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Synthesis of Higher Alcohols over Promoted Copper Catalysts

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A series of copper catalysts, promoted with 0.5% K_2CO_3, was prepared and tested for thermal stability by measuring the surface area after successive 20-h treatments in flowing hydrogen at 250, 275, 300, and 325°C. Four of these catalysts and a commercial $CuO/ZnO/Al_2O_3$ catalyst were tested for activity and selectivity in the synthesis of higher alcohols from a $1H_2 + 2CO$ synthesis gas at 10.5 MPa and 285 to 325°C. Two of these catalysts, $CuO/ZnO/Cr_2O_3$ and $CuO/ZnO/ThO_2$, had about the same initial activity as the commercial preparation. Catalysts which did not contain ZnO, namely, CuO/TiO_2 and CuO/ThO_2, were relatively inactive. The $CuO/ZnO/ThO_2$ and commercial catalysts lost activity and surface area at 325°C, while the activity and surface area of the $CuO/ZnO/Cr_2O_3$ catalyst remained constant during 60 h onstream at the same temperature. The major alcohol products were methanol, 2-methyl-1-propanol, ethanol, and *n*-propanol and the selectivity to higher alcohols increased with increasing temperature. The C_4 alcohol selectivities of the catalysts containing ThO_2 at 325°C were significantly larger than those of the other catalysts. The similar selectivities of these catalysts despite the marked difference in their activities suggests that ThO_2 promotes the production of higher alcohols.

INTRODUCTION

In the higher alcohol synthesis (HAS), mixtures of methanol and higher alcohols, particularly ethanol, 1-propanol, and 2-methyl-1-propanol are produced over a methanol synthesis catalyst promoted with alkali. This process has been studied since the 1930s (*5, 6, 11, 13*) but relatively little work has been done using the modern copper-containing catalysts (*8, 17, 18, 20*). The methanol synthesis is typically carried out over a copper/zinc oxide catalyst at 225 to 275°C and 50 to 100 atm, while higher alcohol production is favored by higher temperatures and pressures.

Mixed alcohols are preferred over methanol as a gasoline octane improver because of the cosolvent effect of the higher alcohols. As straight liquid fuels, the heat of combustion of alcohols on a unit mass or unit volume basis increases with molecular weight.

Smith and Anderson (*16, 17*) showed that higher alcohols could be produced over a commercial $CuO/ZnO/Al_2O_3$ catalyst promoted with K_2CO_3. At 13.2 MPa higher alcohol selectivity was negligible below 260°C and increased with increasing temperature, but catalyst deactivation, presumably due to sintering, was rapid at 300°C. Hydroxides and carbonates of the alkali metals from Li to Cs have been used to promote HAS catalysts. Vedage *et al.* (*20*) tested a number of alkali promoters on a CuO/ZnO catalyst at 7.6 MPa, 288°C, and CO/H_2 ratios of 2.2/1 and 1.1/1 and reported that CsOH promotion gave the largest yields of higher alcohols. This finding is consistent with the earlier work of Morgan *et al.* (*11*). In a subsequent study, Klier *et al.* (*8*), working with a CsOH-promoted catalyst and a $1H_2 + 2.2CO$ feed, found that the 2-methyl-1-propanol/methanol ratio in the products increased by a factor of 7 as the temperature was increased from 288 to 325°C. The catalyst stability at temperatures above 300°C was not discussed.

Methanol catalysts are comprised of CuO and ZnO with a third component, usually Cr_2O_3 or Al_2O_3, added as a structural promoter. While the exact nature of the active

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sites and the role of ZnO in these catalysts is the subject of some debate (*3, 7, 21*), there is little doubt that a fine dispersion of copper is necessary for high activity (*3, 10, 15, 19*). Sintering, with the resultant loss of surface area, is therefore a probable cause of the deactivation observed at elevated temperatures.

In the present work, a number of catalyst formulations were tested for resistance to sintering in flowing H_2 at 250 to 325°C. Several of these catalysts were further evaluated for activity, stability, and selectivity in the higher alcohol synthesis.

EXPERIMENTAL

Catalyst preparation. Most of the catalysts were prepared by coprecipitation from 1 *N* metal nitrate solutions by rapid addition of 1 *N* sodium carbonate at 50 to 60°C. The catalyst supported on titania was made by adding the carbonate solution to a slurry of titania in copper nitrate solution. The titania, supplied by Cabot, was 85% anatase and 15% rutile, and anatase was detected in the X-ray diffraction pattern of the resulting catalyst. The fine nonporous powder had an average particle diameter of 0.03 μm and a surface area of 50 m^2/g.

The precipitates were filtered in a Buchner funnel, thoroughly washed, dried for 20 h at 120°C, broken into small pieces, and calcined in air at 350°C for 4 h. The calcined catalyst was crushed to a fine powder and impregnated with 0.5% K_2CO_3. The crushed, promoted catalysts were used in the thermal stability tests, but before use in activity tests the powders were pelleted, crushed, and sized to 16–25 mesh (0.94 mm).

Thermal stability testing. The thermal stability of the series of supported and promoted copper catalysts was tested by measuring the surface area after successive 20-h treatments in flowing H_2 at 250, 275, 300, and 325°C. Rapid determination of surface areas was obtained using a flow technique (*14*) in which it was assumed that nitrogen formed a monolayer at a relative pressure of 0.09. The estimated surface areas were reproducible to within 1% and were 7 to 24% lower than those estimated using a standard volumetric adsorption apparatus and the BET equation for estimating monolayer volumes.

To allow thermal stability tests to be made on one apparatus, some additional features were built into the system. For the reduction cycles, hydrogen (UHP grade from Canadian Liquid Air) could be routed through the sample tube and then out through a bubble flow meter. The furnace used during the reductions was an insulated cylindrical aluminum block 17 cm long and 11 cm in diameter. A hole, large enough for the sample tube, was drilled axially into the block and surrounded with five symetrically placed cartridge heaters. The furnace could be put into place over the sample tube, or removed, as required. About 1 h was required to heat the furnace and sample from room temperature to the desired temperature.

A thermocouple placed in the center of the catalyst bed was the sensing element for an Electronic Control Systems 16C1 proportional controller. The catalyst bed temperature could be controlled to within 1°C.

X-ray diffraction. X-ray diffraction (XRD) patterns were obtained for the fresh catalysts and the reduced catalysts after the thermal stability tests. The reduced samples were transferred in helium into a few milliliters of collodion (a solution of nitrocellulose in alcohol and ether). The resulting syrupy slurry was transferred to a glass slide and allowed to dry, leaving a thin layer of fine catalyst particles coated with the clear polymer. A blank slide treated with collodion showed no XRD peaks. These precautions prevented oxidation of the catalysts by air.

Activity testing. The apparatus used for activity testing is the same as that used by Smith and Anderson (*16–18*). All activity tests were performed at 10.5 MPa and 285 to 325°C.

A Superpressure air-operated compressor was used to deliver synthesis gas mixtures to an 8.5-liter plastic-lined storage cylinder rated at 34.5 MPa. A rupture disk and a purge line were included between the compressor and the high-pressure storage cylinder. The synthesis gas fed to the compressor was a premixed, certified standard obtained from Matheson, of nominal composition 30/60/10, $CO/H_2/Ar$. The gas flow to the reactor was set using a Matheson pressure regulator and a Whitey needle valve. A charcoal trap, placed between the storage cylinder and the reactor, was used to remove iron carbonyls from the synthesis gas. The reactor exit gases passed through a condenser immersed in an ice bath, a Grove 91W backpressure regulator, and through a bubble flow meter to an exhaust fan. All tubing and ancillaries were made of 316 stainless-steel. Online product analysis was achieved using a heated line from the reactor exit to the sampling valves and two gas chromatographs. A thermal conductivity detector was used to detect H_2, Ar, CO, and CO_2 and a flame ionization detector was used for C_1 to C_4 hydrocarbons plus methanol online and methanol and the other condensed products after each run.

The fixed-bed, single-pass tubular reactor, operated in the integral mode in the present work, consisted of a 51-cm stainless-steel tube, with an o.d. of 1.905 cm and an i.d. of 1.295 cm, lined with a tight fitting copper tube. The reactor was situated coaxially in a cylindrical aluminum block 25 cm long and 14 cm in diameter. Five 250-W cartridge heaters, placed symetrically in the block, provided heating. A thermocouple placed in the middle of the catalyst bed was the sensing element for an Omega 2001 proportional temperature controller. The catalyst bed temperature could be controlled to within 1°C. The catalyst was pretreated with flowing synthesis gas ($1000\ h^{-1}$, $6CO + 3H_2 + 1Ar$) at 300°C and atmospheric pressure overnight. About 45 min were required to heat the reactor to 300°C from room temperature.

In the first set of activity tests, the reactor was operated with each catalyst for successive 20-h periods at 285, 300, and 325°C. Three catalysts, including the commercial catalyst, were selected, based on their activities and selectivities, for further testing in 60-h runs at 325°C.

Characterization of used catalysts. The surface areas of fresh and used catalysts were estimated from the nitrogen isotherms at 77 K. The apparatus used to determine the isotherms was a standard volumetric adsorption apparatus (*1*) and the BET equation was used to estimate the monolayer volume.

RESULTS

Thermal Stability Testing

Thermal stability test results for each of the eight catalysts made in the present work (but not for the commercial catalyst used by Smith and Anderson (*17, 18*)) are presented in Table 1. Coprecipitation of the catalysts apparently yielded high dispersion of copper oxide as evidenced by the broad peaks obtained in the X-ray diffraction patterns. Except for the CuO on TiO_2 all preparations lost a significant fraction of their initial surface areas during thermal stability testing. The $CuO/ZnO/Cr_2O_3$, $CuO/ZnO/ThO_2$, CuO/ThO_2, and CuO on TiO_2 catalysts were chosen, on the basis of the thermal stability tests, for further testing and comparison with the commercial catalyst used by Smith and Anderson (*17, 18*).

Catalyst Activity and Deactivation

The activities of catalysts tested in the present work at 285°C and 10.5 MPa are compared on a plot of conversion versus reciprocal space velocity in Fig. 1. The solid curve was obtained from the rate equation of Smith (*16*), derived from data obtained under the same conditions with the alkalized $CuO/ZnO/Al_2O_3$ catalyst. Of the catalysts containing ZnO, the one promoted with Cr_2O_3 was the most active, while the preparations promoted with ThO_2

TABLE 1

Results of Thermal Stability Testing

Catalyst	Composition (mole % of metal)	Surface area (m^2/g)[a]					Percentage surface area retained	Phases detected (XRD)	
		Fresh oxides	Reduction temperature[b] (°C)					Fresh	Reduced
			250	275	300	325			
CuO	100	1.3	0.52	0.48	0.43	0.41	32	CuO[c]	Cu[c]
CuO/ZnO	50/50	15.6	10.7	9.4	8.0	6.8	44	CuO,ZnO[d]	Cu,ZnO[d]
$CuO/ZnO/Cr_2O_3$	30/60/10	75.0	60.4	53.1	51.5	47.3	63	CuO,ZnO[d]	[e]
CuO/ZnO/MnO	30/60/10	61.4	34.8	25.5	21.2	16.1	26	[e]	[e]
CuO/ZnO/MgO	30/60/10	60.5	28.3	22.0	16.8	12.7	21	CuO,ZnO[c]	Cu,ZnO[c]
$CuO/ZnO/ThO_2$	30/60/10	45.6	36.2	31.1	28.9	26.0	57	[e]	[e]
CuO/TiO_2	30/70	33.4	33.8	33.8	34.2	34.1	102	CuO,TiO_2[d]	Cu,TiO_2[d]
CuO/ThO_2	80/20	36.5	32.7	31.6	31.1	29.6	81	[e]	[e]
$CuO/ZnO/Al_2O_3$	46/46/8[f]	33.6	—	—	—	—	—	CuO,ZnO[c]	Cu,ZnO[c,g]

[a] Weight basis: raw, unreduced catalyst.

[b] Reduced in ~1200 h^{-1} of H_2 for 20 h.

[c] Well-defined peaks.

[d] Broad, low intensity peaks.

[e] No peaks.

[f] Commercial catalyst. Data from Smith (*16*).

[g] Reduced in ~1200 h^{-1} of H_2 at 325°C for 12 h.

and Al_2O_3 had moderate activity. The two catalysts which did not contain ZnO were significantly less active. This finding is consistent with the conclusions of Natta *et al.* (*13*) and Klier (*7*), but at odds with the results of Chinchen *et al.* (*3*) regarding the unique mutual promotion of CuO and ZnO.

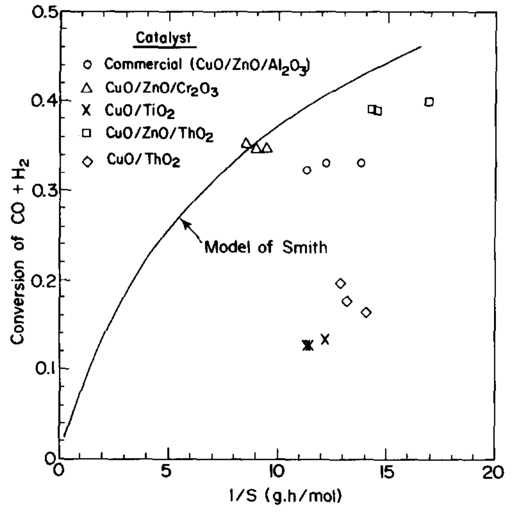

FIG. 1. Comparison of measured reaction rates with model of Smith (*16*) for commercial ($CuO/ZnO/Al_2O_3$) catalyst at 285°C, 10.5 MPa.

The reaction rates at the beginning and end of each of the extended runs along with the surface areas of the catalysts are given in Table 2. The commercial CuO/ZnO/Al_2O_3 and the $CuO/ZnO/ThO_2$ catalysts lost activity and surface area during the runs at 325°C. The $CuO/ZnO/Cr_2O_3$ catalyst, however, maintained constant activity and surface area throughout the 60-h test at 325°C. The surface areas given in Tables 1 and 2 are not directly comparable because (i) the treatment histories are different, especially since the activity testing produces an environment containing CO_2, H_2O, alcohols, and hydrocarbons; (ii) the methods used to estimate the surface areas are different; and (iii) the weight basis of the two sets of data are different. Converting the surface area of reduced $CuO/ZnO/Cr_2O_3$ given in Table 2 (72.65 m^2/g) to square meters per gram of

TABLE 2

Activities and Surface Areas of Fresh and Used Catalysts at 10.5 MPa and 325°C

Catalyst	Reaction rates (mol CO + H_2/h · g) × 100		Surface area (m^2/g catalyst)[c]	
	Initial[a]	Final[b]	Fresh reduced[d]	Final[b]
Commercial	2.82	1.75	42.08	17.13
	2.63	1.77 (1.57)[e]	42.08	—
$CuO/ZnO/Cr_2O_3$	4.00	4.14	72.65	73.50
$CuO/ZnO/ThO_2$	3.88	2.36	42.47	32.39

[a] Initial rates at 285°C: 0.0259, 0.0384, and 0.0253 mol/h · g, respectively.

[b] Run duration about 60 h.

[c] Evacuated at 120°C, 10^{-5} Torr, 12–14 h, weight basis: reduced catalyst.

[d] Reduced $6CO + 3H_2 + 1Ar$, 300°C, 12–14 h.

[e] Rate after 85 h onstream.

raw, unreduced catalyst gives 59.1 m^2/g, in fair agreement with the data in Table 1.

Selectivity

Product distributions for the various catalysts are given in Table 3. Carbon dioxide production tends to increase with temperature as a result of increasing higher alcohol and/or hydrocarbon selectivity (see Fig. 2). The CuO on TiO_2 catalyst had low activity and also the highest selectivity to hydrocarbons of the catalysts tested.

Alcohol selectivities are compared with those of Smith (*16*) and Klier and co-workers (*20*) in Table 4. Alcohols determined in the present work were methanol, ethanol, 1-propanol, 2-butanol, 2-methyl-1-propanol, 1-butanol, and 1-pentanol. Methyl formate (*20*) and 2-propanol (*16*) have been reported in the products of the HAS, but these species were not found in the present work. The alcohol distributions are similar

TABLE 3

Product Selectivities in Higher Alcohol Synthesis at 10.5 MPa

Catalyst	Temperature (°C)	Space velocity (h^{-1})	Carbon selectivity of measured products			
			CO_2	Alcohols	CH_4	Other hydrocarbons
Commercial ($CuO/ZnO/Al_2O_3$)	285	1930	0.194	0.687	0.057	0.062
	300	2144	0.356	0.552	0.037	0.055
	325	2176	0.393	0.458	0.049	0.100
$CuO/ZnO/Cr_2O_3$	285	2095	0.251	0.709	0.018	0.022
	300	2406	0.327	0.613	0.023	0.037
	325	3012	0.373	0.471	0.054	0.102
CuO/TiO_2	285	2121	0.002[a]	0.796	0.160	0.042
	300	2310	0.376	0.339	0.263	0.022
	325	2442	0.448	0.222	0.296	0.034
$CuO/ZnO/ThO_2$	285	1391	0.532	0.392	0.020	0.056
	300	2444	0.490	0.440	0.020	0.050
	325	2608	0.509	0.386	0.036	0.069
CuO/ThO_2	285	2406	0.041[a]	0.822	0.081	0.056
	300	2108	0.034[a]	0.837	0.084	0.045
	325	2423	0.018[a]	0.872	0.063	0.047

[a] Small CO_2 peaks were not always integrated, resulting in low estimates of CO_2 production for these runs.

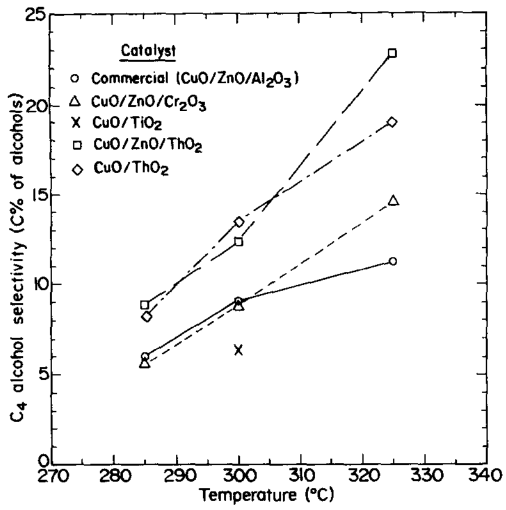

FIG. 2. C_4 alcohol selectivity as a function of temperature, $6CO + 3H_2 + 1Ar$, 10.5 MPa.

for data at 285°C, with methanol, ethanol, 1-propanol, and 2-methyl-1-propanol predominating. The strong effect of temperature on higher alcohol selectivity is shown in Fig. 2 and detailed alcohol selectivities for $CuO/ZnO/Cr_2O_3$ and $CuO/ZnO/ThO_2$ at 285 and 325°C are also presented in Table 4.

Catalyst deactivation was the main interest of the present work and most of the data are not well suited to the estimation of kinetic parameters. However, some observation can be made regarding the rates over the fresh catalysts. At 325°C, for the catalysts of Table 2 promoted with Al_2O_3, Cr_2O_3, and ThO_2, methanol was near equilibrium with respect to $H_2 + CO$, but the higher alcohols were present in substantially lower than equilibrium amounts. The reaction rates over fresh $CuO/ZnO/Al_2O_3$ and $CuO/ZnO/Cr_2O_3$ at 325°C are only slightly greater than those at 285°C (Table 2), possibly a sign of the approach to equilibrium of the synthesis of methanol. This effect is not observed with the ThO_2-promoted catalyst, probably due to its greater selectivity toward higher alcohols.

The selectivities for C_4 alcohols of the catalysts containing ThO_2 are similar despite the marked difference in their activities. The favorable effect of ThO_2 on higher alcohol selectivity recommends it for further testing as a chemical promoter in the HAS. Maj *et al.* (*9*) studying the methanol synthesis at 300 to 360°C and space velocities of 5000 to 10,000 h^{-1} over a ThO_2 catalyst, reported the production of "isobutanol," presumably 2-methyl-1-propanol. Alcohols, particularly 2 methyl-1-propanol,

TABLE 4

Alcohol Selectivities

	Smith (*16*)	Klier (*20*)	Present work					
	$CuO/ZnO/Al_2O_3$	CuO/ZnO	$CuO/ZnO/Al_2O_3$		$CuO/ZnO/Cr_2O_3$		$CuO/ZnO/ThO_2$	
H_2/CO	0.5	0.45	0.5	0.5	0.5	0.5	0.5	0.5
Promoter	K_2CO_3	KOH	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3
Temp. (°C)	285	288	285	325	285	325	285	325
Pressure (MPa)	10.4	7.6	10.5	10.5	10.5	10.5	10.5	10.5
Space velocity (h^{-1})	—	2667	1930	2177	2095	3036	1391	2608
Conversion (% $CO + H_2$)	34.2	—	31.6	25.8	33.7	24.3	30.4	28.3
Selectivities (carbon percentage of alcohols)								
Methanol	75.7	85.6	81.1	80.4	83.6	79.7	83.3	68.6
Ethanol	5.8	6.4	7.8	3.8	6.6	2.6	4.9	3.8
2-Propanol	0.3	[a]	[a]	[a]	[a]	[a]	[a]	[a]
1-Propanol	5.6	4.9	4.5	3.6	3.7	2.1	2.9	3.6
2-Butanol	0.8	[a]	0.7	0.7	1.2	0.7	0.6	0.6
2-Methyl-1-propanol	8.1	3.0	4.0	9.4	3.3	13.2	7.4	20.2
1-Butanol	1.5	0.1	1.3	1.1	1.0	0.7	0.9	1.9
1-Pentanol	2.2	[a]	0.7	1.0	0.5	1.1	0.0	1.2

[a] Not determined/reported.

are produced over ThO_2 catalysts at 300 atm and 375 to 425°C in the isosynthesis (*2*, *4*).

The excellent thermal stability of the $CuO/ZnO/Cr_2O_3$ catalyst makes it a good prospect as a HAS catalyst, and improvements in the higher alcohol selectivity of this catalyst can probably be made by using CsOH as a promoter instead of K_2CO_3 and by promoting the catalyst with ThO_2.

CONCLUSIONS

A coprecipitated $CuO/ZnO/Cr_2O_3$, 30/60/10 catalyst promoted with 0.5% K_2CO_3 was active for the higher alcohol synthesis and showed no deactivation during 60 h on-stream at 325°C. The higher alcohol selectivity was similar to that of a similarly promoted $CuO/ZnO/Al_2O_3$ commercial catalyst but can probably be improved by optimizing the promoter concentration or by using Cs instead of K as the alkali promoter.

The presence of ZnO appears to have a distinct promoting effect on the activity of copper-containing catalysts and in this respect, the present work supports the conclusions of Natta (*12*) and Klier (*7*). The ZnO probably acts as both a structural (Table 1) and a chemical (Fig. 1) promoter.

Thorium dioxide improves the higher alcohol selectivity of HAS catalysts. A coprecipitated $CuO/ZnO/ThO_2$, 30/60/10 catalyst was active in the synthesis of higher alcohols and had a selectivity for C_4 alcohols 50% greater than that of the $CuO/ZnO/Cr_2O_3$ catalyst at 325°C. The ThO_2-promoted catalyst had poor thermal stability and lost 40% of its initial activity during a 60-h run at 325°C.

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