermann et al., 1993; Boz et al., 1994] and the high-temperature zinc chromite catalysts [Natta et al., 1957; Paggini and Sanfilippo, 1986; Forzatti and Tronconi, 1991], the branched alcohols are, along with methanol, the preferred products of the chain growth process. Due to their intrinsic low reactivity, they manifest a terminal behavior: once formed through the evolution of the intermediate species, isobutanol and higher branched oxygenates do not undergo further reactions and are accumulated in the reacting system [Nunan et al., 1988; Lietti et al., 1992]. However, productivities of isobutanol higher than 50 g/kg cat/h have not been reported in the literature for these conventional catalysts. Appreciably higher yields are needed to be economically feasible. The slowest step of the reaction is the low rate of the $C_1 \Rightarrow C_2$ step that initiates the formation of higher oxygenates [Nunan et al., 1988; Tronconi et al., 1992]. The optimization of HAS kinetics through proper manipulation of the operating variables [Beretta et al., 1994], copper-based catalyst composition [Nunan et al., 1989a-c; Stiles et al., 1991; Hu et al., 1991], and the study of new catalyst formulations [Keim and Falter, 1989; Ueda et al., 1993; Minahan and Nagaki, 1994] has been recently pursued in order to improve isobutanol productivity.

In the present work, high productivities and selectivities to isobutanol and higher 2-methyl alcohols have been achieved by an alternative engineering design of HAS. This consists of separating the process into two consecutive steps: (1) the initial synthesis of intermediate oxygenates and (2) their subsequent conversion to the terminal branched species. It is already known from the results of chemical enrichment experiments [Klier et al., 1993; Herman and Lietti, 1994; Lietti et al., 1992] that the addition of C_2 and C_3 intermediates to the reacting system causes a general promotion of HAS and, in particular, the production of branched alcohols. The purpose of the present research is the initial optimization of the production of short-chain alcohols over a Cs-promoted $Cu/ZnO/Cr_2O_3$ catalyst, the study of a Cs-promoted ZnO/Cr_2O_3 catalyst for the selective synthesis of isobutanol, and the engineering of double-bed experiments for the synergic utilization of the two catalysts. Herein, the optimized Cu-based catalyst (used as the first bed) is expected to supply intermediate reactants to the high-temperature catalyst (used as the second bed), and the reactants can be efficiently converted to isobutanol. The results are discussed in light of well-established knowledge about the mechanistic, kinetic, and thermodynamic aspects that govern HAS over both the Cu-based and Cu-free catalysts [Frolich and Cryder, 1930; Anderson et al., 1952; Natta et al., 1957; Calverley and Anderson, 1987; Elliott and Pennella, 1988; Klier et al., 1988; Nunan et al., 1989a-c; Tronconi et al., 1990; Smith et al., 1991; Lietti et al., 1992; Tronconi et al., 1992; Breman et al., 1994; Herman and Lietti, 1994].

Experimental

Catalyst Preparation

A 3.0 mol% Cs/Cu/ZnO/Cr_2O_3 catalyst was synthesized following the procedure reported by Nunan et al. [1989d]. The preparation consisted of the initial coprecipitation of a single-phase hydrotalcite-like precursor [Mihyata, 1983; Busetto et al., 1984; Reichle, 1985; Reichle, 1986], $Cu_{2.4}Zn_{3.6}Cr_2(OH)_{16}CO3{\cdot}4H_2O$, by simultaneous addition of 1 M sodium carbonate and metal nitrate solution to a sodium acetate solution at a constant pH of 9.0 [Nunan et al., 1989d]. After filtering, washing with distilled water, and drying, the precipitate was crushed, sieved to 0.85-2.0 mm particles, and decomposed to a mixture of Cu/Zn/Cr oxides (molar ratio = 30/45/25) by stepwise calcination in air (1.67K/min) to 623K; the final temperature was maintained for 3 hr. Cesium doping was effected by adding the calcined catalyst (2.0-2.5 g) to a N_2-purged aqueous solution of CsOOCH; the solution was slowly evaporated under flowing nitrogen at 323K. The catalyst was finally recalcined in air at 623K for 3 hr. The Cs-doped catalyst was reduced before testing in the synthesis reactor by heating the catalyst to 523K under a flowing H_2/N_2 = 2/98% mixture (60 ml/min) at atmospheric pressure. The reduction treatment was terminated when the concentration of water monitored in the effluent gas dropped significantly.

A 4.0 mol% CsOOCH ZnO/Cr_2O_3 was prepared by an analogous procedure from a commercial zinc chromite catalyst (Harshaw, Zn-0311 T 1/4"), previously sieved to 0.85-2.0 mm and calcined under N_2 at 673K for 4 hr. On the basis of X-ray powder diffraction (XRD) analysis, it was established that the commercial catalyst consisted of two distinct crystalline phases: $ZnCr_2O_4$ with spinel-like structure and microcrystalline ZnO. In line with the treatment adopted by Tronconi et al. [1989] for a similar catalytic system, the doped catalyst was activated by heating to 723K under a flowing H_2/N_2 = 2/98% mixture.
During the treatment, the release of CO_2 and water was monitored by gas chromatography.

Activity Tests

Catalyst testing was carried out in a tubular fixed-bed reactor. The apparatus was described previously by Nunan et al. [1989a], and a schematic diagram is provided in Figure 12. Special arrangements were made to minimize iron carbonyl formation from contact of CO with iron-containing surfaces, since deposition of iron from $Fe(CO)_5$ over Cu-based catalyst sites causes irreversible deactivation [Bogdan et al., 1988]. Charcoal and molecular sieve traps were employed for filtering the CO stream fed from high-pressure stainless steel tanks. In addition, an copper-lined stainless steel reactor and copper thermocouple wells for reading the catalyst temperature were adopted, and a water cooling system was used to keep the temperature of the stainless steel tubing upstream from the reactor below 338K. Indeed, elemental analysis of tested catalysts (500 hr on stream) indicated iron content <60 ppm.

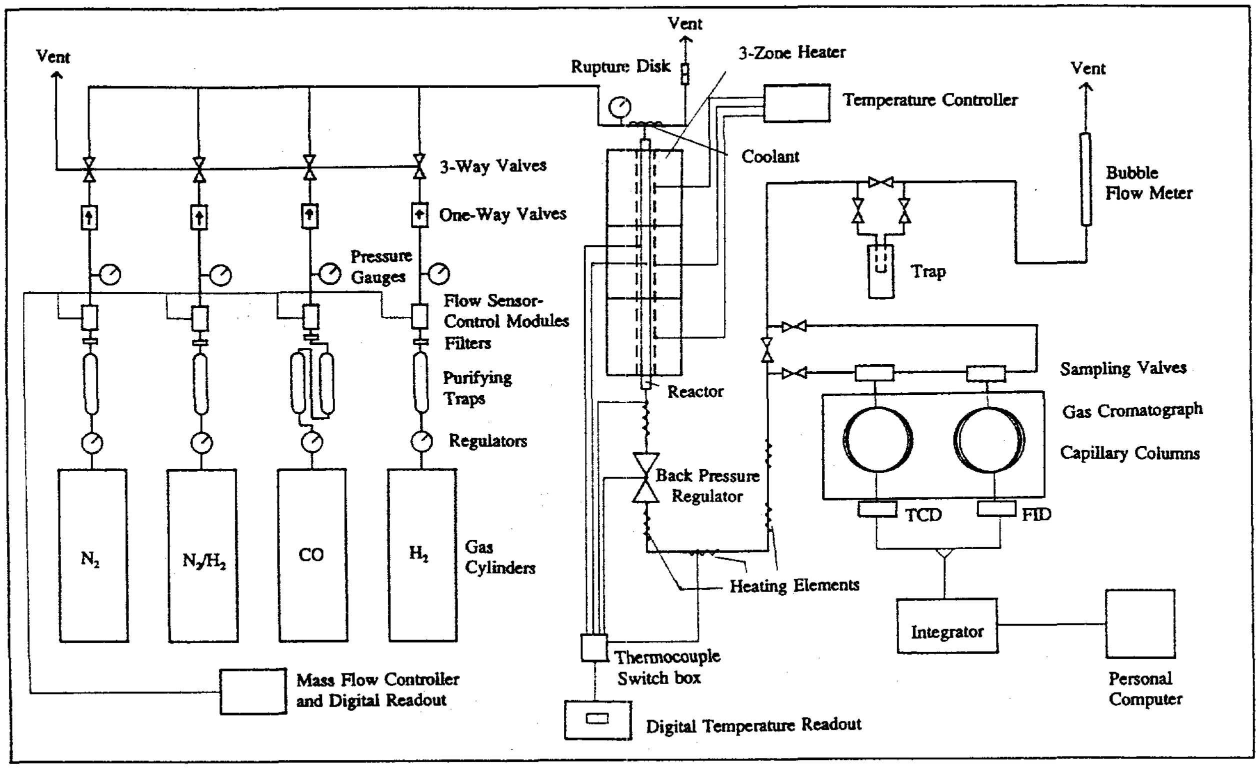

Figure 12. Schematic of the catalyst testing unit.

In the case of the single-bed experiments, 2.0 g of each catalyst were diluted with 0.5 mm Pyrex beads to a total volume of about 7.0 ml. The bed (about 7 cm long) was placed in the center of the reactor tube (1.9 cm I.D. and 55 cm long), using 3.0 mm Pyrex beads as packing material upstream and downstream. In the case of the double-bed experiments, 1.0 g of each catalyst was diluted with the Pyrex beads up to a 4.0 ml volume. As indicated in Figure 13, the $Cs/Cu/ZnO/Cr_2O_3$ bed was loaded in the top portion of the reactor, about 15 cm downstream from the reactor inlet section. The $Cs/Zn/Cr_2O_3$ bed ewas loaded in the bottom portion of the reactor at a distance of about 20 cm below the first bed. The temperatures of the beds were monitored by two independent thermocouples; a copper-thermocouple well was connected to each reactor end.

The catalyst pretreatments in the double-bed reactor required a stepwise procedure. Initially, the Cu-based catalyst was reduced by heating the top portion of the reactor at 523K under flowing $H_2/N_2 = 2/98$ vol% mixture, while the bottom portion of the reactor was kept unheated. When the reduction was completed, the first bed was cooled to room temperature under flowing N_2. Subsequently, the treatment of the zinc chromite catalyst was carried out by heating the bottom portion of the reactor to 723K under a flowing H_2/N_2 mixture. During this phase of the reduction process, in order to "protect" the Cu-based catalyst from possible Cu sintering or over-reduction, the temperature of the first bed was kept below 343K by an external water circulating system.

The gas stream fed to the synthesis reactor consisted of a mixture of H_2, CO, and N_2 ($N_2/CO = 5/95$ mol% in each experiment). Nitrogen behaved as an inert in the reacting system and provided an internal standard for the evaluation of the product yields. The kinetic runs carried out over the $Cs/Cu/ZnO/Cr_2O_3$ catalyst ranged over the following windows of operating variables: T = 583-613K, P = 6.5-7.6 MPa, $H_2/CO = 0.45\text{-}3.5$, gas hourly space velocity (GHSV) = 3,300-18,375 l(STP)/kg cat/hr. The activity tests over the $Cs/ZnO/Cr_2O_3$ catalyst and the double-bed experiments were carried out at constant pressure (7.6 MPa) and synthesis gas composition ($H_2/CO = 0.75$), varying GHSV in the range of 5,450-18,375 l(STP)/kg cat/hr. Over the zinc chromite catalyst, a constant temperature of 678K was maintained. In the double-bed experiments, the first bed was kept at 598K, while the second bed was maintained at 678K. In each experiment, the set of conditions was maintained for a period of 24 hr.

Quantitative Product Analysis

The reactor outlet stream was sampled every 20-60 min using an on-line automated heated sampling valve, and it was analyzed by a Hewlett-Packard 5390 gas chromatograph. The analyses were quantified and averaged for evaluation of product yields and selectivities after a steady-state activity was reached (about 6 hr from the initial setting of the operating conditions). A Molsieve capillary column was used to separate N_2, CH_4, and CO. The column was connected to a thermal conductivity detector (TCD).

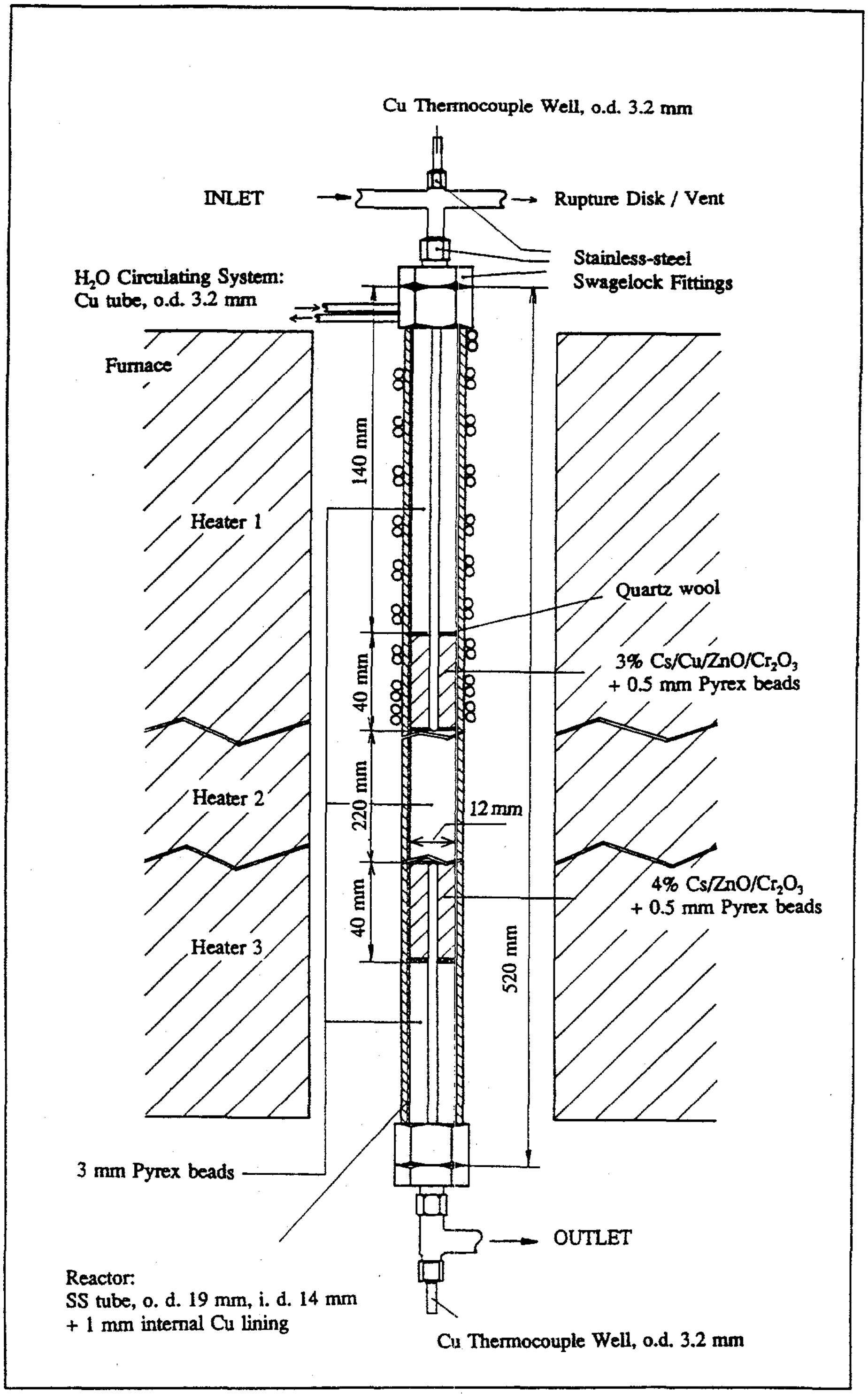

Figure 13. Scaled drawing of the synthesis reactor in the double-bed experiments. Note that the water circulating system was employed during the catalyst pretreatments, but it was removed during the activity testing experiments. The same cooling system was used during the testing of the 3 mol% Cs/Cu/ZnO/Cr_2O_3 catalyst to maintain the temperature of the stainless steel tubing upstream from the reactor below 338K.

The CO/N_2 and CH_4/N_2 %CO molar ratios were applied as follows to evaluate CO conversion (mol%) and methane production (g/kg cat/hr): conversion = 1 - $(CO/N_2)_{outlet}/(CO/N_2)_{inlet}$, and CH_4 productivity = CH_4/N_2 * N_2 Molar Flow Rate * MW_{CH4}.

Knowledge of methane productivity provided for the quantification of the oxygenates and hydrocarbons separated in a capillary CP13 column and analyzed by a flame ionization detector (FID). The same column was temporarily connected to the TCD to determine CO_2 and H_2O yields. The FID response factors were determined by a thorough calibration of the instrument, resulting in significant deviations from the literature data. The identification of products was based on comparison of the retention times with those of known standards and on fragmentation patterns obtained from analyses of liquid samples by a Hewlett Packard gas-chromatograph/mass spectrometer. Carbon balances were calculated in each experiment by comparing the overall amount of carbon detected in the outlet product mixture with the measure of CO conversion; relative errors were always lower than 10%.

Results

HAS Over the 3 mol% Cs-Promoted $Cu/ZnO/Cr_2O_3$ Catalyst

The product distribution observed over the $Cs/Cu/ZnO/Cr_2O_3$ catalyst is represented in Table 2 for typical operating conditions involving low reaction temperature (583K) and low H_2/CO feed ratio (0.45). Linear primary C_1-C_6 alcohols, the C_4-C_7 2-methyl branched primary alcohols, C_3-C_7 secondary alcohols, the corresponding carbonyl species (aldehydes and ketones), methyl esters, traces of dimethyl ether, and C_1-C_6 hydrocarbons were detected and analyzed, and these are indicated in the table by the following abbreviations:

Me	Methyl	MF	Methylformate
Et	Ethyl	MAc	Methylacetate
Pr	Propyl	MPr	Methylpropionate
Bu	Butyl	MiBu	Methylisobutyrate
Pent	Pentyl	MBu	Methylbutyrate
Hex	Hexyl	DME	Dimethylether
2m	2-methyl	HC	Hydrocarbon
3m	3-methyl		

Higher molecular weight products were also formed in small quantities. Methanol (whose synthesis approaches the thermodynamic equilibrium under the conditions employed), ethanol, propanol and isobutanol were the major oxygenated products. Methane and ethane were the most abundant hydrocarbons. The formation of oxygenates and hydrocarbons was accompanied by the production of water, most of which was converted to CO_2 through the water gas shift reaction [Tronconi et al., 1990]. The data reported in Table 2 are in close agreement with those obtained in previous work by Nunan et al. [1989c]. This demonstrates the good reproducibility of the catalyst and of the experiments reported herein; this work has also been verified by repetition of catalyst preparations and of selected kinetic runs.

Table 2. Product distribution observed over the 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst (2 g) under the reference operating conditions with $H_2/CO = 0.45$ synthesis gas at 583K, 7.6 MPa, and with GHSV = 5,450 l(STP)/kg cat/hr.
Abbreviations are defined in the test.

Species	Productivity (g/kg cat/hr)	Species	Productivity (g/kg cat/hr)
Primary Alcohols:		Methyl Esters:	
MeOH	231.0	MF	8.3
EtOH	22.3	MAc	7.4
PrOH	28.6	MPr	5.6
BuOH	6.1	MiBu	6.7
PentOH	1.3	MBu	2.8
HexOH	1.0		
2m-PrOH	28.0	Hydrocarbons:	
2m-BuOH	5.0	Methane	5.1
2m-PentOH	1.5	Ethene	0.02
2m-HexOH	1.5	Ethane	5.9
		Propene	0.1
Secondary Alcohols:		Propane	1.8
2-PrOH	0.1	Buta(e)nes	1.7
2-BuOH	1.5	Penta(e)nes	0.6
3m-2-BuOH	2.9	Hexa(e)nes	0.6
3-PentOH	2.1		
2m-3-PentOH	1.8	Others:	
		DME	1.8
Aldehydes:		C_{7+} Oxygenates	22.5
Acetaldehyde	0.7	CO_2	638
Propionaldehyde	1.1	H_2O	3.4
Isobutyraldehyde	0.9		
Ketones:		CO Conv.	20.2%
Acetone	0.2		
2-Butanone	1.5		
3m-2-Butanone	1.7		
3-Pentanone	1.9		
2m-3-Pentanone	3.0		

The results reported in Figure 14 show the changes observed in the product distribution when the reaction temperature was increased from 583 to 613K. Methanol productivity decreased significantly due to the mentioned thermodynamic constraint. In addition, the production of linear primary alcohols, especially ethanol and propanol, appeared to be disfavored by higher reaction temperature. In effect, the increase in temperature promoted the conversion of the intermediate oxygenates to the terminal species, resulting in a significant enhancement in the production of branched primary alcohols, especially isobutanol. Similarly, the formation of intermediate ketones and secondary alcohols (e.g., 2-butanone and 2-butanol) slightly decreased with increasing temperature, while the production of 2-methyl-3-pentanone and 2-methyl-3-pentanol was significantly enhanced. The formation of methane and higher hydrocarbons also increased at higher reaction temperature; the overall CO_2-free carbon selectivity to hydrocarbons grew from 6.7% at 583K to 15.4% at 613K.

Figure 15 shows the results obtained by varying the H_2/CO synthesis gas ratio in the range of 0.45-3.5. The gradual enrichment of hydrogen in the reactant mixture caused a progressive increase in methanol production. In contrast, the C_{2+} oxygenates exhibited a trend toward a maximum, followed by a plateau sustained at the maximum value. As is known, an initial increase in the H_2/CO ratio promotes the overall chain growth process by favoring CO hydrogenation; an excess of hydrogen tends to slow down the formation of higher oxygenates due to a preferential conversion of the C_1 surface species to methanol [Klier, 1982]. In the case of high-temperature catalysts, the effect of H_2/CO ratio on higher alcohol synthesis has been associated with the inhibiting effect of water, whose concentration increases with increasing H_2 partial pressure [Tronconi et al., 1992]. Figure 15 shows a maximum formation of C_{2+} oxygenates for a H_2/CO value of 0.75. Further experiments have indicated that the position of this maximum does not change with varying reaction temperature. The rate of formation of methane was rather unaffected by the feed composition in the range investigated (CH_4 productivity = 11.17 g/kg cat/hr at $H_2/CO = 0.45$ and 11.24 g/kg cat/hr at $H_2/CO = 3.5$), while the productivity of higher hydrocarbons was reduced from about 30 g/kg cat/hr to 10 g/kg cat/hr upon increasing the H_2/CO ratio from 0.45 to 3.5. This trend, together with the observation that the hydrocarbon products do not fit an Anderson-Schultz-Flory distribution, supports a relationship between higher oxygenate and higher hydrocarbon formation.

At the intermediate temperature of 598K and at the optimal synthesis gas ratio of $H_2/CO = 0.75$, the effect of contact time has been explored by varying GHSV in the range of 3,300-18,375 l(STP)/kg cat/hr. The results are shown in Figure 16 for the most abundant species. More detailed product distributions are reported for selected runs in Table 3 in order to facilitate the following comparison of the performance of the Cu-based catalyst with those of the zinc chromite catalyst and the double-bed system. As shown in Figure 16a for the reaction pressure of 7.6 MPa, increasing the reactant flow rate resulted in a significant enhancement in methanol productivity, amounting to 1.2

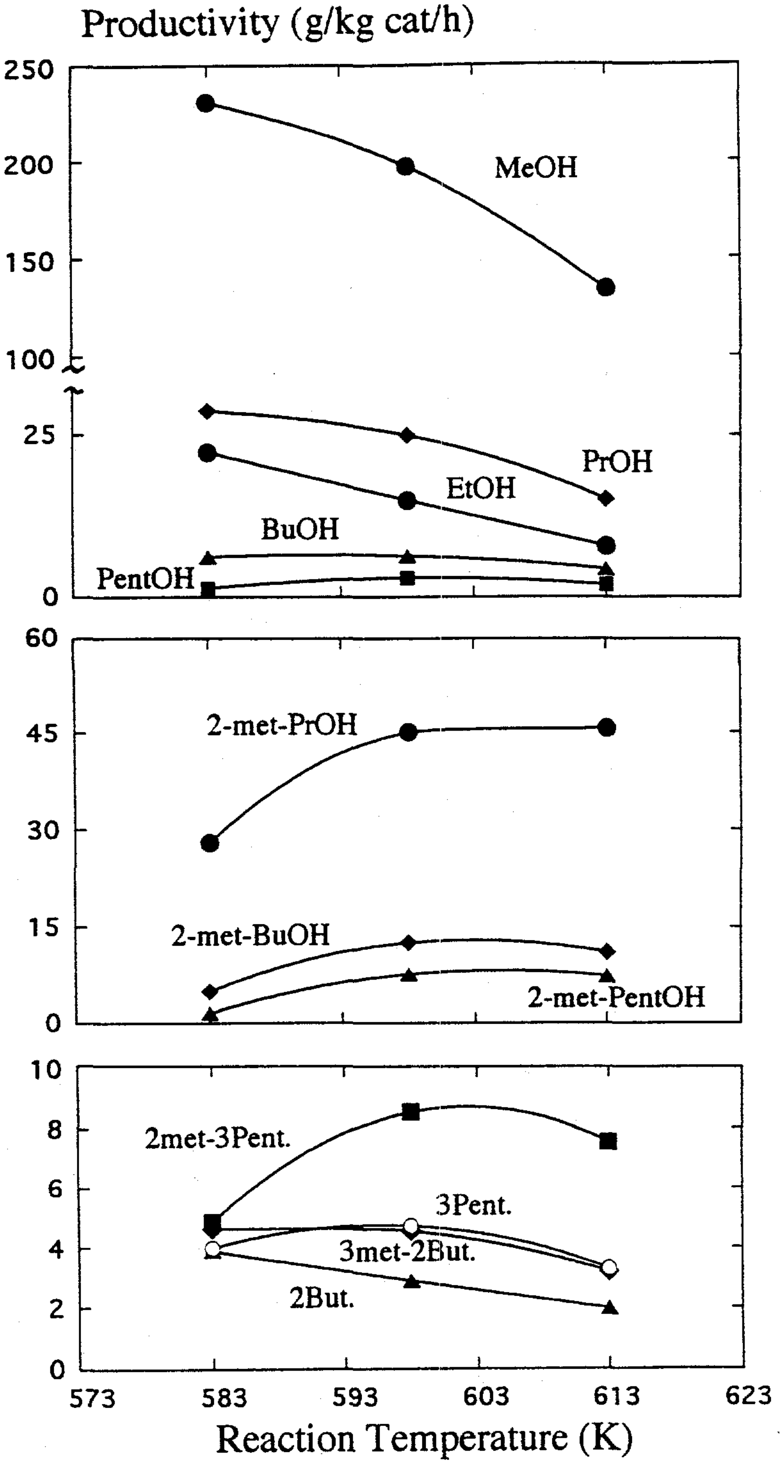

Figure 14. Effect of the reaction temperature on the oxygenate product productivities and distribution observed over the 3 mol% Cs/Cu/ZnO/Cr_2O_3 catalyst. Operating conditions were $H_2/CO = 0.45$, GHSV = 5,450 l(STP)/kg cat/hr, and P = 7.6 MPa. The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

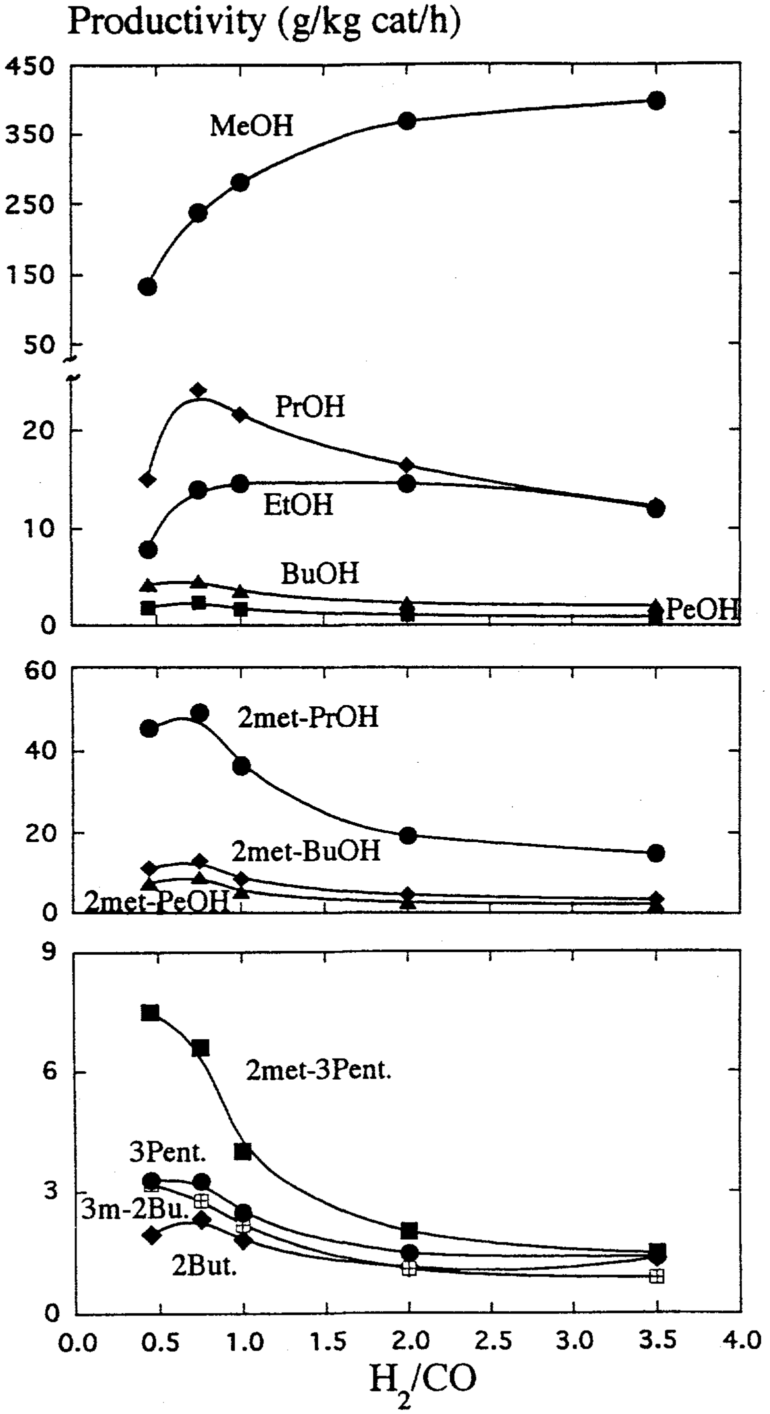

Figure 15. Effect of the synthesis gas composition on the oxygenate product productivities and distribution over the 3 mol% Cs/Cu/ZnO/Cr_2O_3 catalyst. Operating conditions were T = 583K, GHSV = 5,450 l(STP)/kg cat/hr, and P = 7.6 MPa. The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

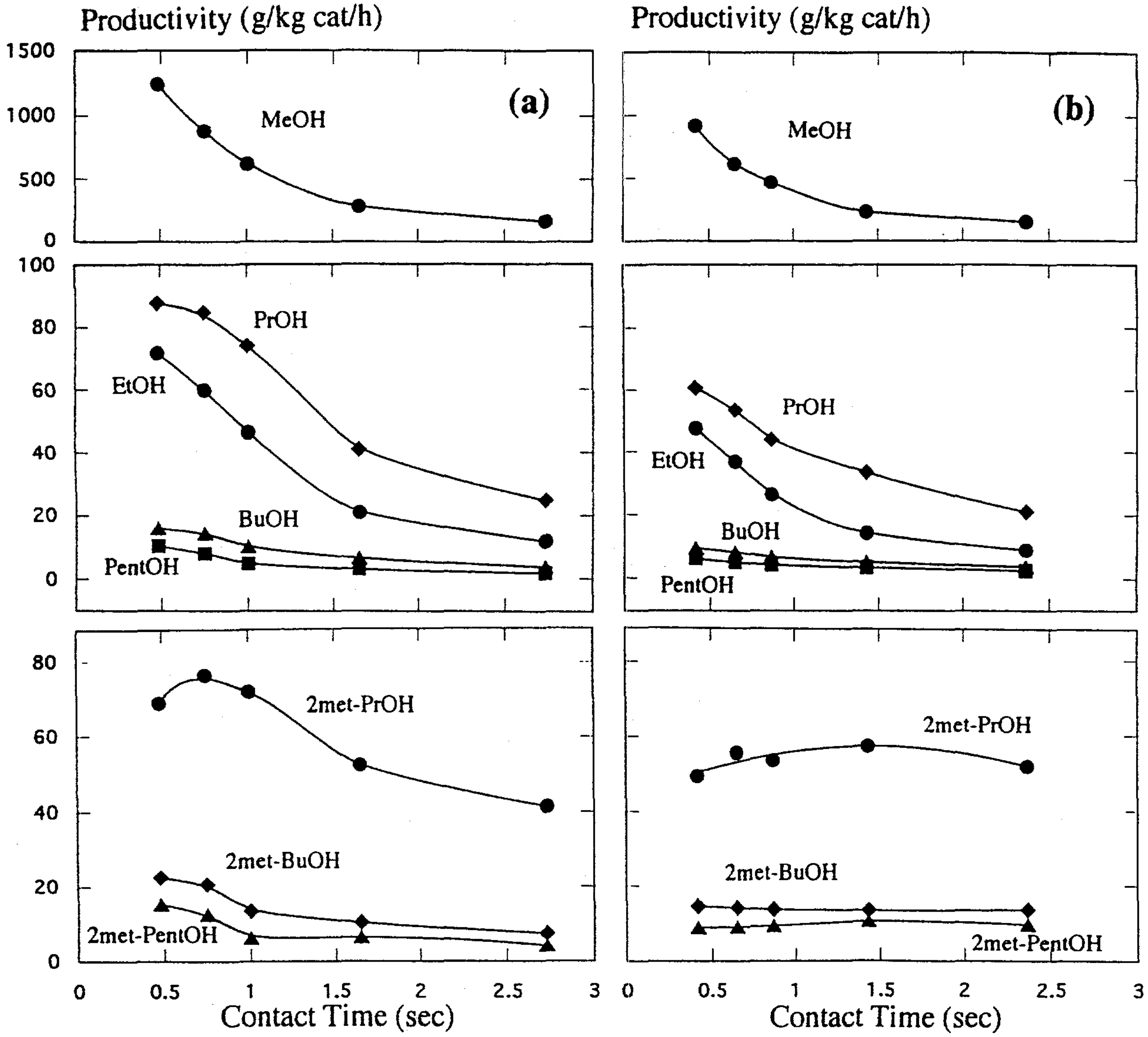

Figure 16. Effect of contact time on the oxygenate product productivities and distribution over the 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst.
Operating conditions were (a) T = 598K, $H_2/CO = 0.75$, and P = 7.6 MPa and (b) T = 598K, $H_2/CO = 0.75$, and P = 6.5 MPa.

Table 3. Higher alcohol synthesis over the 3 mol% Cs/Cu/ZnO/Cr_2O_3 catalyst (2 g) using $H_2/CO = 0.75$ synthesis gas at 598K and 7.6 MPa.

The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

Product	GHSV = 5,450 l(STP)/kg cat/hr (g/kg cat/hr)	GHSV = 12,000 l(STP)/kg cat/hr (g/kg cat/hr)	GHSV = 18,375 l(STP)/kg cat/hr (g/kg cat/hr)
MeOH	268.0	844.5	1200.
EtOH	20.0	59.1	68.7
PrOH	38.8	83.4	83.2
BuOH	6.5	14.1	15.2
PentOH	2.8	8.0	9.6
HexOH	2.3	7.6	10.0
2m-PrOH	52.1	75.9	65.6
2m-BuOH	10.9	21.4	21.0
2m-PentOH	4.8	13.7	14.4
2m-HexOH	5.9	10.1	13.5
2-BuOH	4.5	8.3	9.7
3m-2-BuOH	5.0	8.9	10.2
3-PentOH	4.2	10.2	10.2
2m-3-PentOH	7.4	14.0	16.0
MF	4.2	14.1	20.4
MAC	3.6	11.3	11.7
DME	3.1	5.3	5.3
C_{7+}oxygenates	41.8	61.1	53.9
CH4	11.0	11.0	10.4
C_2 HC	8.1	6.9	6.2
C_3 HC	2.7	2.0	1.2
C_4 HC	2.2	1.4	0.6
% CO Conv. (CO_2-free)	19.7%	13.8%	11.7%

kg/kg cat/hr at GHSV = 18,375 l(STP)/kg cat/hr. This result alone is remarkable in that the synthesis gas initially contained no CO_2, a well-known promoter of methanol synthesis over copper-based catalysts [Klier et al., 1982]. At the same time, the productivity of the higher oxygenates increased with increasing flow rate. However, at extremely high GHSV values, the formation of C_{2+} species tended to be reduced due to short contact times. Thus, the plots of higher alcohol yields exhibited maxima that, in line with the reaction mechanism, were observed to shift towards longer contact times with an increasing number of carbons in the oxygenate (more chain growth steps involved). In particular, the still increasing profile of ethanol at high flow rates, the slightly bent profile of propanol, and the fully bent profile of isobutanol clearly exemplified the sequence of steps leading to the formation of isobutanol, ethanol $\Rightarrow$ propanol $\Rightarrow$ isobutanol, that were identified in earlier ^{13}C isotope labeling work [Nunan et al., 1988 and 1989a,b]. The maximum productivity to isobutanol has been observed at GHSV = 12,000 l(STP)/kg cat/hr and corresponded to 76 g/kg cat/hr. This represents an improvement of over 150% with respect to catalyst performance under the typical operating conditions adopted for Cu-containing catalysts (see Table 2).

The qualitative trends of methanol and higher alcohol productivities as a function of contact time did not change at the lower pressure of 6.5 MPa, as shown in Figure 16b. However, the decrease in pressure caused a strong reduction in methanol formation. A slower rate of higher oxygenate synthesis was also evident at short contact times, when the productivity of linear and branched alcohols was significantly lower than that observed at 7.6 MPa. In contrast, at longer contact times, the formation of C_{2+} oxygenates at 7.6 MPa was comparable to that obtained at the lower pressure of 6.5 MPa; this was possibly due to surface saturation by adsorbed oxygenates at the longer contact times, which moderated the effect of higher partial pressures of the reactants at the higher total reaction pressure. The analysis of the combined effects of flow rate and total pressure indicates that moderate values of flow rate and the lower pressure represent the best conditions for obtaining the highest C_{2+} oxygenates/methanol selectivities.

HAS Over the 4 mol% Cs-Promoted ZnO/Cr_2O_3 Catalyst

Selected experiments were performed over the Cs-promoted commercial zinc chromite catalyst at a constant temperature (678K), feed composition ($H_2/CO = 0.75$) and pressure (7.6 MPa), while the GHSV was varied in the range of 5,450-18,375 l(STP)/kg cat/hr. The results are summarized in Table 4. A lower conversion of CO was observed compared to the Cu-based catalyst, due in particular to the lower equilibrium amount of methanol produced at high temperature. The formation of C_{2+} oxygenates over the $Cs/ZnO/Cr_2O_3$ catalyst at 678K was comparable in amount to that observed over the $Cs/Cu/ZnO/Cr_2O_3$ catalyst at 598K. However, major differences in the distribution of the higher oxygenates were observed over the two catalysts. The data in Table 4 indicate a very low productivity in intermediate species and a selective formation of isobutanol over the Cu-free catalyst. In addition, very small quantities of secondary alcohols and ketones

Table 4. Higher alcohol synthesis over the 4 mol% Cs/ZnO/Cr_2O_3 catalyst (2 g) with H_2/CO = 0.75 synthesis gas at 678K and 7.6 MPa.

The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

Product	GHSV = 5,450 l(STP)/kg cat/hr (g/kg cat/hr)	GHSV = 12,000 l(STP)/kg cat/hr (g/kg cat/hr)	GHSV = 18,375 l(STP)/kg cat/hr (g/kg cat/hr)
MeOH	52.8	132.8	173.4
EtOH	0.8	2.1	2.7
PrOH	3.8	8.7	11.5
BuOH	0.3	0.7	0.9
PentOH	0.2	0.5	0.6
HexOH	0.1	0.2	0.3
2m-PrOH	39.5	69.1	74.1
2m-BuOH	4.2	7.9	8.3
2m-PentOH	2.4	7.0	5.3
2m-HexOH	0.2	0.7	0.9
2-BuOH	1.8	1.2	2.5
3m-2-BuOH	0.4	0.9	0.9
3-PentOH	0.4	0.7	1.2
2m-3-PentOH	2.9	5.4	5.5
MF	2.4	1.2	1.1
MAC	0.2	0.7	0.8
DME	2.9	4.5	4.7
C_{7+}oxygenates	51.6	79.0	78.0
CH4	2.8	3.9	4.1
C_2 HC	5.1	7.5	7.9
C_3 HC	3.3	4.5	4.6
C_4 HC	2.5	5.0	3.1
% CO Conv. (CO_2-free)	8.1%	4.9%	4.5%

were observed. In line with the low production of methanol, methyl esters and dimethyl ether were only minor products. Methyl esters were also low because of thermodynamic constraints, and dimethyl ether was also low because of the low acidity of the catalysts due to the relatively high basic Cs dopant contents. The formation of methane was significantly lower than observed over the Cu-based catalyst. On the contrary, the formation of higher hydrocarbons (mainly olefins) was enhanced. The productivity of oxygenates and hydrocarbons was observed to increase with increasing flow rate. At high values of GHSV, the distribution of the higher alcohols maintained a high selectivity to isobutanol, which, along with methanol, was the only major product observed.

HAS Over the Double-Bed 3 mol% Cs-Promoted Cu/ZnO/Cr_2O_3 and 4 mol% Cs-Promoted ZnO/Cr_2O_3 Catalysts

Double-bed kinetic runs were carried out under the following conditions: $T_{\text{first bed}}$ = 598K, $T_{\text{second bed}}$ = 678K, P = 7.6 MPa, H_2/CO = 0.75, and GHSV = 5,450-18,375 l(STP)/kg cat/hr. Equal amounts of the 3% Cs/Cu/ZnO/Cr_2O_3 and 4% Cs/ZnO/Cr_2O_3 catalysts were used in the first and second beds, respectively. The results of the experiments are summarized in Table 5. The amount of methanol produced over the double-bed configuration was comparable to that obtained over the zinc chromite catalyst alone. The productivity of intermediate linear alcohols appeared significantly lower and slightly higher than obtained over the single Cu-based and Cu-free catalysts, respectively. The productivities of isobutanol, isobutanal, and higher 2-methyl branched oxygenates were significantly higher than those observed over either of the two catalysts. At GHSV = 5,450 l(STP)/kg cat/hr, the enhancement of isobutanol productivity with the double-bed configuration was 40% of the amount produced by the single Cu-based catalyst and 80% of the amount produced by the zinc chromite catalyst. The formation of secondary alcohols and ketones was intermediate to the performances of the two single catalysts. The formation of high molecular weight oxygenates (C_{7+}) did not seem to be affected by the double-bed configuration at low flow rates, with similar productivities over all three catalysts; see Tables 3-5. With increasing GHSV, the productivities of these oxygenates first increased with moderate GHSV and then decreased at high GHSV, as expected for high molecular weight secondary products. This C_{7+} oxygenate productivity was especially enhanced at moderate GHSV over the double-bed catalysts, with an apparent maximum at somewhat above GHSV = 12,000 l(STP)/kg cat/hr. The productivity of methane observed over the combined catalysts was comparable to the amount observed over the Cu-based catalyst, while the productivity of higher hydrocarbons (mainly olefins) was enhanced with respect to the individual catalysts.

The same quantitative comparison of the performances of the double-bed systems with those of the single beds apply at each value of GHSV investigated. With increasing flow rate, high productivities of isobutanol and 2-methyl oxygenates were observed, while the desirable high selectivities were retained. However, methanol productivity increased

Table 5. Higher alcohol synthesis over the double-bed 3 mol% Cs/Cu/ZnO/Cr_2O_3 and 4 mol% Cs/ZnO/Cr_2O_3 catalyst with H_2/CO = 0.75 synthesis gas at 7.6 MPa. The operating conditions were: top bed = 3 mol% Cs/Cu/ZnO/Cr_2O_3 (1 g) at 598K and bottom bed = 4 mol% Cs/ZnO/Cr_2O_3 (1 g) at 678K. The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

Product	GHSV = 5,450 l(STP)/kg cat/hr (g/kg cat/hr)	GHSV = 12,000 l(STP)/kg cat/hr (g/kg cat/hr)	GHSV = 18,375 l(STP)/kg cat/hr (g/kg cat/hr)
MeOH	56.6	114.3	178.8
EtOH	1.1	3.9	7.0
PrOH	6.5	18.7	23.5
BuOH	1.3	3.3	4.2
PentOH	1.1	2.3	3.1
HexOH	1.3	1.9	2.3
2m-PrOH	76.8	114.6	138.8
2m-BuOH	16.2	27.1	32.9
2m-PentOH	8.9	16.0	21.7
2m-HexOH	7.5	17.4	24.0
2-BuOH	1.0	4.4	5.2
3m-2-BuOH	2.8	6.9	7.2
3-PentOH	2.3	6.8	7.7
2m-3-PentOH	10.5	19.7	23.1
MF	6.1	8.9	11.3
MAC	2.1	2.0	1.7
DME	2.9	4.4	4.8
C_{7+}oxygenates	46.9	135.5	81.5
CH4	10.5	12.4	12.0
C_2 HC	9.5	19.9	18.1
C_3 HC	3.0	3.5	4.8
C_4 HC	4.5	2.2	5.1
% CO Conv. (CO_2-free)	12.0%	9.4%	6.6%

faster than the C_{2+} oxygenates productivities with increasing GHSV. Consequently, the molar ratio of methanol/2-methyl branched alcohols varied in the three experiments; they were 1.17, 1.62, and 2.05 at GHSV = 5,450, 12,000, and 18,375 l(STP)/kg cat/hr, respectively.

Discussion

The kinetic investigation over the ternary Cs-doped, Cu-based catalyst indicated that the overall yield of higher oxygenates was enhanced with increasing temperature and was optimal for a H_2/CO syngas ratio of 0.75. As did methanol formation, the production of C_{2+} species increased with gas hourly space velocity and total pressure. Under the optimized operating conditions (598K, $H_2/CO = 0.75$, GHSV = 12,000 l(STP)/kg cat/hr, and 7.6MPa), the productivities of both the higher alcohols and methanol were significantly higher than those reported in the literature for other higher alcohol synthesis catalysts [Nunan et al., 1989a-c; Forzatti and Tronconi, 1991; Boz et al., 1994].

The typical feature of the C_{2+} product distribution over the $Cs/Cu/ZnO/Cr_2O_3$ catalyst is an extensive formation of light alcohols. As intermediates of the chain growth process, they represent a considerable potential for further improvement in the production of terminal branched species. It can be easily calculated that a complete and selective conversion of ethanol and propanol could double the observed productivities of isobutanol. The abundance of ethanol and propanol in the reacting system is related to the abundance of methanol. It is known that the first C-C bond formation is the rate-determining step of the chain growth process. Over the ternary Cu-based catalyst, apparently, a high surface concentration of C_1 reactive species can in part compensate for the intrinsic low rate of the $C1 \Rightarrow C2$ step. As previously observed, the formation of C_2-C_3 primary alcohols decreases significantly with increasing reaction temperature, while a more selective formation of the terminal branched species takes place. This trend is favorable for maximizing the formation of 2-methyl alcohols. However, at temperatures beyond the range explored, the reduced concentration of surface C_1 species is likely to become a limiting factor for the formation of higher oxygenates. Moreover, an increase in reaction temperature is generally accompanied by a decrease in catalyst stability. At 613K, a constant catalytic activity (constant CO conversion and constant product distribution) was observed over a period of 150 hr only. At the intermediate temperature of 598K, all the above-mentioned factors (supply of C_1 species, relative rates of the chain growth routes, stability of the catalyst) appeared to be compromised, as high productivities of isobutanol and 2-methyl alcohols could be obtained only with significant formation of methanol and short chain alcohols. At this temperature, the catalyst performance was shown to be stable over a period of 300-350 hr.

Conversely, the product distribution observed over the Cs-promoted commercial ZnO/Cr_2O_3 catalyst is characterized by low selectivities to ethanol and propanol and high selectivities to isobutanol. The chemical pathway

$$C_2 \xrightarrow{+C_1} C_3 \xrightarrow{+C_1} iC_4 \qquad (1)$$

appears to prevail over any competitive route, as indicated by the low quantities of C_4-C_6 oxygenates produced *via* cross condensations of the C_2 and C_3 intermediates. The high rate of the C_n + C_1 steps is most probably related to the high reaction temperature employed. Nevertheless, it must be noted that neither the ternary Cu-based catalyst tested at the same temperature nor other Zn/Cr/O catalysts with different compositions [Forzatti and Tronconi, 1991] have achieved the selectivity for isobutanol as the currently used Cs-promoted commercial catalyst. A specific contribution of the 4% Cs/ZnO/Cr_2O_3 catalyst in promoting the pathway (1) must therefore be taken into account.

The double-bed configuration combines the complementary features of the two catalytic systems, wherein each is allowed to operate under its own optimal temperature regime for the production of higher oxygenates. The 3% Cs/Cu/ZnO/Cr_2O_3 catalyst, operating at 598K as the first bed, produced methanol, ethanol and propanol in abundance; the 4% Cs/ZnO/Cr_2O_3 catalyst, operating at 678K as the second bed, efficiently converted the supplied C_2 and C_3 intermediates to the terminal branched alcohols. In other terms, the double-bed design takes advantage of the separation of the overall HAS process into two subsequent steps: the initial low-temperature formation of the first C-C bond and the following high-temperature carbon chain growth process. The former step controls the rate of the overall oxygenates formation, while the latter effects the high selectivity to the 2-methyl alcohols, primarily isobutanol. As a result, at GHSV = 18,375 l(STP)/kg cat/hr, the overall formation of 2-methyl oxygenates over the double-bed configuration amounts to over 215 g/kg cat/hr, which represents an improvement of 90% with respect to the performance of the single Cs/Cu/ZnO/Cr_2O_3 catalyst, and 145% with respect to the single Cs/ZnO/Cr_2O_3 catalyst.

It must be noted that the double-bed configuration is penalized with respect to the single Cu-based catalyst by a considerable "loss" of CO conversion. A comparison of results obtained over the double-bed system at GHSV = 5,450 l(STP)/kg cat/hr with those obtained over the single Cu-based catalyst at approximately twice the space velocity (12,000 l(STP)/kg cat/hr) allows the estimate that almost 80% of methanol produced over the first bed is decomposed over the high-temperature bed to CO and H_2. However, as already pointed out, the net result of the reduced amount of methanol and the increased formation of branched species over the double-bed configuration is a very favorable methanol/2-methyl-oxygenates molar ratio.

It is finally observed that the enhanced formation of higher oxygenates over the double-bed configuration is accompanied by an increase in C_{2+} hydrocarbons, probably due to the dehydration and decarboxylation reactions of higher alcohols that occur over the high-temperature catalysts [Forzatti and Tronconi, 1991]. However, the molar carbon selectivity to C_{2+} oxygenates is still more than one order of magnitude higher than the carbon selectivity to C_{2+} hydrocarbons.

Conclusions

A thorough kinetic investigation has provided evidence for a remarkably high activity of the 3% $Cs/Cu/ZnO/Cr_2O_3$ catalyst in both methanol and higher alcohol synthesis. The specific property of the ternary Cu-based catalyst in producing large amounts of short chain oxygenates can be exploited to enhance the formation of branched alcohols. This has been demonstrated by designing a double-bed system wherein the 3% $Cs/Cu/ZnO/Cr_2O_3$ catalyst, operating as the first low-temperature bed, initiates the chain growth process by forming C_1-C_3 oxygenated intermediate species, while a 4% $Cs/ZnO/Cr_2O_3$ catalyst, operating as the second high-temperature bed, terminates HAS with the formation of branched alcohols, primarily isobutanol. Such a configuration results in the selective production of methanol and 2-methyl branched alcohols mixtures with molar ratios close to 1.

It is noted that not all the reaction parameters in the present double-bed experiments have been optimized. The operating conditions were chosen to guarantee maximum production of C_2 and C_3 intermediates over the ternary copper-based catalyst. A further increase in isobutanol productivity could be achieved by exploring the effect of varying the temperature of the second bed, the total pressure, and the relative amounts of catalysts in the two beds. However, this optimization research appears more suitable for a theoretical approach based on the simulation of the specific reaction kinetics of the two catalysts. In general, the research reported here points out that the manipulation of HAS by means of reaction engineering (i.e., effecting the process through steps in tandem) represents a valid alternative to the development of new and more active catalysts for the synthesis of isobutanol.

III. EFFECT OF REACTION PRESSURE ON HIGHER ALCOHOL SYNTHESIS OVER THE DOUBLE-BED Cs-PROMOTED CATALYSTS

Introduction

The production of valuable gasoline octane enhancers from CO hydrogenation reactions has recently received much interest [Brown, 1993; Zhou, 1994]. Production of methanol from $H_2/CO/CO_2$ synthesis gas mixtures over $Cu/ZnO/(Al_2O_3$ or $Cr_2O_3)$ catalysts at moderate pressures and temperatures is a well-established commercial process [Klier, 1982; Rogerson, 1984; Supp and Quinkler, 1984; Bridger and Spenser, 1989; Herman, 1991]. In this process, selectivity to methanol is nearly 100%, with space time yields as high as several kilograms per kilogram of catalyst per hour. It has been proposed in the literature that certain octane or cetane enhancers, such as methyl tertiary-butyl ether (MTBE) and methyl isobutyl ether (MIBE), can be synthesized by the direct or indirect coupling of methanol and isobutanol [Nunan et al., 1985; Keim and Falter, 1989; Klier et al., 1992; Klier et al., 1993a,b; Sanfilippo, 1993]. This concept has been demonstrated for the direct one-step synthesis of MIBE [Nunan et al., 1985] and for the indirect synthesis of MTBE *via* a continuous two-stage process using two different catalysts [Herman et al., 1994]. With MTBE in mind, it is desirable to increase isobutanol yields in the higher alcohol synthesis process that utilizes CO_2-free synthesis gas.

It is known that over catalysts investigated for higher alcohol synthesis, such as alkali-doped, low-temperature, copper-based catalysts [Klier et al., 1984; Nunan et al., 1989a-c; Hindermann et al., 1993; Boz et al., 1994] and high temperature copper-free ZnO/Cr_2O_3 catalysts [Natta et al., 1957; Paggini et al., 1986; Forzatti and Tronconi, 1991], the major products of CO hydrogenation are methanol and branched alcohols. Once formed, the branched alcohols are stable and do not react further in the chain growth process [Nunan et al., 1988; Smith et al., 1990 and 1991; Lietti et al., 1992]. However, the rate-determining step is the $C_1 \Rightarrow C_2$ step that initiates the chain growth process, and, by virtue of its low rate, limits the production of higher oxygenates. Few reports of significant isobutanol yields over the above-mentioned catalysts are found in the literature [Beretta et al., 1995 and 1996]; however, it is clear that high productivities must be achieved if isobutanol is to be used in the synthesis of high-value products like MTBE. Recent work in this area has focused on the optimization of reaction conditions over cesium-promoted catalysts [Nunan et al., 1989a and 1989c; Beretta et al., 1994], the development of new catalysts [Keim and Falter, 1989; Ueda et al., 1993; Minihan and Nagaki, 1994], and new process engineering concepts [Beretta et al., 1996].

It is known from the results of chemical enrichment experiments [Nunan et al., 1989a; Lietti et al., 1992; Klier et al., 1993a; Herman and Lietti, 1994] that the addition of C_2 and C_3 intermediates to the reaction system generally promotes HAS productivity, in particular the production of branched alcohols. Recent studies [Beretta et al., 1995 and 1996] have demonstrated a new concept of producing these branched alcohols in a single reactor using CO_2-free H_2/CO synthesis gas as a reactant mixture. In that scheme, a double catalyst bed configuration was employed, wherein the top bed supplied methanol and C_2-C_3 intermediate oxygenates that were then converted to branched alcohols by the bottom-bed catalyst. In the current study, the effect of higher reaction pressure was examined in a continuing effort to improve isobutanol yields.

Experimental

Catalyst Preparation

The copper-based catalyst was prepared by the coprecipitation method described previously [Nunan et al., 1989d]. This method consisted of the initial precipitation of hydroxycarbonate precursors from nitrate solutions of Cu, Zn, and Cr at a constant pH of 9.5 using sodium carbonate as the precipitating agent. The resulting precursors were filtered and washed free of sodium, and then dried, crushed, sieved and calcined at 623K for 3 hr. The Cu-free ZnO/Cr_2O_3 catalyst (obtained from Harshaw) was calcined in N_2 at 673K for 4 hr. After calcination, both catalysts were cesium doped in the same manner, wherein the samples were added to a N_2-purged solution of cesium formate that was subsequently evaporated to dryness under flowing N_2 at a constant temperature of 323K. After doping, samples were re-calcined in air at 623K for 3 hr.

Catalytic Testing

Catalyst testing was carried out in a tubular, fixed-bed, downflow, stainless steel reactor described previously [Nunan et al., 1989a] and shown in an earlier section of this report. In order to minimize the formation of iron carbonyl, the reactor was lined with copper, and charcoal traps were placed in the reactant feed streams.

The double-bed experiments were performed with 1.0 g of each catalyst, diluted with 5 ml of 0.5-mm Pyrex beads. The reactor was loaded such that the top and bottom beds were separated by approximately 22 cm of 3-mm Pyrex beads. The temperature of each bed was monitored and controlled by thermocouples contained in individual copper-wells. In the case of the single-bed experiments, a 2.0-g portion of catalyst was diluted with 7 ml of 0.5-mm Pyrex beads and loaded into the center of the reactor.

Kinetic testing was carried out with H_2/CO ratios of 0.75 and 1.0 and a gas hourly space velocity (GHSV) of 18,375 l(STP)/kg cat/hr. In the double-bed configuration, the top bed was maintained at 598K, while the bottom bed was varied from 613 to 678K. Reaction temperature ranged from 613 to 703K in the single-bed experiments. The system pressure was varied from 7.6 to 12.4 MPa. Under each set of conditions, steady-state activity was attained within 4 hr, and conditions were held constant for at least 24 hr. Before testing, the catalysts were reduced *in situ* with a flowing 2% H_2/N_2 gas mixture. Copper-based catalysts were reduced at a temperature of 523K, while copper-free catalysts were reduced at 723K. The reduction process was monitored by H_2O production as detected by gas chromatography (GC). Reduction was considered complete when the intensity of the peak for water decreased and became insignificant on the chromatogram.

Reaction products were monitored and analyzed by an online, dedicated Hewlett-Packard Model 5890 gas chromatograph coupled to a Hewlett-Packard 3396 integrator and a personal computer for data collection. The reactor exit stream was sampled every 20-60 min *via* an automated in-line heated Valco sampling valve. Peak identification was achieved by liquid product collection followed by GC/MS analysis. Space-time yields (STY) of the products were calculated by carbon balance.

Results

HAS Over the Double-Bed 3 mol% Cs-Cu/ZnO/Cr_2O_3 and 4 mol% Cs-ZnO/Cr_2O_3 Catalysts

Higher alcohol synthesis research over cesium-promoted copper-containing and copper-free ZnO/Cr_2O_3-based catalysts at 7.6 MPa, both alone and in tandem, has been reported here, as well as in the literature [Beretta et al., 1995 and 1996]. In this current investigation, a new batch of catalyst was synthesized and tested under the same conditions to determine reproducibility. In addition, the pressure dependence of HAS activity was studied. Figure 17 shows the distribution of major products at a H_2/CO ratio of 0.75 and at pressures of 7.6 and 10.3 MPa. It can be seen that higher pressure favors the production of most of the products, with the exception of 3-methyl-2-butanol (3m-2-BuOH), 3-pentanol, and C_2-C_4 hydrocarbons. Under these conditions, the major products observed were methanol and isobutanol. Methanol productivity showed the strongest pressure dependence, increasing from 173 g/kg cat/hr at 7.6 MPa to 398 g/kg cat/hr at 10.3 MPa. Production of isobutanol exhibited a milder dependence upon pressure, with an STY of 125 g/kg cat/hr at 7.6 MPa and 166 g/kg cat/hr at 10.3 MPa.

A more complete listing of the products formed at the two pressures of 7.6 and 10.3 MPa are given in Table 6. It is evident that the quantities of the esters and C_{7+} oxygenates formed under these reaction conditions were not significantly affected by the reaction pressure. Increasing the pressure by 35.5% increased CO conversion to products by 36.1% when reaction conditions of $H_2/CO = 0.75$ synthesis gas mixture were employed.

Testing of this catalyst system was continued after changing the synthesis gas mixture to $H_2/CO = 1.00$. The pressure was changed stepwise from 12.4 to 10.3 to 7.6 MPa, while the temperatures of the two catalyst beds were maintained constant at 598K (top) and 678K (bottom). The productivity of four major products (methanol, isobutanol, propanol, and hydrocarbons) obtained at the H_2/CO ratio of 1.00 is illustrated in Figure 18. All products demonstrated decreasing productivities with decreasing reaction pressure, with the exception of the C_2-C_4 hydrocarbons, as shown in Table 7. Similar to the results obtained with a H_2/CO ratio of 0.75 (Figure 17), the pressure dependence of methanol

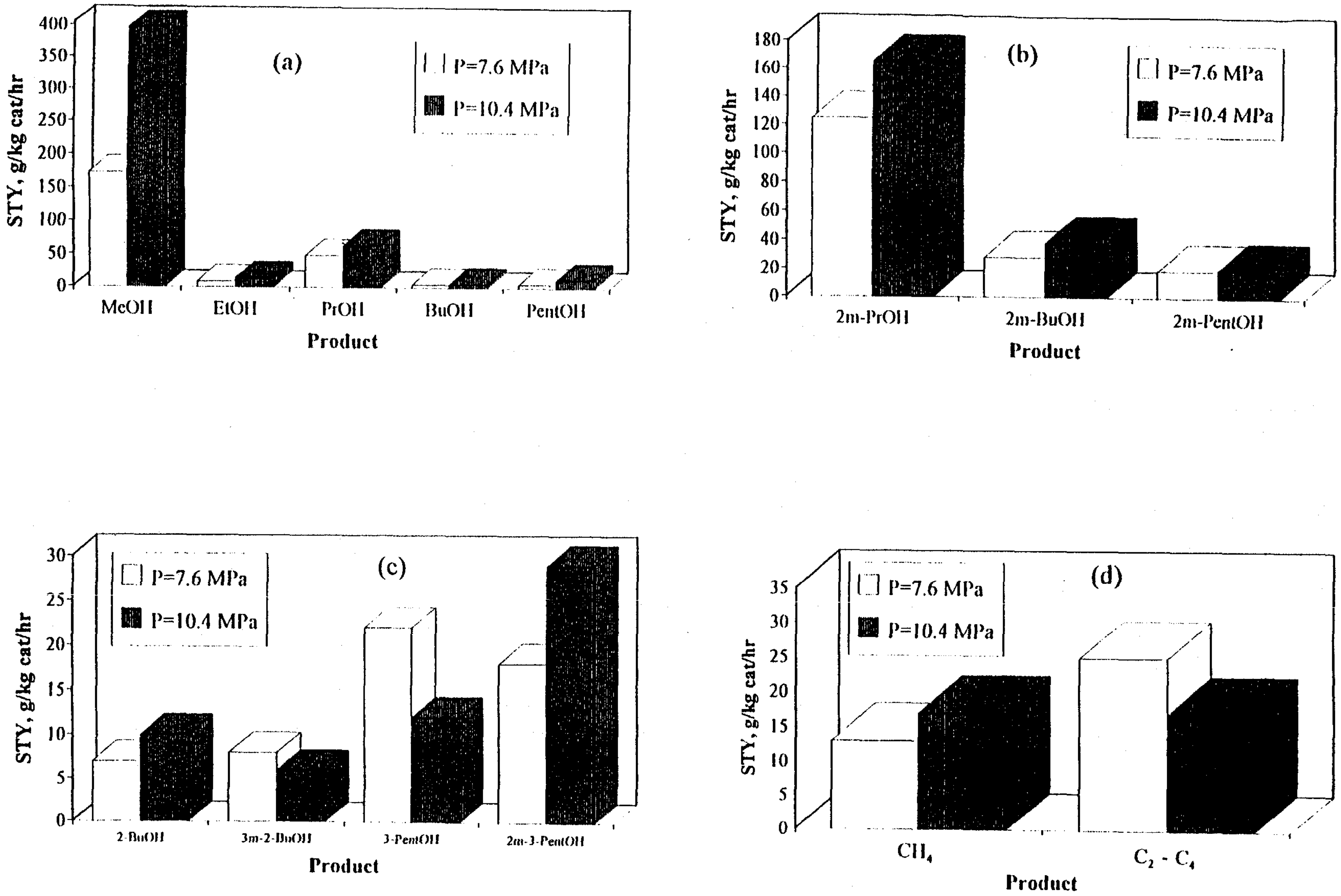

Figure 17. Product distributions, expressed in terms of space time yields (STY), over the double-bed 3 mol% Cs-Cu/ZnO/Cr_2O_3 and 4 mol% Cs-ZnO/Cr_2O_3 catalysts with $T_{top\ bed}$ = 598K, $T_{bottom\ bed}$ = 678K, H_2/CO = 0.75 and GHSV = 18,375 l(STP)/kg cat/hr at reaction pressures of 7.6 and 10.3 MPa for (a) primary alcohols, (b) branched alcohols, (c) secondary alcohols, and (d) hydrocarbons.

Table 6. Productivities (g/kg cat/hr) of products formed during higher alcohol synthesis from $H_2/CO = 0.75$ synthesis gas over the double-bed 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ (top bed) and 4 mol% $Cs/ZnO/Cr_2O_3$ (bottom bed) catalysts with $T_{top\ bed} = 598K$, $T_{bottom\ bed} = 678K$, and GHSV = 18,375 l(STP)/kg cat/hr. The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols.

Product	P = 7.6 MPa (g/kg cat/hr)	P = 10.3 MPa (g/kg cat/hr)
MeOH	173	398
EtOH	9	14
PrOH	49	64
BuOH	5	6
PentOH	6	6
2m-PrOH	125	166
2m-BuOH	28	38
2m-PentOH	19	20
2-BuOH	7	10
3m-2-BuOH	8	6
3-PentOH	22	12
2m-3-PentOH	18	29
MF	6	8
MAC	0	0
DME	4	8
C_{7+}oxygenates	7	7
CH_4	13	17
C_2-C_4 HC	25	17
% CO Conv. (CO_2-free)	6.1	8.3

productivity was the strongest, increasing approximately 300% when the reaction pressure was increased from 7.6 to 12.4 MPa. Propanol STY varied from 18 to 81 g/kg cat/hr over the pressure range studied. Reaction pressure had a less significant effect on the observed isobutanol productivity, which was 96 and 153 g/kg cat/hr at pressures of 7.6 and 12.4 MPa, respectively.

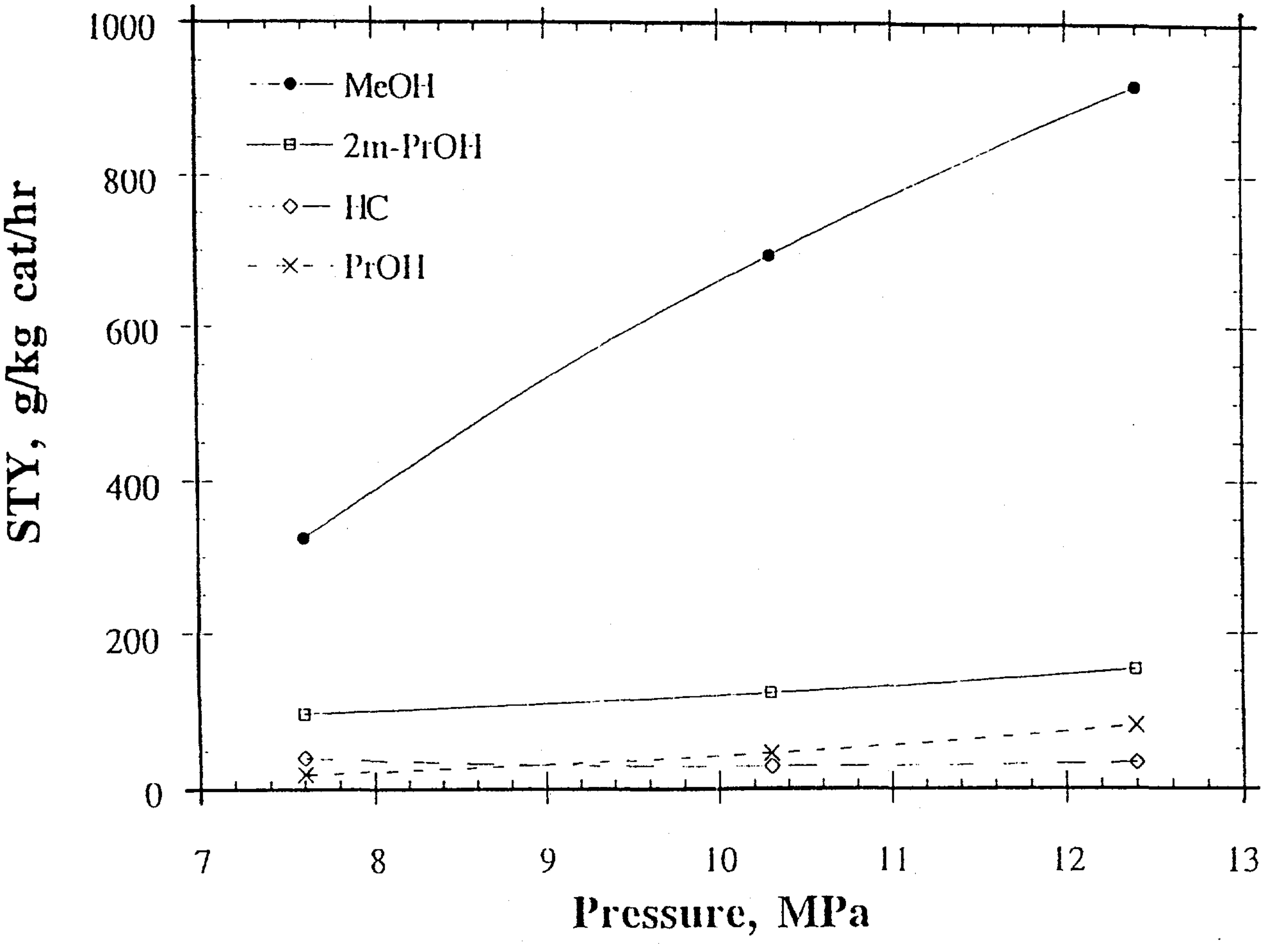

Figure 18. Effect of reaction pressure on productivity over the double-bed 3 mol % Cs-Cu/ZnO/Cr_2O_3 and 4 mol% Cs-ZnO/Cr_2O_3 catalysts with $T_{top\ bed}$ = 598K, $T_{bottom\ bed}$ = 678K, H_2/CO = 1.00 and GHSV = 18,375 l(STP)/kg cat/hr.

Table 7. Productivities (g/kg cat/hr) of products formed during higher alcohol synthesis from $H_2/CO = 1.00$ synthesis gas over the double-bed 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ (top bed) and 4 mol% $Cs/ZnO/Cr_2O_3$ (bottom bed) catalysts with $T_{top\ bed} = 598K$, $T_{bottom\ bed} = 678K$ and GHSV = 18,375 l(STP)/kg cat/hr.
The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols.

Product	P = 12.4 MPa (g/kg cat/hr)	P = 10.3 MPa (g/kg cat/hr)	P = 7.6 MPa (g/kg cat/hr)
MeOH	902	696	324
EtOH	22	12	5
PrOH	81	45	18
BuOH	9	3	1
PentOH	3	2	1
2m-PrOH	153	122	96
2m-BuOH	29	17	13
2m-PentOH	13	9	9
2-BuOH	5	3	2
3m-2-BuOH	5	2	1
3-PentOH	9	10	9
2m-3-PentOH	21	19	13
MF	5	5	3
MAC	0	0	0
DME	21	18	9
C_{7+}oxygenates	9	7	7
CH4	20	17	14
C_2-C_4 HC	13	11	26
% CO Conv. (CO_2-free)	11.6	8.3	4.9

The space time yields of the products obtained with $H_2/CO = 1.00$ synthesis gas and varying reaction pressure are summarized in Table 7. In addition to the major products mentioned above, small amounts of methylformate (MF) and dimethyl ether (DME) were produced. The productivity of DME varied directly as the space time yield of methanol varied, but the quantity of MF varied little as the pressure was altered. Also included in the table are the CO conversions under the various reaction conditions. As expected, CO conversion was enhanced by the higher reaction pressures.

HAS Over the Single-Bed 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ Catalyst at High Temperature

The 3 mol% Cs $Cu/ZnO/Cr_2O_3$ catalyst has been studied under HAS conditions up to a reaction temperature of 613K [Beretta et al., 1996]. One of the goals of this study was to further probe the viable working temperature range of this copper-based catalyst. To this end, the catalyst was studied in a single-bed configuration at reaction temperatures in the range of 613 to 703K, and the results are shown in Figure 19. All of the major products decreased with increasing reaction temperature. Methanol STY dropped significantly from 122 g/kg cat/hr at 613K to 18 g/kg cat/hr at 703K. The decrease in isobutanol STY was much less significant, falling from 73 to 40 g/kg cat/hr as the reaction temperature increased from 613 to 703K. Reaction temperature also influenced CO conversion, which decreased from 9.6% at 613K to 4.2% at 703K, as shown in Table 8.

Discussion

The current study has shown that both cesium-doped copper-based and copper-free ZnO/Cr_2O_3 catalysts are active in higher alcohol synthesis at high temperatures and pressures. Our previous studies indicated the advantage of combining the Cu-based and Cu-free catalysts in a double-bed configuration [see Section II of this report and Beretta et al., 1996]. Indeed, Beretta et al. [1996] showed that by utilizing the double-bed configuration, the productivity of 2-methyl oxygenates could be increased by as much as 90% compared with a single Cu-based bed and 145% compared with a single Cu-free bed. In the present study, a new batch of catalyst was prepared according to the procedure reported by Beretta et al. [1996]. This procedure involves several steps of drying, calcination, doping under N_2, and temperature-programmed *in situ* reduction. Testing under the same conditions demonstrated that the newly prepared catalyst was comparable to the original catalyst. In fact, the space time yields and product distributions were the same, within experimental error, for each sample, indicating that the preparation was reproducible.

In continuation of this group's higher alcohol synthesis research, the reaction pressure range was extended to 12.4 MPa, while other reaction variables were held constant. As expected from thermodynamic considerations, all products exhibited an increase in productivity with higher pressure. Although higher pressure favored the formation of all products by enhancing CO conversion levels, productivities did not increase uniformly. The significant increase in methanol productivity with increasing pressure was not

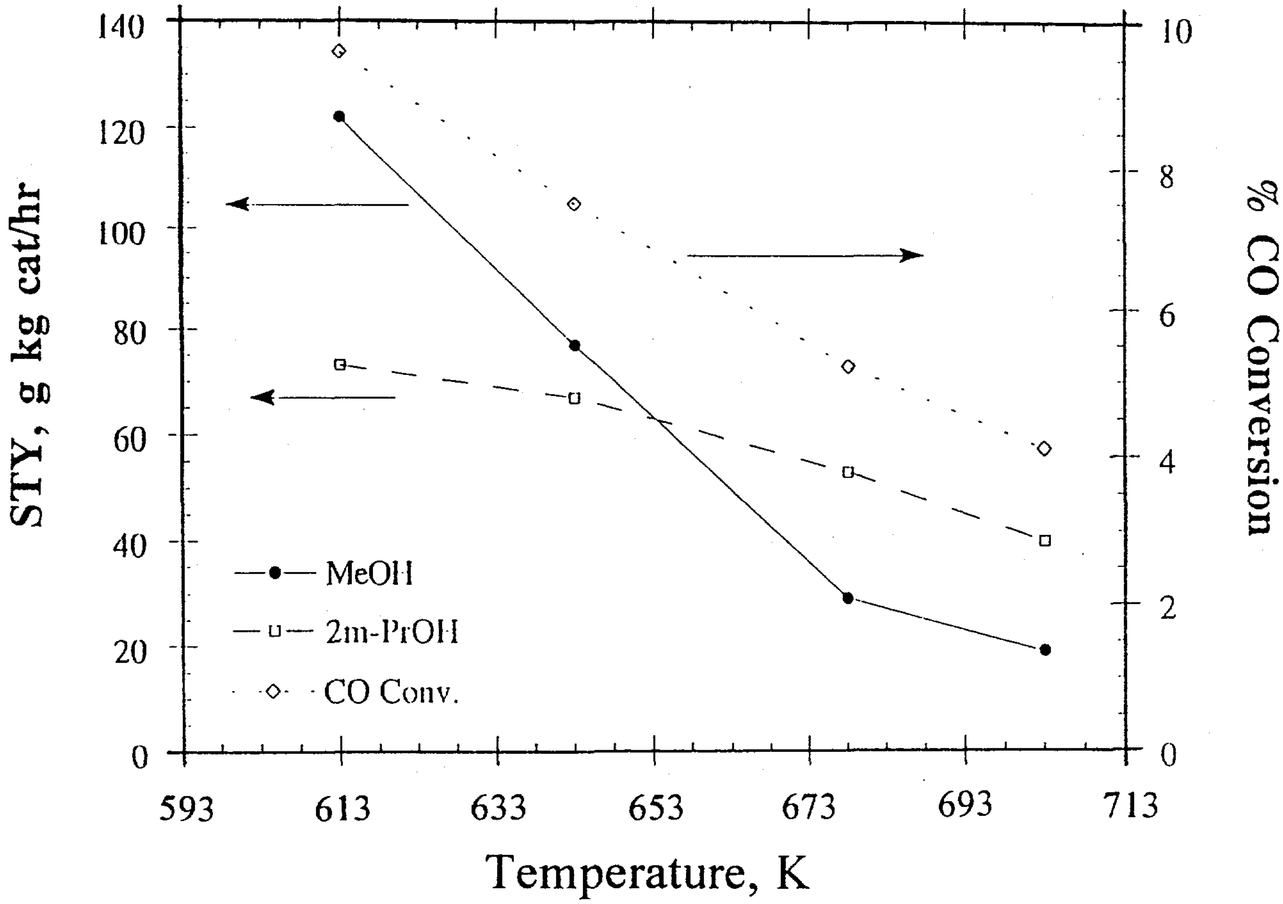

Figure 19. Effect of reaction temperature on methanol and isobutanol (2m-PrOH) productivity and CO conversion (CO_2-free) over the single-bed 3 mol% Cs-Cu/ZnO/Cr_2O_3 catalyst with $H_2/CO = 0.45$ and GHSV = 5450 ℓ/kg cat/hr at a pressure of 7.6 MPa.

Table 8. The productivities and distribution of products formed over the 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst (2 g) with $H_2/CO = 0.45$ synthesis gas at 7.6 MPa with GHSV = 5,450 l(STP)/kg cat/hr as temperature (T) was increased from 613 to 703K. The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols. Abbreviations used are Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pent = pentyl, 2m = 2-methyl, 3m = 3-methyl, MF = methylformate, MAC = methylacetate, DME = dimethylether, and HC = hydrocarbon.

	T = 613K (g/kg cat/hr)	T = 643K (g/kg cat/hr)	T = 678K (g/kg cat/hr)	T = 703K (g/kg cat/hr)
MeOH	122	77	29	19
EtOH	4	1	1	1
PrOH	22	13	4	3
BuOH	3	0	0	1
PentOH	3	0	1	1
2m-PrOH	73	67	53	40
2m-BuOH	20	13	8	4
2m-PentOH	12	10	4	2
2-BuOH	5	6	5	2
3m-2-BuOH	3	4	1	1
3-PentOH	5	6	4	3
2m-3-PentOH	12	10	7	6
MF	1	4	6	9
MAC	1	2	1	3
DME	2	3	3	1
C_7^+-Oxygenates	9	9	11	10
CH_4	7	10	14	18
C_2-C_4 HC	11	10	15	15
%CO Conv. (CO_2-free)	9.6	7.5	5.3	4.2

proportionally reflected in the trend of isobutanol production. At a synthesis gas ratio of $H_2/CO = 0.75$, methanol STY rose from 173 to 398 g/kg cat/hr as pressure increased from 7.6 to 10.3 MPa, respectively. Within this same pressure increment, isobutanol productivity changed from 125 to 166 g/kg cat/hr. Similarly, when pressure was increased from 7.6 to 12.4 MPa with a H_2/CO ratio of 1.00, methanol STY increased to 920 from 324 g/kg cat/hr, while isobutanol STY increased from 96 to 153 g/kg cat/hr. Interestingly, the rate of change of isobutanol productivity relative to pressure with $H_2/CO = 1.00$ was approximately the same as with $H_2/CO = 0.75$. This observation suggests that isobutanol productivity should reach a level of 200-220 g/kg cat/hr at a reaction pressure of 12.4 MPa with $H_2/CO = 0.75$, while methanol productivity would be appreciably below 1000 g/kg cat/hr.

The current consensus in the literature indicates that copper-based catalysts should not be used at higher temperatures due to sintering of copper particles [Bridger and Spenser, 1989]. In this study the copper-based catalyst was tested at temperatures as high as 703K, and while alcohol production was lower at higher temperature, the product distribution did not change. It is suggested that this decrease in overall productivity was not due to catalyst deactivation, but rather it was caused by equilibrium limitations, especially for methanol, arising from the unfavorable (high temperature) reaction conditions. BET surface area measurements support this suggestion, since the surface area of the Cs-$Cu/ZnO/Cr_2O_3$ catalyst after testing (90 m^2/g) was comparable to that measured before testing (97 m^2/g), indicating that copper particles did not sinter significantly. It was recently reported that chromia stabilizes the surface structure of the Cu/ZnO system [Campos-Martin et al., 1995]. This may explain why the catalyst in the current study was able to sustain temperatures as high as 703K for up to 24 hr. Another possibility is that Cs prevents the migration of copper and sintering of copper particles and helps maintain the high surface area of the catalyst.

Conclusions

This study investigated several important aspects of higher alcohol synthesis over cesium-doped copper-based (i.e., $Cs/Cu/ZnO/Cr_2O_3$) and copper-free (i.e., $Cs/ZnO/Cr_2O_3$) catalysts, both individually and in tandem in a single reactor. The reproducibility of preparation and testing of the Cs-promoted catalysts and of the tandem-bed reactor configuration was demonstrated. It was shown that increased reaction pressure, extending up to 12.4 MPa, enhanced yields of both methanol and higher alcohols in the double-bed configuration. However, the promotion of the methanol synthesis reaction was more pronounced than that for isobutanol formation. A productivity of 166 g isobutanol/kg cat/hr was achieved at a reaction pressure of 10.3 MPa from $H_2/CO = 0.75$ synthesis gas, where the methanol/isobutanol mass ratio corresponded to 2.4 (correspondingly, the isobutanol/methanol mass ratio = 0.42). A cesium-doped copper-based catalyst exhibited stability, at least on a short-term basis, at high temperatures (>673K).

IV. DOUBLE-BED Cs/Cu/ZnO/Cr_2O_3 CATALYST FOR HIGHER ALCOHOL SYNTHESIS

Catalytic Testing Results

A comparison of the results of the single-bed copper-based catalyst at high temperature (described in the previous section) with the copper-free catalyst reported by Beretta et al. [1996] suggested that the former could be effectively used as the bottom bed in a double-bed configuration. The relative stability of the cesium-doped copper-based catalyst at high temperatures, along with its high selectivity toward isobutanol synthesis, indicated that this catalyst could be used to improve upon the previous double-bed experiment by increasing the isobutanol yield. Indeed, the single-bed study of the copper-based catalyst demonstrated that this catalyst was more active toward isobutanol production at lower temperatures (613 and 643K) than the copper-free catalyst at high temperature (678K). In order to maximize isobutanol production, the copper-based catalyst was utilized in a double-bed configuration. In this manner, the temperatures of the two beds of equal volume could be controlled separately in order to achieve higher isobutanol productivity. Figure 20 shows the distribution of major products at two different bottom-bed temperatures (613 and 643K). It is seen that the space time yields of these products were lower at the higher bottom-bed temperature. As a group, the linear, primary alcohols showed the strongest temperature dependence. The remaining products (branched primary alcohols, secondary alcohols, and hydrocarbons) exhibited a weaker dependence upon temperature.

Table 9 lists all of the products observed under the HAS conditions specified in Figure 20. As can be seen, at the higher bottom-bed temperature of 643K, small amounts of butanol and pentanol were also produced. CO conversion, also listed in Table 9, was disfavored at the higher bottom-bed temperature. With the bottom-bed temperature maintained at 613K, CO conversion was 8.5%, but it decreased to 6.2% when the bed temperature was increased to 643K.

This experiment shows that by modifying the double-bed higher alcohol synthesis by using the Cs/Cu/ZnO/Cr_2O_3 catalyst in both beds but at different temperatures, isobutanol productivity increased significantly, as did the production of methanol. When the copper-based catalyst was used as the bottom bed and maintained at 340°C, isobutanol STY was 202 g/kg cat/hr, compared to 125 g/kg cat/hr (see Table 6) when the bottom bed consisted of the copper-free catalyst at 678K, an increase of 62%. Similarly, methanol production was greatly increased by the copper-containing bottom bed, reaching a value of 574 g/kg cat/hr. Product distribution was influenced by the temperature of the copper-based bottom bed. High yields of methanol are expected at the lower reactant temperature due to equilibrium constraints at higher temperatures. Lower temperature is also expected to increase the overall productivity of the copper-based catalyst. This was

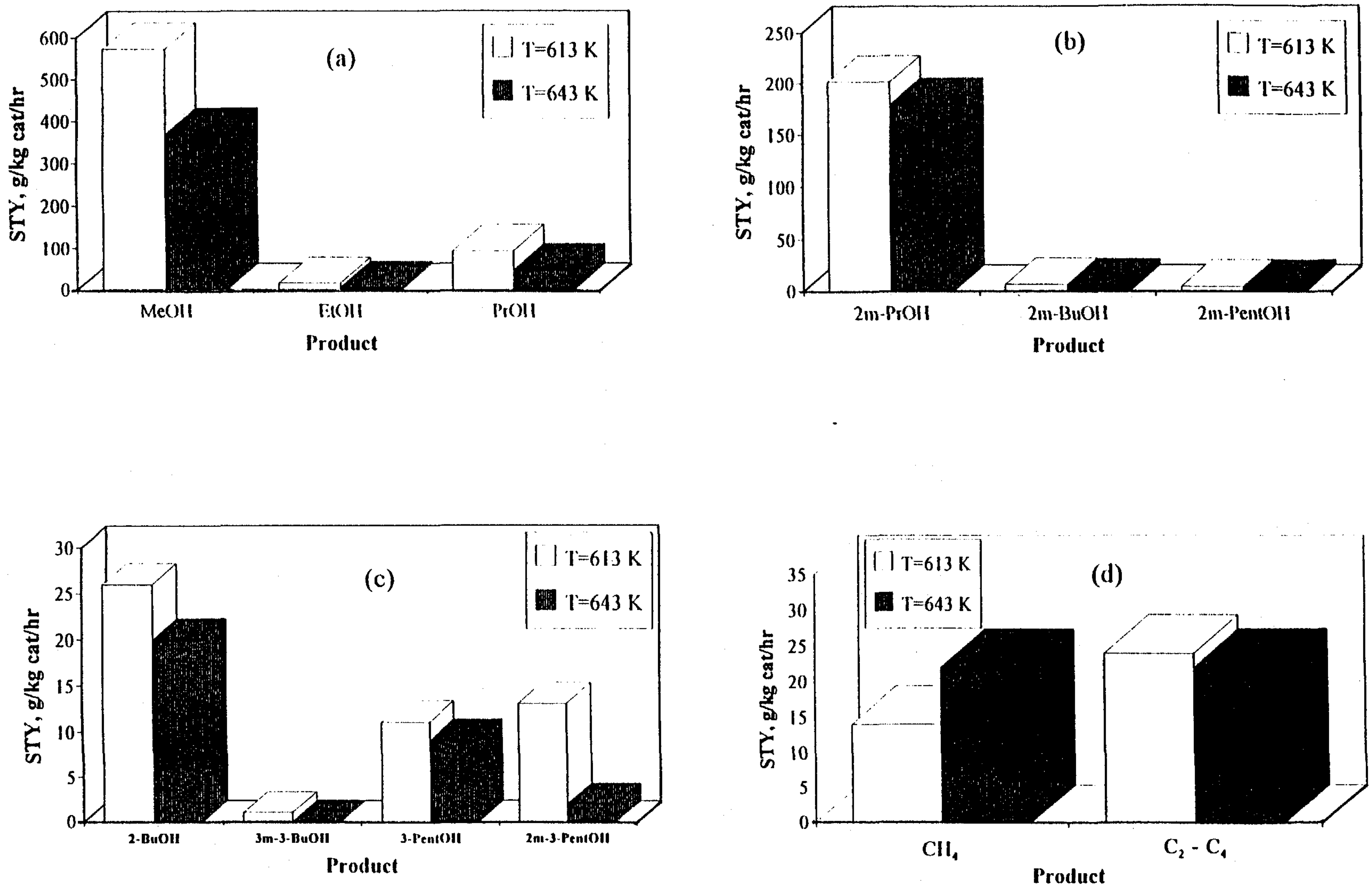

Figure 20. Product distribution over the double-bed 3 mol % Cs-Cu/ZnO/Cr_2O_3 (both beds) catalyst with $T_{top\ bed}$ = 598K, H_2/CO = 0.75 and GHSV = 18,375 l(STP)/kg cat/hr at a reaction pressure of 7.6 MPa with bottom-bed temperatures of 613 and 643K for (a) primary alcohols, (b) branched alcohols, (c) secondary alcohols, and (d) hydrocarbons.

TABLE 9. Higher alcohol synthesis over two portions of the 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst held in a double-bed configuration, where the top bed (1 g) was held at 598K and the lower bed (1 g) was maintained at 613 or 643K. The synthesis gas consisted of $H_2/CO = 0.75$ at 7.6 MPa with GHSV = 18,375 l(STP)/kg cat/hr. The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols. Abbreviations used are Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pent = pentyl, 2m = 2-methyl, 3m = 3-methyl, and HC = hydrocarbon.

	Top = 598K Bottom = 613K (g/kg cat/hr)	Top = 598K Bottom = 643K (g/kg cat/hr)
MeOH	574	369
EtOH	15	5
PrOH	93	47
BuOH	0	1
PentOH	0	1
2m-PrOH	202	180
2m-BuOH	7	6
2m-PentOH	5	5
2-BuOH	26	20
3m-2-BuOH	1	0
3-PentOH	11	9
2m-3-PentOH	13	2
CH_4	14	22
C_2-C_4 HC	24	22
%CO Conv. (CO_2-free)	8.5	6.2

reflected in the CO conversion level, which increased from 6.2 to 8.5% when the reaction temperature was decreased. With the copper-based bottom bed, the selectivity of isobutanol among the other 2-methyl alcohols was greatly increased, as well.

Conclusions

This study used the recently demonstrated concept of employing two sequential catalysts at different reaction temperatures to enhance the productivity of isobutanol from synthesis gas. It was shown that the $Cs/Cu/ZnO/Cr_2O_3$ catalyst could be utilized to advantage as the second-bed catalyst at 613-643K instead of the previously used copper-free $Cs-ZnO/Cr_2O_3$ catalyst at the higher temperature of 678K. High space time yields of *202 g/kg cat/hr for isobutanol* and high selectivity toward isobutanol/methanol mixtures were achieved by coupling two beds of the $Cs/Cu/ZnO/Cr_2O_3$ catalyst at different reaction temperatures in a double-bed configuration. The isobutanol/methanol mass ratios were about 0.35 and 0.5 for the lower bed temperatures of 613 and 643K, respectively. The selectivity of the isobutanol and methanol products was notable. At the lower bed temperature of 613K, 67% of the C in the products shown in Table 9 was in the isobutanol and methanol products. If n-propanol is included along with isobutanol and methanol, then 80% of the carbon found in the alcohol and hydrocarbon products was obtained in these three alcohols.

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LIST OF PUBLICATIONS TO-DATE

- **Publications Based on the Research Carried out During this Project**:

"Higher Alcohol Synthesis Over Cs-Doped Cu/Zn/Cr Oxide Catalysts: Effect of Reaction Temperature on the Product Distribution and Catalyst Stability," A. Beretta, Q. Sun, R. G. Herman, and K. Klier, Preprints, Div. Fuel Chem., ACS, **40(1)**, 142-147 (1995).

"Synthesis of 2-Methylpropan-1-ol/Methanol Mixtures From H_2/CO Synthesis Gas Over Double-Bed Cs/Cu/ZnO/Cr_2O_3 and Cs/ZnO/Cr_2O_3 Catalysts," A. Beretta, Q. Sun, R. G. Herman, and K. Klier, J. Chem. Soc., Chem. Commun., 2525-2526 (1995).

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"High Pressure Methanol Synthesis Over Zirconia Supported Copper Catalysts," Y. Cai, M. M. Burcham, B. Roy, R. G. Herman, and K. Klier, J. Catal., manuscript under revision.

"Higher Alcohol Synthesis Over Cesium-Promoted Cu/ZnO/Cr_2O_3 and ZnO/Cr_2O_3 Catalysts in a Double Bed Reactor Configuration at High Temperatures and Pressures," M. M. Burcham, Y. Cai, R. G. Herman, and K. Klier, Ing. Eng. Chem. Res., manuscript under revision.

- **Recent Publications Resulting From the Ether Synthesis Research carried out during the Previous Research Period**:

"Coupling of Alcohols to Ethers: the Dominance of the Surface S_N2 Reaction Pathway," K. Klier, Q. Sun, O. C. Feeley, M. Johansson, and R. G. Herman, in "*11th Intern. Congr. Catal.-40th Ann.*," (Studies in Surface Science and Catalysis), **101A**, ed. by J. W. Hightower, W. N. Delgass, E. Iglesia, and A. T. Bell, Elsevier, Amsterdam, 601-610 (1996).

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"Selective Isotopic Oxygen Incorporation into C_5 and C_6 Ethers *via* Solid Acid Catalyzed Reaction of Methanol and Ethanol with Isobutanol," O. C. Feeley, Q. Sun, R. G. Herman, M. Johansson, L. Lietti, and K. Klier, Catal. Letters, **35**, 13-22 (1995).

"Mechanistic Studies of the Pathways Leading to Ethers *via* Coupling of Alcohols," Q. Sun, L. Lietti, R. G. Herman, and K. Klier, Preprints, Div. Fuel Chem., ACS, **40(1)**, 138-141 (1995).

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