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The Effect of Cobalt Concentration, Methanol, and Ethanol on the Alcohol Synthesis over a CuZnCr Catalyst

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Doping CuZnCr (38/38/24) with Co (0–5 mol%), and adding methanol or ethanol to a CO + H_2 reactant mixture led to considerable modifications in catalytic activity and selectivity. Modification of the reducibility of the catalyst and copper aggregation were attributed to the presence of Co. The introduction of methanol inhibited production of other oxygenated compounds. On the contrary, the introduction of ethanol enhanced it. Results obtained with ethanol in the reactant flow for both Co-modified and unmodified catalysts suggest that production of methanol and ethanol are related and that the active sites for methanol synthesis are the same as those for higher alcohol synthesis under low-pressure reaction conditions. © 1994 Academic Press, Inc.

INTRODUCTION

The synthesis of alcohols has been studied since about 1930 (1). Early studies were focussed on high-temperature Zn–Cr oxide catalysts that were typical for methanol synthesis until the 1960s. Modern industrial catalysts are constituted by Cu-containing mixed oxide systems (CuO–ZnO–M_2O_3, where M = Al, Cr, Mn, V) which are usually produced by coprecipitation methods.

Recently, it has been reported that the presence of cobalt and potassium in low-temperature methanol catalysts shifts the selectivity toward higher alcohols (2). Fischer–Tropsch catalysts are obtained when small amounts of cobalt are added to methanol synthesis catalysts (3, 4). It has been proposed that the active sites for methanol production in the catalyst may be blocked off by cobalt atoms, which are responsible for hydrocarbon production (5).

On the other hand, even when methanol is incorporated directly into higher alcohol products (6), the latter's yield is strongly dependent on methanol concentration in CO_2-free synthesis gas flow (7). Few data have been presented on the effects of methanol and ethanol since, in most studies of higher alcohols synthesis (HAS), the reactions of these alcohols are at equilibrium and their concentrations are not treated as independent variables.

The purpose of the present work is to study the effects of cobalt, methanol, and ethanol on the alcohol synthesis over a CuZnCr catalyst at atmospheric pressure. Differently from other works (3, 8, 9), the cobalt is coprecipitated with the other components, and only the Cu/Zn/Cr ratio is maintained constant rather than the M^{2+}/M^{3+} and (Cu + Co)/Zn ratios.

EXPERIMENTAL

Catalyst Preparation

CuZnCr and CuZnCrCo catalysts (Cu/Zn/Cr = 38/38/24) were prepared by a coprecipitation method similar to that adopted by Herman *et al.* (10). An aqueous solution of Na_2CO_3 (1.5 M) was added dropwise to a mixed solution of metal nitrates (Total metal concentration = 1 M) at 80°C until the pH reached 8.0. Precipitates formed were aged in the mixed solution at 80°C for 1 h, maintaining the pH of the solution at 8.0–8.3. Thereafter the precipitate was filtered out, washed with distilled–deionized water, and dried in air at 90°C overnight. The subsequent calcination was carried out in air by heating the catalysts in a furnace from 150 to 350°C in increments of 50°C every 30 min with the maximum temperature maintained for 24 h.

Catalyst Characterization

XRD powder patterns were obtained with Fe-filtered CoK_α radiation (λ = 1.7902 Å) using a Philips Goniometer. All XRD spectra were obtained in air.

Surface areas of the catalysts were obtained with N_2 adsorption on a Perkin–Elmer Sorptometer 1020A.

TPR analyses were carried out using an apparatus consisting of a flow system connected to a thermal conductivity cell to follow changes in the composition of the reducing gas (15 vol% of H_2 in N_2). The samples were placed into a tubular reactor which was heated at a constant rate (10°C min^{-1}). Water produced was removed with a liquid nitrogen trap at the outlet of the reactor. Thus, the observed signal was related only to hydrogen consumption.

XPS spectra were measured on a Leybold LH-11 spec-

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trometer using MgK_α and AlK_α radiation. The anode was operated at about 400 W. The base pressure during analysis was 10^{-6} mbar. All binding energies (BE) were referenced to the carbon 1*s* level (284.6 eV) due to adventitious carbon always observed on the solids.

Catalysts after reaction were kept in a helium flow until room temperature was reached and then were sealed in bulbs attached to the top of the reactor. Bulbs were only opened at the moment of the analysis. For XPS analysis, sample holders were filled at inert conditions. This procedure was followed in order to avoid air reoxidation of the used catalysts.

Catalyst Activity

Catalytic tests of the calcined samples were carried out in a fixed-bed-type reactor with a continuous flow system at atmospheric pressure. The reactions were followed by analysis of the gases with two gas chromatographs connected on-line to the system: one with a TC detector to follow CO conversion and the other with a FI detector for the products. A complete analysis of the products was made by collecting them in a liquid nitrogen trap at the reactor outlet and analyzing them by GC-MS, using Kratos MS25RFA equipment.

Methanol and ethanol were injected into the reactant flow by saturation of the synthesis gas, bubbling the gas into a reservoir which was kept at a suitable temperature to attain the desired alcohol concentration. Experimental conditions were as follows: temperature = 280°C, $H_2/CO = 3.0$, GHSV = 4300 $l\ h^{-1}\ kg^{-1}$.

RESULTS

XRD Analysis

Figure 1 shows XRD spectra of the catalysts employed. After calcination (Fig. 1A), all catalysts show a spinel-type phase as the main phase, together with considerable amounts of CuO and ZnO. The catalysts prepared here are more amorphous than reported CuZnCr catalysts obtained by similar coprecipitation methods (9–11). Also, the concentration of simple oxides seems to be higher in our catalysts than in those reported before (9). The presence of cobalt has no effect in simple oxide concentration. Surface areas of the solids were found to be similar and independent of cobalt content. Formation of cobalt oxides was never observed, but their presence in small amounts could not be excluded.

After reaction, the XRD spectra obtained (Fig. 1B) show a signal due to metallic copper. The presence of CuO bands in the XRD spectrum of the unmodified CuZnCr catalyst should be emphasized. A CuO phase was not detected for the catalyst with 5.0 mol% of cobalt. In the used catalysts, the main phase still is the spinel-type one, and the ZnO concentration seems to have no variation during reaction.

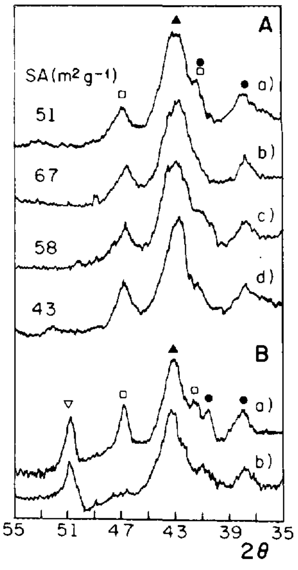

FIG. 1. XRD powder patterns of Co-modified CuZnCr catalysts. (A) Calcined catalysts with Co content of (a) 0.0, (b) 0.5, (c) 1.0, and (d) 5.0 mol%. (B) Used catalysts with Co content of (a) 0.0 and (b) 5.0 mol%. (▲) Spinel-type phase; (□) CuO; (●) ZnO; (▽) Cu. (Surface area of the calcined catalysts is shown on each XRD spectrum.)

Temperature Programmed Reduction (TPR)

TPR spectra (Fig. 2) show a reduction peak at about 270°C for all the calcined catalysts, together with a shoulder of low intensity between 540–740°C. All these reduction signals are not appreciably affected by the presence of cobalt in the catalysts.

After reaction, reduction signals are still found from the catalysts but hydrogen consumption is considerably lesser. Reduction temperatures are almost invariable for the Co-modified CuZnCr catalyst, but a shift to 185°C of the low-temperature signal is observed for the CuZnCr catalyst. The high-temperature shoulder is not affected by reaction and it is also insensible to cobalt content. Identical spectra, not presented here, were found when samples were prereduced in the TPR reactor (15 vol% of H_2 in N_2, 280°C, 24 h), confirming that catalysts are not totally reduced during reaction.

XPS Analysis

XPS analysis (Table 1) shows that differences from bulk composition were observed after calcination. Surface enrichment of zinc takes place during calcination, lowering Cu and Cr concentration, and also Co surface content for the Co-modified CuZnCr catalyst. Noteworthy is the fact that zinc surface concentration still increases after reaction. Cobalt concentration is also higher after reaction in

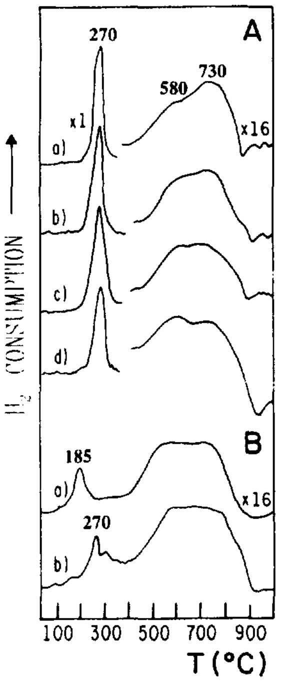

FIG. 2. TPR profiles of Co-modified CuZnCr catalysts. (A) Calcined catalysts with Co content of (a) 0.0, (b) 0.5, (c) 1.0, and (d) 5.0 mol%. (B) Used catalysts with Co content of (a) 0.0 and (b) 5.0 mol%.

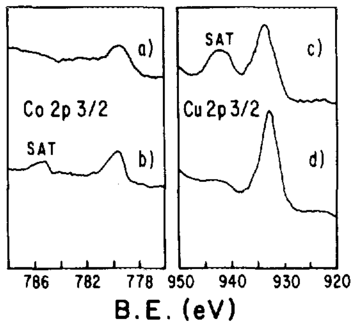

FIG. 3. Co $2p^{3/2}$ and Cu $2p^{3/2}$ XPS signals for the 5.0 mol% Co–CuZnCr catalyst after calcination (a and c) and reaction (b and d).

the Co-modified catalyst. Copper surface content is the same for the calcined and used CuZnCr catalysts. However, an important decrease in its concentration is observed for the used Co–CuZnCr catalyst.

In the calcined samples, Cu is in the Cu^{2+} state (Fig. 3c). Reduction of copper is observed after reaction, as it is deduced from both the absence of satellite structure and the Cu $2p_{3/2}$ peak shift to 932.6 eV (Fig. 3d). Cobalt is in the Co^{2+} state in the catalysis after reaction. This is mainly proved by the typical high-intensity satellite structure at about 6 eV from the Co $2p_{3/2}$ band (9) (Fig. 3b). In the calcined samples, differentiation between Co^{2+} and Co^{3+} was not possible due to a poor resolution of the spectrum (Fig. 3a). However, the later cobalt state has been reported to be present in similar catalysts (9). Thus, the presence of Co^{3+}, or Co^{3+} and Co^{2+}, mixtures could not be excluded.

Chromium is present in the Cr^{3+} state for the CuZnCr catalyst after calcination and after reaction (Table 1). Shifts in the Cr $2p_{3/2}$ band are observed for the Co-modified catalyst. Even when the shifts still are in the range of Cr^{3+} (12, 13), they could be related here to Cr^{3+} in different chemical environments.

Two types of oxygen are observed on the calcined cata-

TABLE 1

XPS Analysis Data of Co-Modified CuZnCr Catalysts

Co (mol%)	Metal bulk composition	Metal surface composition		Binding energy (eV)		Chemical state	
		After calcination	After reaction	After calcination	After reaction	After calcination	After reaction
0.0	Cu 38.0	36.0	31.6	Cu 933.8	932.6	Cu^{2+}	Reduced Cu
	Zn 38.0	47.7	54.2	Zn 1021.4	1021.3	Zn^{2+}	Zn^{2+}
	Cr 24.0	16.3	14.3	Cr 576.4	576.3	Cr^{3+}	Cr^{3+}
				O 530.9	530.4	Simple oxide	Mixed oxide
				529.6		Mixed oxide	
5.0	Cu 36.3	34.1	20.8	Cu 933.8	932.6	Cu^{2+}	Reduced Cu
	Zn 36.3	46.7	56.0	Zn 1021.4	1021.3	Zn^{2+}	Zn^{2+}
	Cr 22.3	17.1	18.1	Cr 576.4	576.3	Cr^{3+}	Cr^{3+}
	Co 5.0	2.1	5.1	Co 780.3	779.7	Co^{2+}	Co^{2+}
				O 531.2	530.4	Simple oxide	Mixed oxide
				529.7		Mixed oxide	

lysts (Table 1). These bands are related to oxygen of simple oxides (531 eV) and to oxygen in mixed oxides (530 eV) (14). XPS spectra of the samples after reaction only show the oxygen band related to mixed oxides.

Catalytic Activity

Figure 4 shows the catalytic behavior of the catalysts employed. All catalysts present a strong deactivation within the first hour of reaction, but deactivation is more pronounced for those catalysts with cobalt incorporated. However, a slightly higher catalytic activity is observed for the 5.0 mol% Co-modified catalyst, but it is still lower than that observed for the CuZnCr catalyst.

Figure 5 shows the selectivity at comparable CO conversion of the different catalysts used. Methanol is the main product over the CuZnCr catalyst at high CO conversion (Fig. 5A). It is important to note that when CO conversion is lower (Fig. 5B) the selectivity to methanol presents an important drop and CO_2 (not shown in Fig. 5) is produced in large quantities. Also, at low CO conversion the present CuZnCr catalyst shows a strong hydrocarbon-forming tendency that seems to be unusual for this well-known methanol synthesis catalyst. However, methanol prevails over hydrocarbons in the products.

When cobalt is added, an important change in selectivity toward hydrocarbons is observed as cobalt content increases (Fig. 5), and C_2–C_4 paraffins and olefins become the main products at cobalt content above 0.5 mol%. Methanol production, as for the CuZnCr catalyst, decreases as CO conversion does, but for the Co-modified samples the lack of methanol production observed is reflected in a higher hydrocarbon production.

Table 2 shows the effects in terms of oxygenate yield over the CuZnCr catalyst when methanol and ethanol are added to the reactant flow. Methanol conversion is almost complete but its unreacted amount in the products increases as its feed to the reactor increases. Ethanol is only found among the products when no methanol is introduced to the reactant flow, but in very small amounts. No oxygenates are found when methanol is added. Only an increase in methane, C_2–C_3 hydrocarbons, and CO_2 is observed.

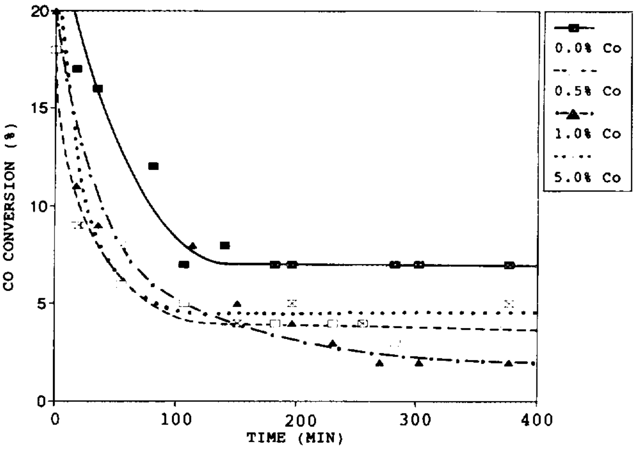

FIG. 4. Catalytic activity in the H_2 + CO reaction of Co-modified CuZnCr catalysts. Reaction conditions: T = 280°C; P = 1 atm; H_2/CO = 3.0; GHSV = 3400 l h^{-1} kg^{-1}.

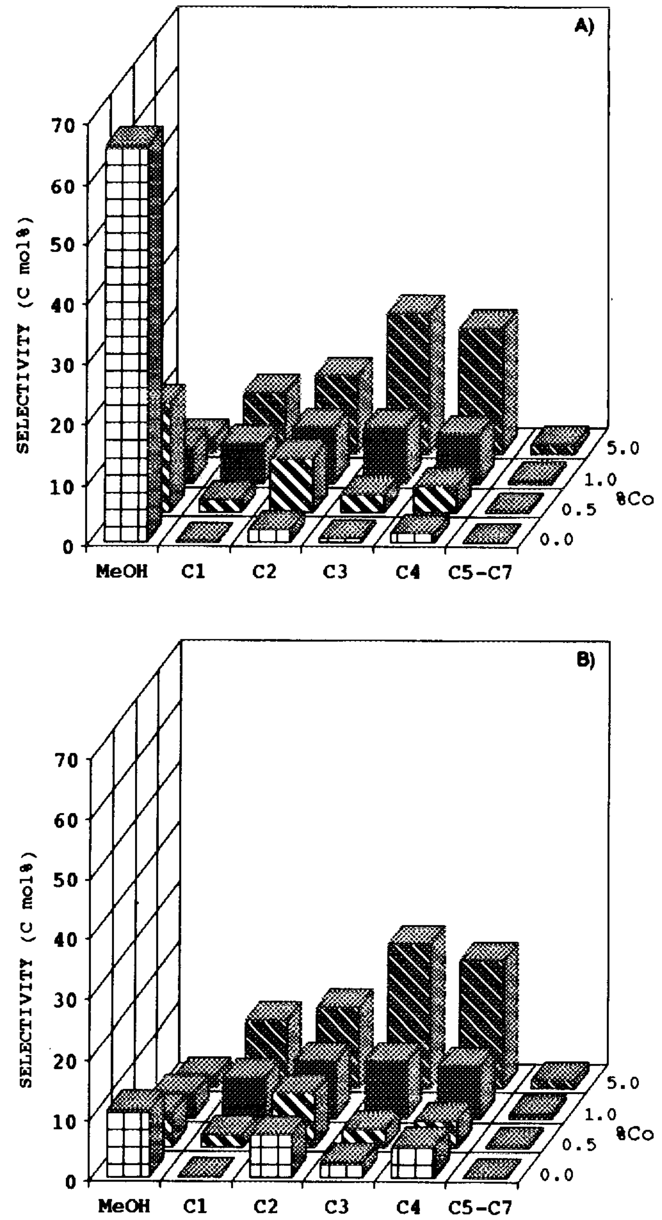

FIG. 5. Selectivity (on C mol basis) for Co-modified CuZnCr catalysts. CO conversion for the different catalysts is (A) 18–22 mol% and (B) 8–9 mol%. C_1–C_7; Hydrocarbons (paraffins + olefins). Reaction conditions are as in Fig. 4.

On the other hand, production of higher alcohols is enhanced when ethanol is added into the reactor. *n*-Butanol is the main higher alcohol found, together with

TABLE 2

Effects of Methanol and Ethanol on the Oxygenate Production over CuZnCr Catalyst

Oxygenated products	Product yield (mmol h^{-1} $gcat^{-1}$)					
	Methanol feed (mmol h^{-1} $gcat^{-1}$)			Ethanol feed (mmol h^{-1} $gcat^{-1}$)		
	0.0	10.0	13.6	3.6	10.4	14.6
Methanol	0.250	0.343	0.573	1.00	3.50	4.12
Ethanol	0.001			0.66	4.20	7.30
n-Propanol				tr	0.01	0.01
2-Methyl-1-propanol				tr	0.02	0.02
n-Butanol				0.18	0.27	0.35
Ethyl acetate				0.22	0.52	0.63
Ethyl butanoate				0.02	0.06	0.08
Methyl acetate				0.01	0.04	0.06
Methyl formate				0.01	0.02	0.03
Other oxygenates[a]				0.20	0.25	0.30

[a] Other oxygenates are aldehydes, ketones, and ethers.

n-propanol and 2-methyl-1-propanol. C_5 and C_6 alcohols are produced only in traces. Together with primary alcohols, ester production is important, and ethyl acetate is the major C_{3+} oxygenated product found when ethanol is added. Ketones and aldehydes are also found among the products. Production of oxygenates increases with ethanol concentration in the reactant flow. Ethanol conversion decreases as its amount in the reactant flow increases, and methanol production is the main reaction at any ethanol feed. The amounts of methanol and ethanol in the products do not inhibit higher oxygenate production.

Figure 6 shows that when ethanol is added to the reactor cobalt content in the catalysts has the same effect as for the CO/H_2 reaction. Ethanol conversion decreases as cobalt concentration in the catalysts increases. Activity at the beginning of the reaction is almost the same for all catalysts, but as the reaction proceeds deactivation of the Co-modified catalysts is higher. With ethanol in the reactant flow, a strong change in alcohol conversion is found for the 5.0 mol% Co–CuZnCr catalyst.

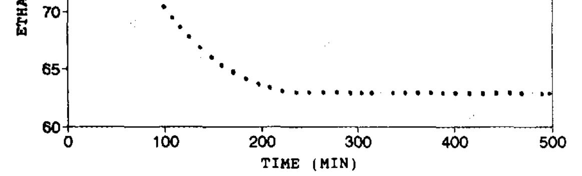

FIG. 6. Catalytic activity in the EtOH + H_2/CO reaction of Co-modified CuZnCr catalysts. Reaction conditions: T = 280°C; P = 1 atm; H_2/CO = 3.0; GHSV = 3400 l h^{-1} kg^{-1}; %EtOH = 5.0 mol%.

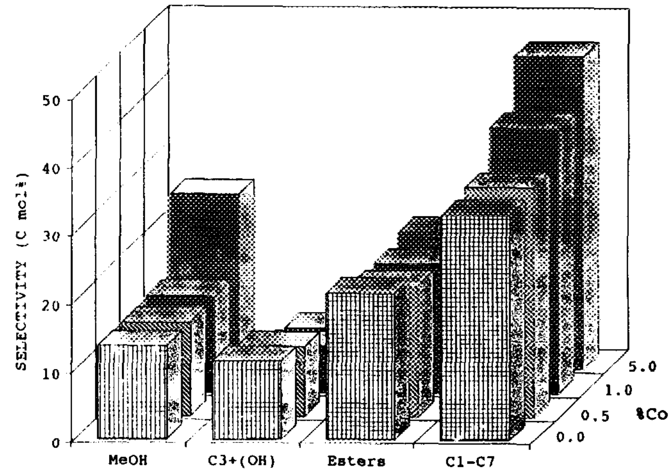

FIG. 7. Steady state selectivity (on C mol basis) in the EtOH + H_2/CO reaction of Co-modified CuZnCr catalysts. C_1–C_7: hydrocarbons (paraffins + olefins); C_{3+}(OH): alcohols with 3 or more carbon atoms. Reaction conditions are as in Fig. 5.

Figure 7 shows that the yield of C_{3+} alcohols in the reaction EtOH + H_2/CO is affected by the presence of cobalt in the catalyst, and decreases as Co content increases. Ester production is almost independent of cobalt concentration. Hydrocarbons and methanol yields are found to increase with cobalt content. As mentioned above, the present CuZnCr catalyst shows a strong hydrocarbon-forming tendency, and in Fig. 7 it could be observed that hydrocarbons are the principal products formed over this catalyst when ethanol is injected into the reactant flow.

DISCUSSION

Effect of Cobalt

The addition of small amounts of cobalt produces a strong deactivation of the CuZnCr catalysts with a minimum of activity for the 1.0 mol% Co-modified catalyst (Fig. 4). A higher content of Co is responsible for an increase in catalytic activity, but it is still considerably lower than for the CuZnCr catalyst.

On the other hand, the catalyst selectivity changes as the amount of cobalt increases from 0.0 to 5.0 mol% (Fig. 5). For the CuZnCr catalyst methanol prevails over hydrocarbons even when a strong change in the selectivity to methanol is observed as the reaction proceeds and CO conversion becomes lower. With only 0.5 mol% of Co in the catalyst, methanol yield is considerably reduced and C_2–C_4 hydrocarbons become the major products. The 5.0 mol% Co-modified catalyst shows the typical behavior of a Fischer–Tropsch catalyst, producing hydrocarbons, in carbon numbers from C_1 to C_7, with only traces of methanol. These results are in agreement with data reported for Co- and Fe-based catalysts (15, 16). However, methanation in the present catalysts is not as important as in the reported ones.

It must be pointed out that the deactivation observed for the Co-modified catalysts cannot be related to textural factors, since all the calcined catalysts show similar BET surface areas (Fig. 1). The changes observed in catalytic activity and selectivity may be attributed to destabilization of copper active sites for alcohol production during reaction due to the presence of cobalt.

Structurally, no appreciable differences are found for the calcined catalysts as cobalt content increases. The amounts of CuO and ZnO seem to be unaffected by cobalt concentration, as observed by XRD (Fig. 1). The reducibility of the catalysts is also insensitive to Co content (Fig. 2). On the other hand, no changes in the high-temperature shoulder of the TPR spectra are observed as cobalt concentration increases. It is at high temperatures where the reduction of cobalt ions to the metallic form is expected (17, 18). TPR results, together with XPS analysis (Table 1, Fig. 3) suggest that cobalt may be in the Co^{2+} state after calcination, possibly forming part of a spinel-type phase as suggested by XRD analysis. It has been reported that spinel phases are capable of stabilizing M^{2+} ions, which become resistant to reduction (19, 20). It must be pointed out that such a cobalt phase does not affect the surface concentration of Cu^{2+} in the calcined catalysts (Table 1).

Important changes in the catalysts due to the presence of cobalt are observed after reaction, indicating that reaction conditions could be promoting the deactivating role of cobalt. It could be inferred from TPR spectra of the used catalysts (Fig. 2) that the presence of cobalt is related to the formation of less reactive species. Reduction profiles show that the used CuZnCr catalyst is easier to reduce than the used Co-modified CuZnCr catalysts. Thus, cobalt could be promoting the synterization of an active copper phase, causing the observed catalytic deactivation. Also, it has been reported before that a decrease in catalytic activity when small amounts of cobalt are added may be attributed to specific Cu–Co interactions involving the formation of mixed phases, stable at the reaction conditions (5, 9).

The results obtained by XPS (Table 1) show that the surface concentration of copper in the 5.0 mol% Co–CuZnCr used catalyst is lower than for the calcined catalyst; an increase in the surface cobalt content, and also in the surface Zn and Cr contents, is observed. A decrease in the surface Cu content is not observed for the used CuZnCr catalyst. Copper could be in the Cu^+ state in the catalysts after reaction. Herman *et al.* (10) have reported that a Cu^+/ZnO solution is responsible for the high activity to methanol synthesis, and for the IFP catalysts it has been reported that Cu^+–M^{3+} phases are the active sites for alcohol formation (21, 22). It is possible that a displacement of copper from those active phases by Co could take place during reaction, causing the observed catalytic deactivation.

However, the trends observed in metal surface composition are consistent with agglomeration and particle size growth of metallic copper, a phase that is expected to be the predominant copper phase on the catalyst after reaction (8–10). Thus, the differences observed in the surface Cu content between the used CuZnCr and Co-modified catalysts could indicate that cobalt favors the agglomeration of the Cu^0 phase during reaction, which is reflected in the catalytic deactivation showed here.

The effect of cobalt over the reducibility of the modified catalyst is also observed in the XRD spectra (Fig. 1). A CuO phase is still present in the CuZnCr catalyst after reaction while this phase is absent in the used 5 mol% Co-modified catalyst. XPS and XRD results seem to corroborate that the catalytic deactivation and selectivity changes observed in the present work could be related to an extensive reduction and agglomeration of the catalysts, which are promoted by small amounts of Co added to the CuZnCr catalyst.

Effect of Methanol and Ethanol

When methanol is added to the reactant flow it is almost totally consumed because of the approach of methanol synthesis to equilibrium and the increased importance of the reverse reaction. The moles of methanol in the products increase as methanol concentration in the reactor increases (Table 2). No oxygenated compounds are detected in the products when methanol is added. Ethanol is only produced, in very small amounts, when no methanol is fed to the reactant flow. As reported before (7), methanol seems to inhibit HAS as its concentration in the reactor increases. The inhibition role of methanol could be associated with a competition for adsorption sites in the catalyst with other intermediate species. So, competition of methanol with CO, or alkyl fragments, for catalytic sites could lead to inhibition of chain growth and, therefore, of higher alcohol production.

Contrary to methanol, ethanol in the reactant flow enhances alcohol synthesis (Table 2). Primary alcohols are the favored alcohols produced and among them, *n*-butanol is the main one. Aldehydes and ketones, corresponding to the primary and secondary alcohols observed, are also produced. Thermodynamical limitations are responsible for the important amounts of *n*-butyraldehyde found, for example (23). Several authors have proposed that chain growth of alcohols occurs via condensation of aldehydic intermediates (24, 25). Esters are also produced under the present conditions, and ethyl acetate is the main one. Methyl esters have been found in small amounts. It is not surprising that with ethanol in the reactor, ethyl esters become the major products by ethanol carbonylation. The variety of oxygenated compounds produced when ethanol is added to the reactor gives an indication of the number of reactions involved in alcohol synthesis.

Ethanol concentration in the reactor does not inhibit HAS. On the contrary, the amounts of *n*-butanol, for example, increase with ethanol concentration in the reactant flow. The amounts of methanol found when ethanol is added to the reactor (Table 2) could indicate the approach to equilibrium of the reaction

$$CH_3OH + CO + 2H_2 \rightarrow CH_3CH_2OH + H_2O.$$

Thus, formation of ethanol and higher alcohols over the present catalyst may proceed by a mechanism that is related with methanol formation in one of the following ways: (i) it may involve methanol as an intermediate and (ii) it may involve an intermediate that is common to the synthesis of both methanol and ethanol. What seems to be clear is that formation of both alcohols is related and that the differences observed when methanol and ethanol are present in the reactant flow support the conclusions of other workers (1, 26) that production of ethanol is the slow step in HAS and that subsequent conversion of ethanol is kinetically favorable.

On the other hand, high methanol amounts in the products do not affect HAS as they do when added to the reactant flow (Table 2). So, strong methanol adsorption over the catalyst is not favored under high ethanol contents, or if it still adsorbs, the presence of adsorbed species from ethanol rapidly react with methanol to give higher oxygenated compounds.

As was observed for the H_2/CO reaction, cobalt in the catalyst also affects activity and selectivity when ethanol is added to the reactant flow (Figs. 6 and 7). Conversion of ethanol over the catalyst decreases as cobalt content increases (Fig. 6). Selectivity toward higher alcohols (Fig. 7) also decreases when small amounts of cobalt are added to the catalyst, indicating that, as are the active sites for methanol production, the catalytic sites for higher alcohols formation are also affected by cobalt. This result could indicate that the active sites for both methanol and higher alcohols production are the same. However, selectivity toward methanol increases with cobalt content. This result could suggest that Co-modified catalysts could provide sites for ethanol to methanol reaction but not for HAS. Ester production is not affected by cobalt content, indicating that catalytic sites for ester synthesis may be unmodified by cobalt. However, it is important to note that Co is known as a good catalyst for alcohol carbonylation (27), and thus could compensate any change affecting the active sites for ester production in the CuZnCr catalyst.

Finally, it is important to mention the strong hydrocarbon-forming tendencies of the present CuZnCr catalyst. As is observed in Fig. 5, selectivity to methanol over the present CuZnCr catalyst is lower than reported before (9, 10), and it also has an important drop as the catalyst deactivates (reflected on a lower CO conversion) during reaction. At a lower CO conversion, hydrocarbon production is unusual for this type of catalyst. This tendency is corroborated when ethanol is added to the reactant flow, where hydrocarbons are the major compounds found among the products (Fig. 7).

It is observed by XRD that the present catalysts are more amorphous than reported CuZnCr catalysts, obtained by similar coprecipitation methods (9–12). Also, it has been mentioned above that the concentration of simple oxides seems to be higher in our catalysts than in those reported before (9). Thus, the changes in selectivity at different CO conversion and the unusual hydrocarbon production over the present CuZnCr catalyst could be related to the genesis of the solid. Shen *et al.* (11) have shown that the preparation conditions of the precursors of Cu/ZnO catalysts have a marked effect upon the local concentration of the copper cations, resulting in differences in the final structures of the precipitates.

CONCLUSIONS

The results presented here show that small amounts of cobalt in a CuZnCr catalyst have important effects on catalytic activity and selectivity. These results seem to indicate that the deactivating role of cobalt is related to an extensive reduction and agglomeration of the catalysts during reaction.

Contrary to methanol, which seems to inhibit HAS when it is present in the reactant flow, ethanol enhances oxygenate production when it is added into the reactor. Important amounts of methanol are produced from ethanol, suggesting that both methanol and ethanol formation are related. The differences observed when methanol or ethanol is added into the reactor could indicate that ethanol production is the slow step in HAS.

Cobalt in the catalyst has the same effect observed in the H_2/CO reaction when ethanol is in the reactant flow. As was observed for methanol, selectivity toward higher alcohols decreases when cobalt is added. This result may indicate that active sites for methanol formation are probably the same as for higher alcohol production.

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