

II. Cs/Cu/ZnO/Cr₂O₃ AND Cs/ZnO/Cr₂O₃ CATALYSTS AS SINGLE BEDS AND IN A DOUBLE-BED CONFIGURATION FOR HIGHER ALCOHOL SYNTHESIS

Introduction

The current interest in higher alcohol synthesis (HAS) from H₂/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 C₁ ⇒ C₂ 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 C₂ and C₃ 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/Cr₂O₃ catalyst, the study of a Cs-promoted ZnO/Cr₂O₃ 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/Cr₂O₃ 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}Cr₂(OH)₁₆CO₃·4H₂O, 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 N₂-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 H₂/N₂ = 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/Cr₂O₃ 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 N₂ 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: ZnCr₂O₄ 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 H₂/N₂ = 2/98% mixture.

During the treatment, the release of CO₂ 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 $\text{Fe}(\text{CO})_5$ 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, a 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.

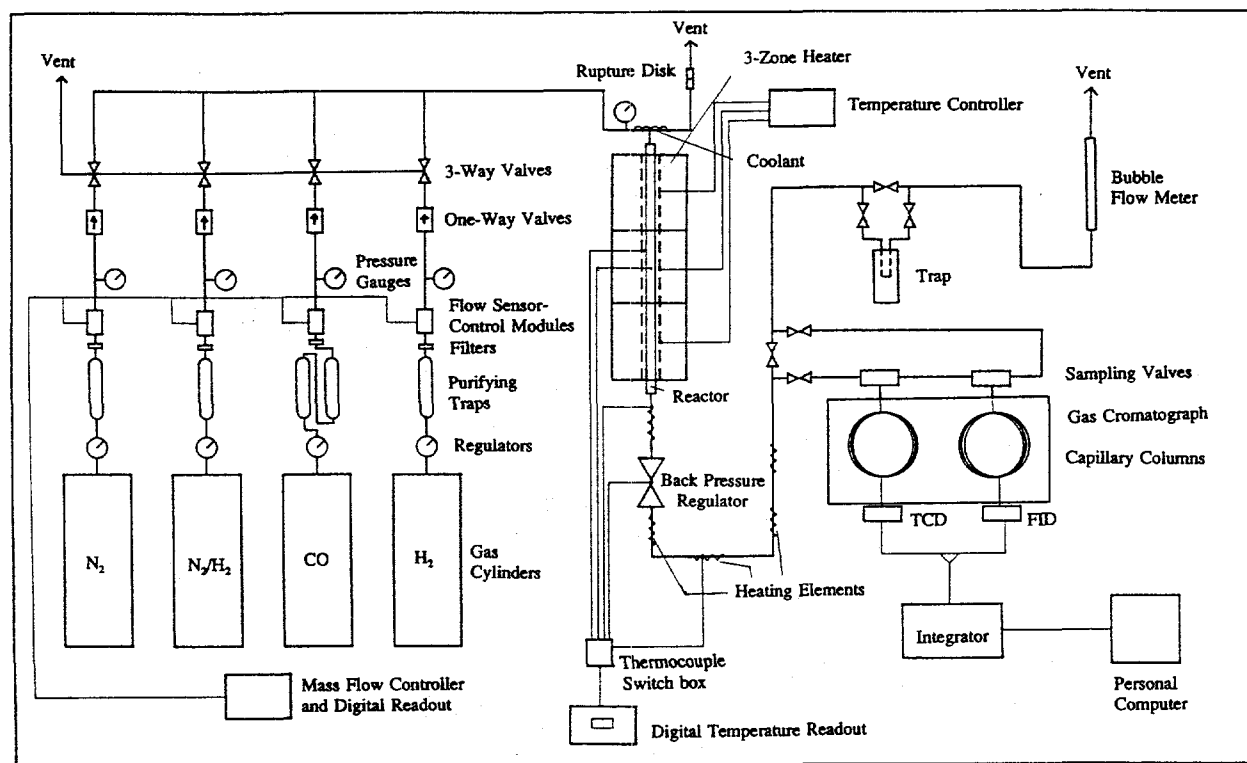


Figure 12. Schematic of the catalyst testing unit.

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/Cr₂O₃ bed was loaded in the top portion of the reactor, about 15 cm downstream from the reactor inlet section. The Cs/Zn/Cr₂O₃ bed was 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 H₂/N₂ = 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 N₂. Subsequently, the treatment of the zinc chromite catalyst was carried out by heating the bottom portion of the reactor to 723K under a flowing H₂/N₂ 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 H₂, CO, and N₂ (N₂/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/Cr₂O₃ catalyst ranged over the following windows of operating variables: T = 583-613K, P = 6.5-7.6 MPa, H₂/CO = 0.45-3.5, gas hourly space velocity (GHSV) = 3,300-18,375 l(STP)/kg cat/hr. The activity tests over the Cs/ZnO/Cr₂O₃ catalyst and the double-bed experiments were carried out at constant pressure (7.6 MPa) and synthesis gas composition (H₂/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 N₂, CH₄, and CO. The column was connected to a thermal conductivity detector (TCD).

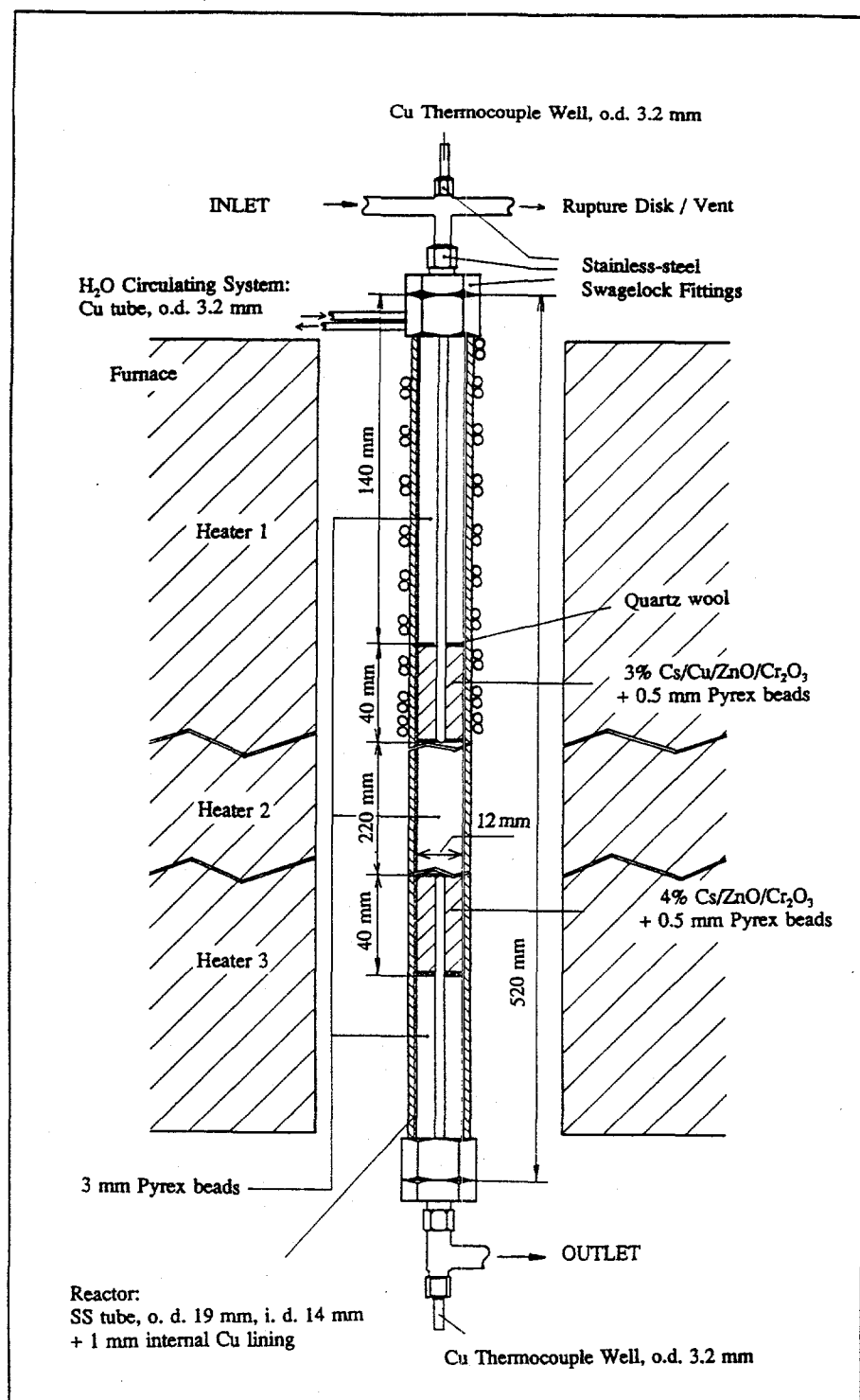


Figure 13. Scaled drawing of the synthesis reactor in the double-bed experiments.
Note that the water circulating system was employed during the catalyst pretreatments, but it was removed during the activity testing experiments. The same cooling system was used during the testing of the 3 mol% Cs/Cu/ZnO/Cr₂O₃ 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 = $1 - (\text{CO}/\text{N}_2)_{\text{outlet}}/(\text{CO}/\text{N}_2)_{\text{inlet}}$, and CH_4 productivity = $\text{CH}_4/\text{N}_2 * \text{N}_2 \text{ Molar Flow Rate} * \text{MW}_{\text{CH}_4}$.

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/Cr₂O₃ Catalyst

The product distribution observed over the Cs/Cu/ZnO/Cr₂O₃ 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 C₁-C₆ alcohols, the C₄-C₇ 2-methyl branched primary alcohols, C₃-C₇ secondary alcohols, the corresponding carbonyl species (aldehydes and ketones), methyl esters, traces of dimethyl ether, and C₁-C₆ 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 CO₂ 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/Cr₂O₃ catalyst (2 g) under the reference operating conditions with H₂/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)
<u>Primary Alcohols:</u>		<u>Methyl Esters:</u>	
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	<u>Hydrocarbons:</u>	
2m-BuOH	5.0	Methane	5.1
2m-PentOH	1.5	Ethene	0.02
2m-HexOH	1.5	Ethane	5.9
		Propene	0.1
<u>Secondary Alcohols:</u>		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	<u>Others:</u>	
		DME	1.8
<u>Aldehydes:</u>		C ₇₊ Oxygenates	22.5
Acetaldehyde	0.7	CO ₂	638
Propionaldehyde	1.1	H ₂ O	3.4
Isobutyraldehyde	0.9		
		<u>CO Conv.</u>	20.2%
<u>Ketones:</u>			
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 CO₂-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 H₂/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 C₂₊ oxygenates exhibited a trend toward a maximum, followed by a plateau sustained at the maximum value. As is known, an initial increase in the H₂/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 C₁ surface species to methanol [Klier, 1982]. In the case of high-temperature catalysts, the effect of H₂/CO ratio on higher alcohol synthesis has been associated with the inhibiting effect of water, whose concentration increases with increasing H₂ partial pressure [Tronconi et al., 1992]. Figure 15 shows a maximum formation of C₂₊ oxygenates for a H₂/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 (CH₄ productivity = 11.17 g/kg cat/hr at H₂/CO = 0.45 and 11.24 g/kg cat/hr at H₂/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 H₂/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 H₂/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

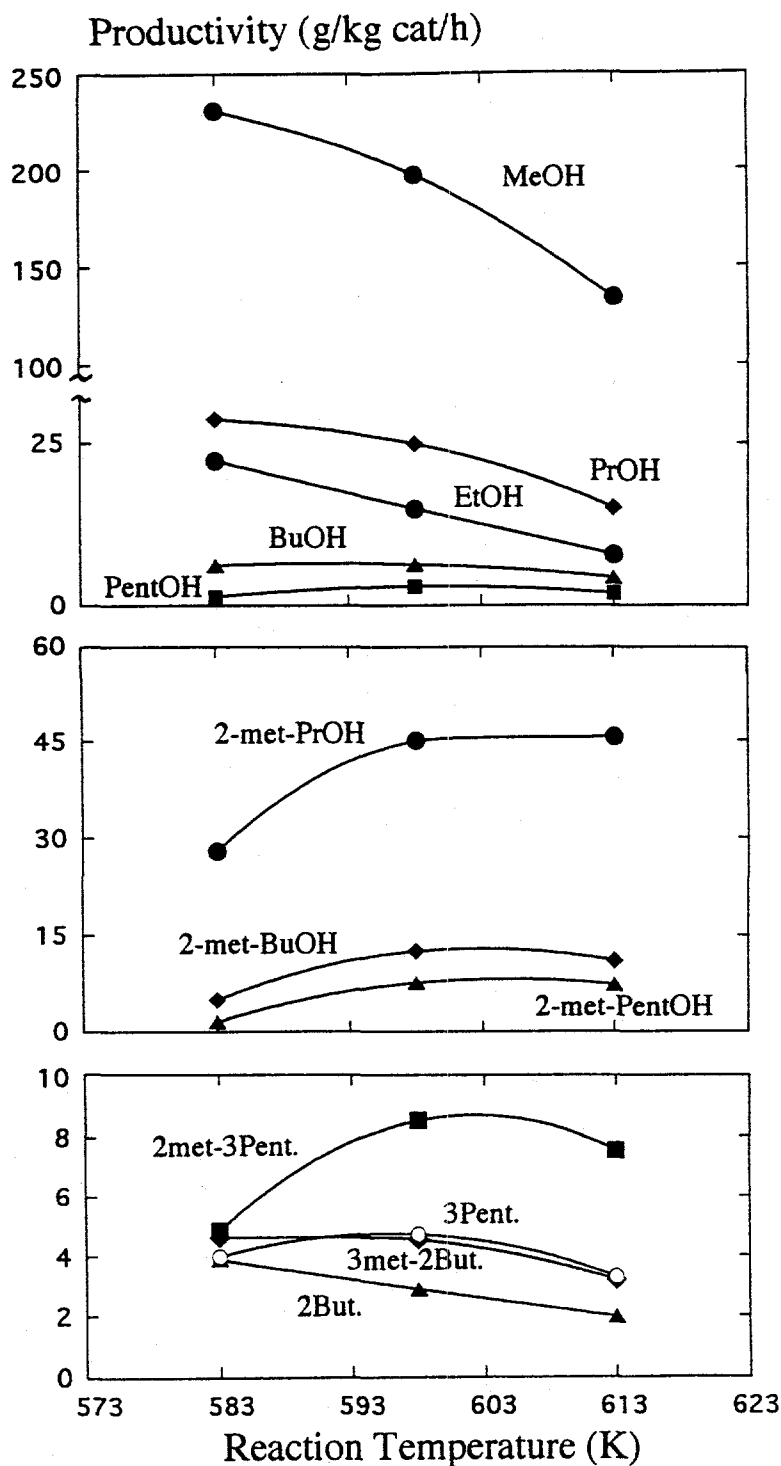


Figure 14. Effect of the reaction temperature on the oxygenate product productivities and distribution observed over the 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst. Operating conditions were H₂/CO = 0.45, GHSV = 5,450 l(STP)/kg cat/hr, and P = 7.6 MPa. The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

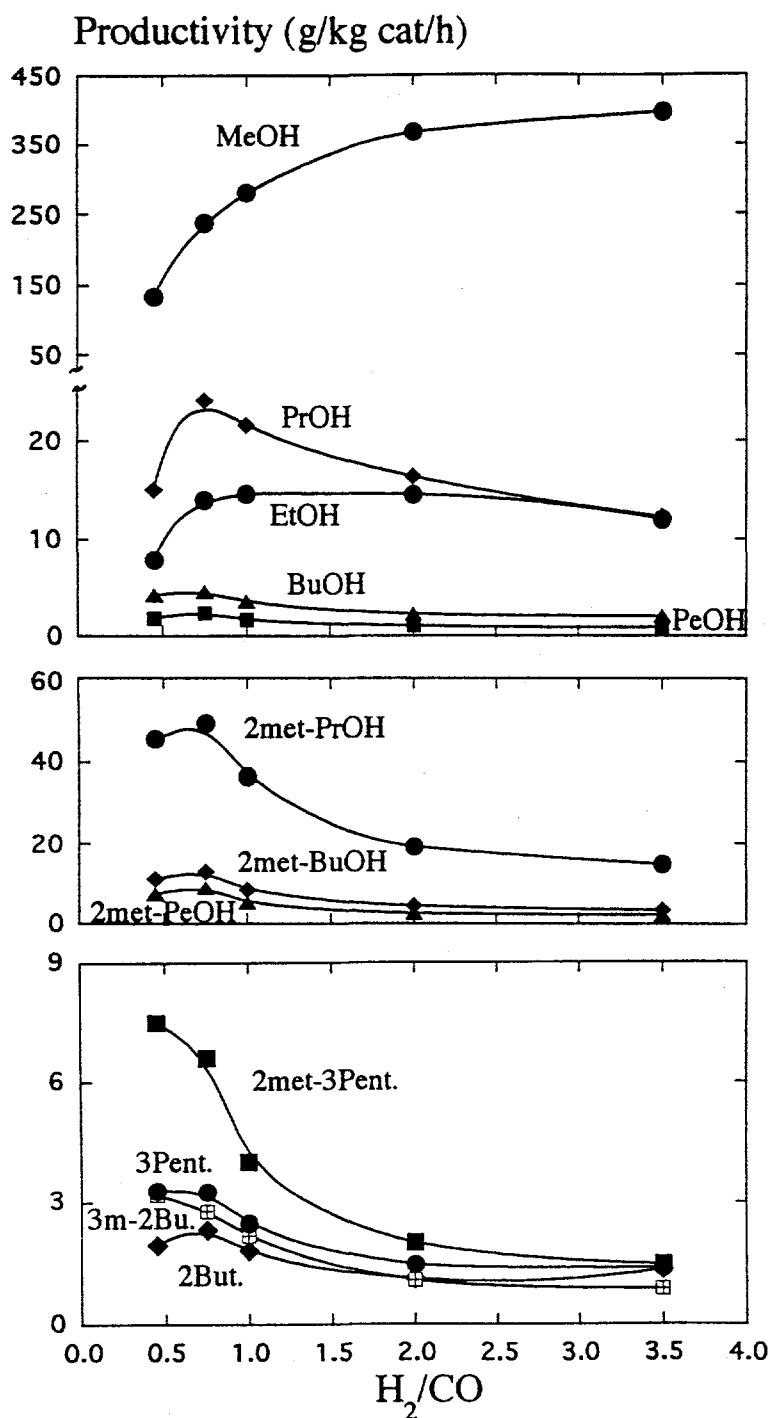


Figure 15. Effect of the synthesis gas composition on the oxygenate product productivities and distribution over the 3 mol % Cs/Cu/ZnO/Cr₂O₃ catalyst. Operating conditions were T = 583K, GHSV = 5,450 l(STP)/kg cat/hr, and P = 7.6 MPa. The productivities of aldehydes and ketones have been summed to those of the corresponding primary and secondary alcohols, respectively.

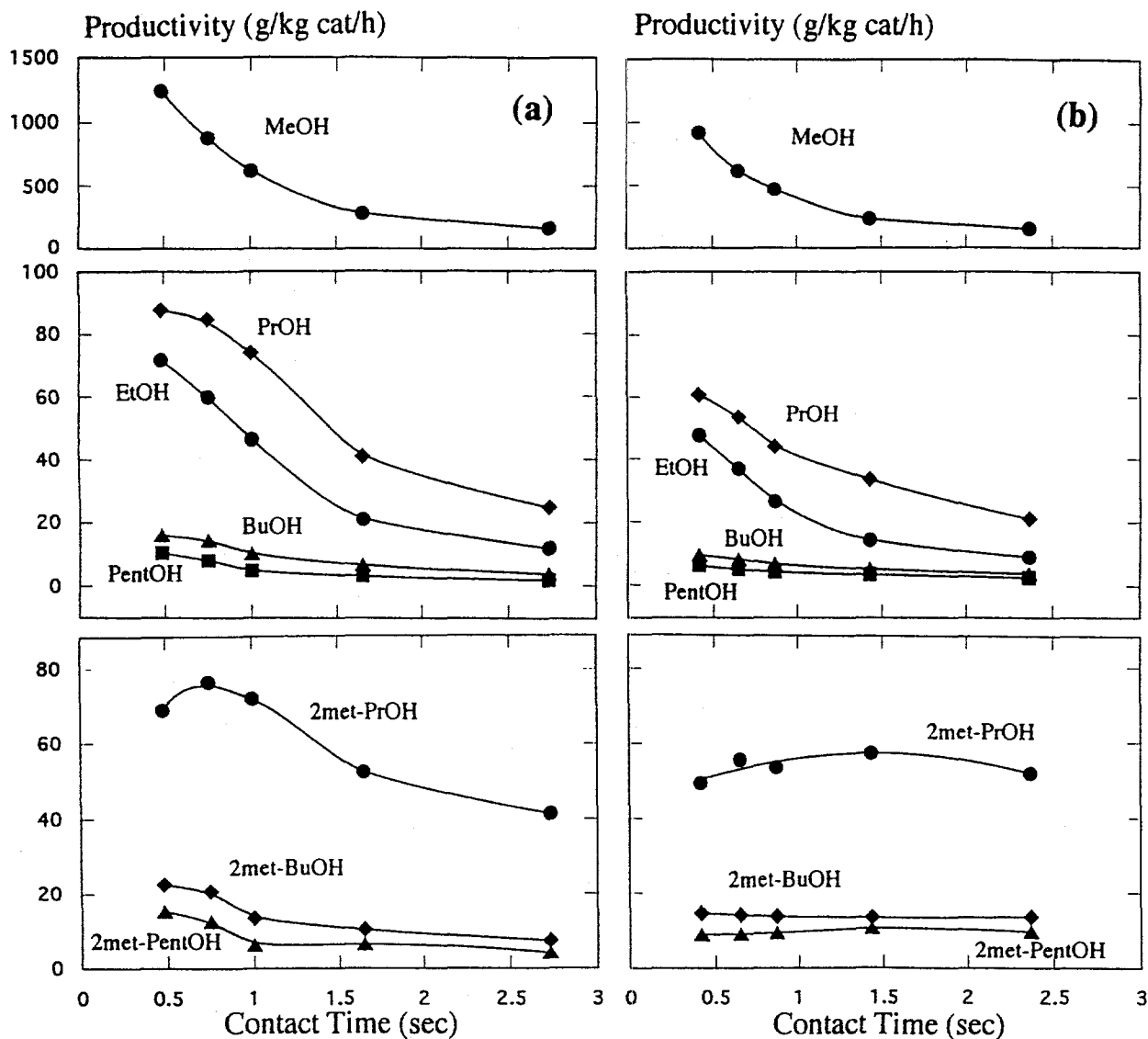


Figure 16. Effect of contact time on the oxygenate product productivities and distribution over the 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst.
 Operating conditions were (a) T = 598K, H₂/CO = 0.75, and P = 7.6 MPa and (b) T = 598K, H₂/CO = 0.75, and P = 6.5 MPa.

Table 3. Higher alcohol synthesis over the 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst (2 g) using H₂/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
CH ₄	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 CO₂, 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 C₂₊ 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 ¹³C 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 C₂₊ 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 C₂₊ oxygenates/methanol selectivities.

HAS Over the 4 mol% Cs-Promoted ZnO/Cr₂O₃ Catalyst

Selected experiments were performed over the Cs-promoted commercial zinc chromite catalyst at a constant temperature (678K), feed composition (H₂/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 C₂₊ oxygenates over the Cs/ZnO/Cr₂O₃ catalyst at 678K was comparable in amount to that observed over the Cs/Cu/ZnO/Cr₂O₃ 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/Cr₂O₃ catalyst (2 g) with H₂/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
CH ₄	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/Cr₂O₃ and 4 mol% Cs-Promoted ZnO/Cr₂O₃ Catalysts

Double-bed kinetic runs were carried out under the following conditions: $T_{\text{first bed}} = 598\text{K}$, $T_{\text{second bed}} = 678\text{K}$, $P = 7.6\text{ MPa}$, $\text{H}_2/\text{CO} = 0.75$, and $\text{GHSV} = 5,450\text{--}18,375\text{ l(STP)/kg cat/hr}$. Equal amounts of the 3% Cs/Cu/ZnO/Cr₂O₃ and 4% Cs/ZnO/Cr₂O₃ 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, isobutanol, and higher 2-methyl branched oxygenates were significantly higher than those observed over either of the two catalysts. At $\text{GHSV} = 5,450\text{ l(STP)/kg cat/hr}$, 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 $\text{GHSV} = 12,000\text{ l(STP)/kg cat/hr}$. 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/Cr₂O₃ and 4 mol% Cs/ZnO/Cr₂O₃ catalyst with H₂/CO = 0.75 synthesis gas at 7.6 MPa.

The operating conditions were: top bed = 3 mol% Cs/Cu/ZnO/Cr₂O₃ (1 g) at 598K and bottom bed = 4 mol% Cs/ZnO/Cr₂O₃ (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
CH ₄	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/Cr₂O₃ 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 $C_1 \Rightarrow C_2$ 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/Cr₂O₃ catalyst is characterized by low selectivities to ethanol and propanol and high selectivities to isobutanol. The chemical pathway



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/Cr₂O₃ 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/Cr₂O₃ catalyst, operating at 598K as the first bed, produced methanol, ethanol and propanol in abundance; the 4% Cs/ZnO/Cr₂O₃ 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/Cr₂O₃ catalyst, and 145% with respect to the single Cs/ZnO/Cr₂O₃ 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 H₂. 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/Cr₂O₃ 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/Cr₂O₃ 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/Cr₂O₃ 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.