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

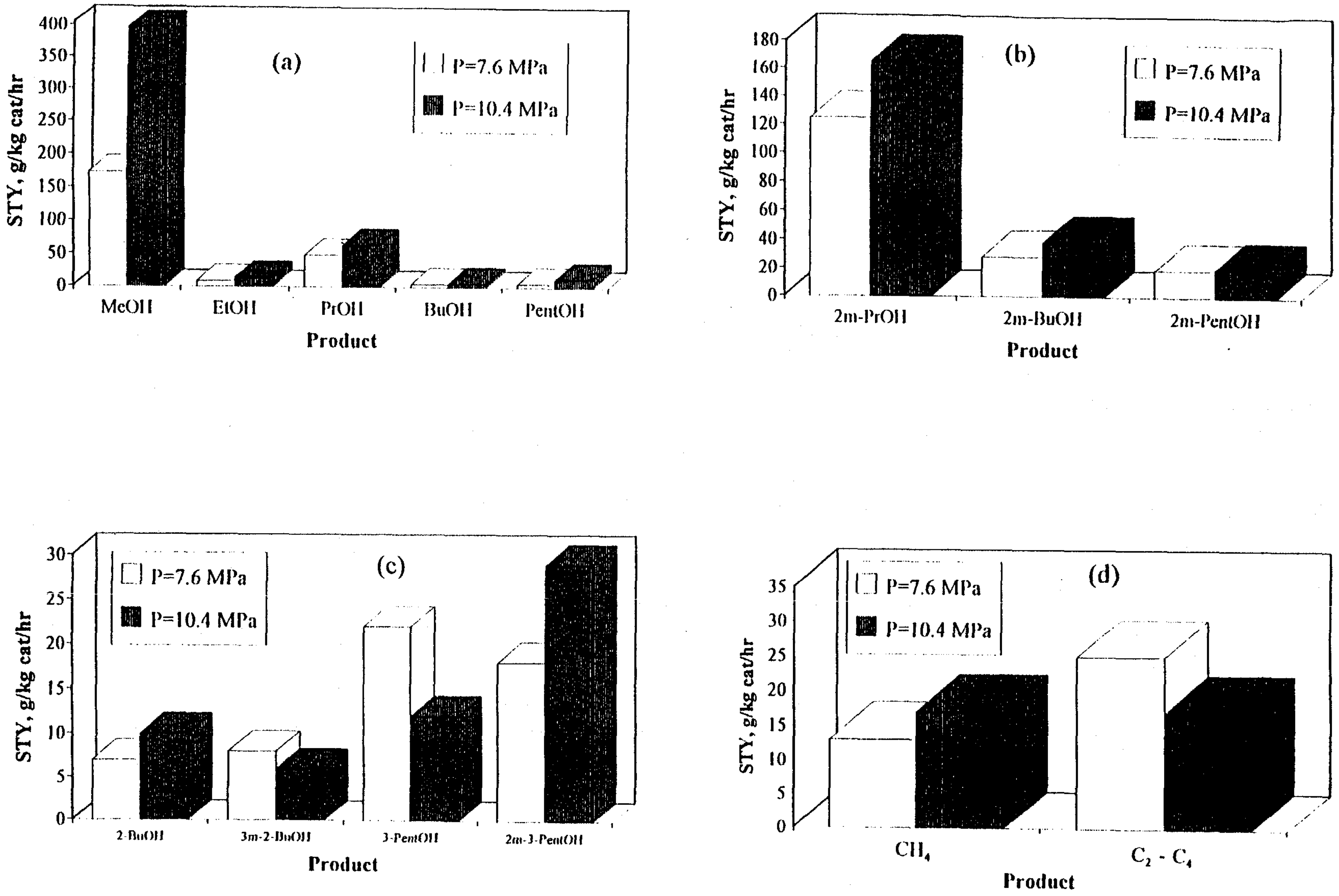

Figure 17. Product distributions, expressed in terms of space time yields (STY), over the double-bed 3 mol% Cs-Cu/ZnO/Cr_2O_3 and 4 mol% Cs-ZnO/Cr_2O_3 catalysts with $T_{top\ bed}$ = 598K, $T_{bottom\ bed}$ = 678K, H_2/CO = 0.75 and GHSV = 18,375 l(STP)/kg cat/hr at reaction pressures of 7.6 and 10.3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

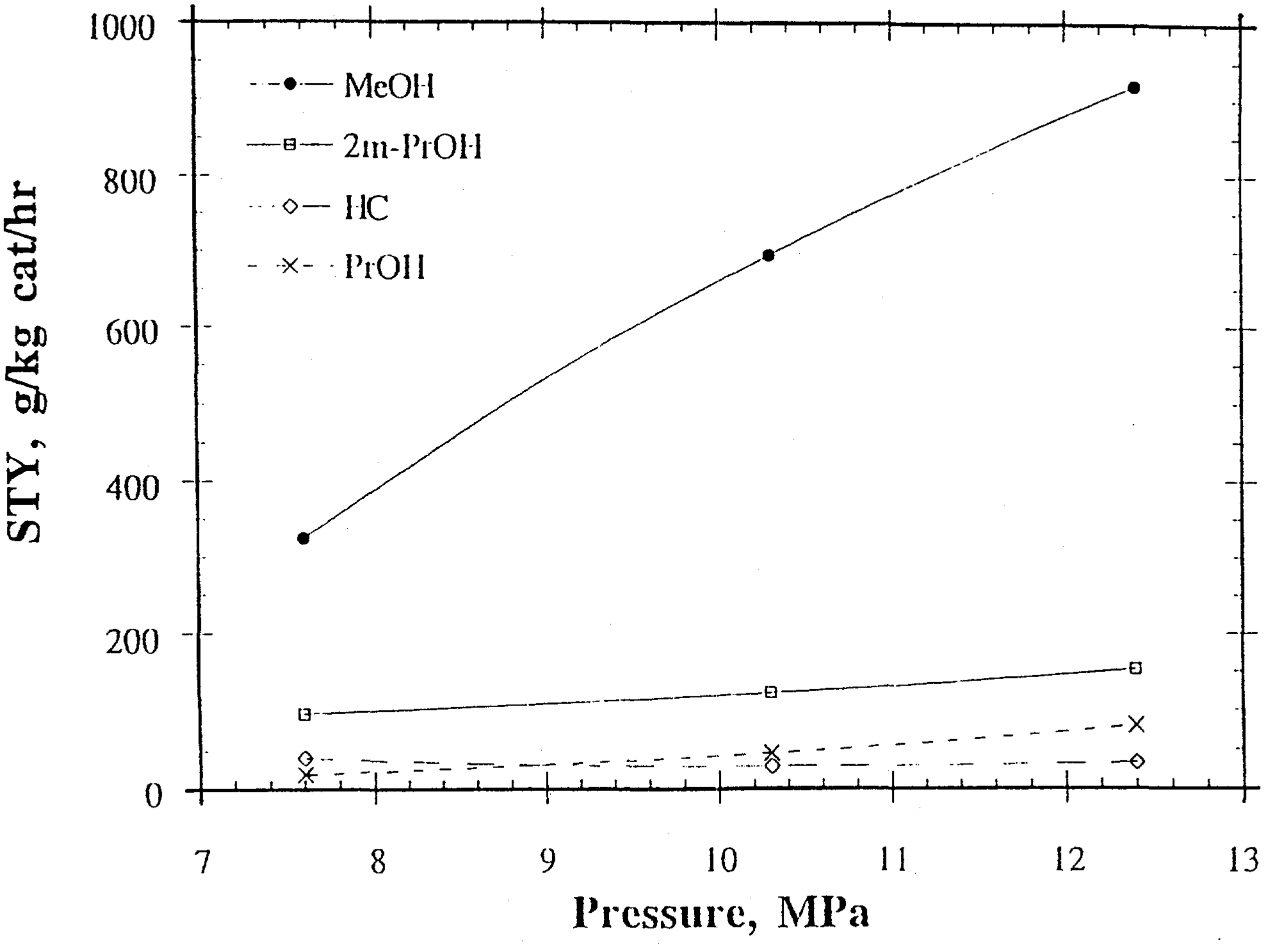

Figure 18. Effect of reaction pressure on productivity over the double-bed 3 mol % Cs-Cu/ZnO/Cr_2O_3 and 4 mol% Cs-ZnO/Cr_2O_3 catalysts with $T_{top\ bed}$ = 598K, $T_{bottom\ bed}$ = 678K, H_2/CO = 1.00 and GHSV = 18,375 l(STP)/kg cat/hr.

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

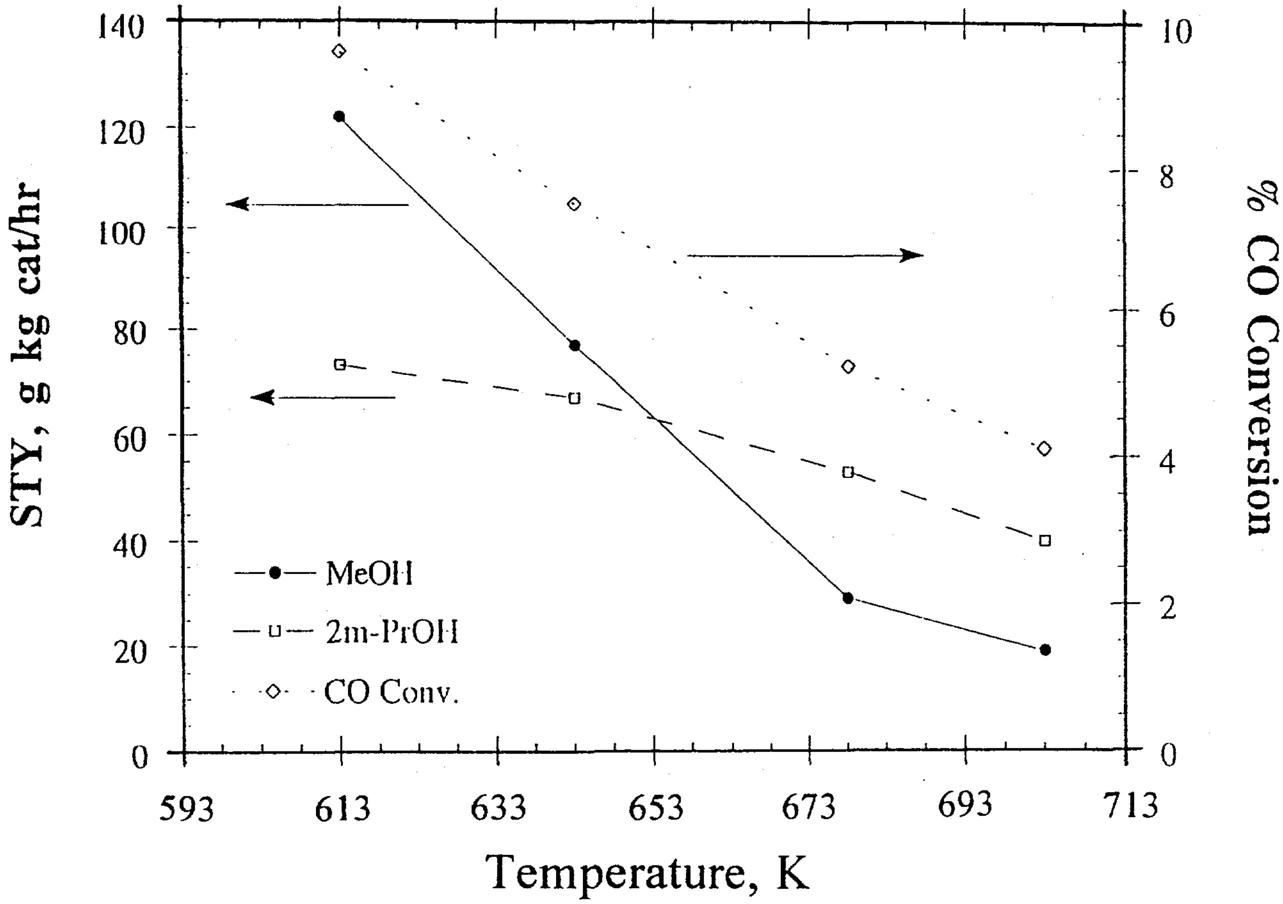

Figure 19. Effect of reaction temperature on methanol and isobutanol (2m-PrOH) productivity and CO conversion (CO_2-free) over the single-bed 3 mol% Cs-Cu/ZnO/Cr_2O_3 catalyst with $H_2/CO = 0.45$ and GHSV = 5450 ℓ/kg cat/hr at a pressure of 7.6 MPa.

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).