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# Effects of Transition Metals on Cu/ZnO Alcohol Synthesis Catalysts

Recently it was reported that the addition of small incremental amounts of cobalt (0–2%) to a conventional Cu/ZnO methanol catalyst systematically destroyed the methanol synthesis activity of the catalyst (*1*). We have now studied the influence on the same catalyst of several other group VIII metals and of metals of the lower groups. This note summarizes the effects produced by these metals on the catalytic properties of Cu/ZnO under methanol synthesis conditions.

## EXPERIMENTAL

*Catalysts.* The Cu/ZnO base catalyst used in this study was a commercial preparation (*1*) supplied by UCI in the form of $\frac{1}{4}$-in. extrudate. Before use, the catalyst was crushed, sieved to $\frac{16}{40}$ mesh size, and calcined in air at 673 K. The metal additives were introduced onto the catalyst by impregnation with an aqueous solution of a metal salt, using the incipient wetness technique. Solutions of the metal nitrates were used for Co, Ru, Rh, Pd, and Zr, and of the ammonium salts for V, Mo, W, and Re. Titanium was deposited as $(NH_4)_2TiO(C_2O_4)_2$, and iridium as $[Ir(NH_3)_5H_2O](NO_3)_3$, which was prepared according to methods in the literature (*2*) from $[Ir(NH_3)_5Cl]Cl_2$. After impregnation the catalysts were dried at 140°C overnight.

*Methods.* The activity of each catalyst was determined in a single pass continuous flow system with a fixed-bed tubular reactor. The catalyst charge, 5 $cm^3$, was reduced *in situ* in flowing hydrogen at 1 atm and 573 K for 4 h before the activity measurements were made. In each catalytic test the reactant mixture (66.7% $H_2$, 31.3% CO, 2% $CO_2$) was passed over the catalyst at a rate of 7.2 liters/$cm^3$ catalyst/hr at 523 K and 65 atm. Liquid products were condensed from the reactor effluents in a trap at 275–277 K and at reactor pressure, and the off-gas was analyzed at regular intervals using a multicolumn Applied Automation gas chromatograph (Model 21). The composition of the liquid products was determined by gas chromatography using a Porapak Q column.

## RESULTS

For each catalyst the rate of methanol formation determined from the liquid sample collected during the first 4 h on stream was used as a measure of the catalytic activity. The effects on the methanol synthesis activity produced by the addition of the transition metals to the base catalyst are shown in Table 1. The selectivity to methanol of the base catalyst was greater than 99%, and no measurable changes in selectivity were produced by any of the added transition metals. Among the metals of group VIII, cobalt produced the most deleterious effects; at equivalent atomic concentration Ru, Ir, and Pt also produced significant poisoning of the catalyst, while Rh and Pd had little influence on the catalytic activity. Among the metals of the lower groups only molybdenum and rhenium poisoned the catalyst. The less easily reducible metals, Ti, Zr, V, and W did not produce any significant decrease in the formation of methanol. Rhenium was the strongest poison of all the metals studied.

The dependence of the catalytic activity on the amount of metal added was determined for Re and Ru. The results are shown in Table 2 and in Fig. 1. Rhenium, which was studied only at low concentra-

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TABLE 1

Effects of Various Metals on the Methanol Synthesis Activity of Cu/ZnO at 523 K and 65 atm

| Additive | M : Cu atom ratio | Yield (g/g cat/h) | Surface area ($m^2/g$) |
|---|---|---|---|
| None | — | 1.23 | 39 |
| 0.29% Co | 0.008 | 0.36 | 41 |
| 0.51% Ru | 0.010 | 0.54 | 36 |
| 0.52% Rh | 0.010 | 1.08 | 46 |
| 0.53% Pd | 0.012 | 1.00 | 51 |
| 0.84% Ir | 0.008 | 0.75 | 45 |
| 0.83% Pt | 0.010 | 0.61 | 46 |
| 0.90% Re | 0.009 | 0.021 | 44 |
| 0.95% Mo | 0.020 | 0.45 | 44 |
| 1.80% W | 0.019 | 1.13 | 49 |
| 0.25% V | 0.012 | 1.16 | 45 |
| 0.24% Ti | 0.010 | 1.07 | 43 |
| 0.47% Zr | 0.010 | 1.23 | — |

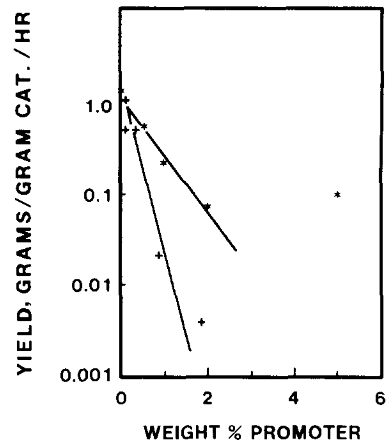

FIG. 1. Methanol yield at 523 K as a function of promoter concentration for Ru (*) and Re (+).

tion levels, showed an increasingly deactivating effect with increasing concentration throughout the entire concentration range. With increasing Ru content the methanol formation decreased in the low concentration range (0–2%), and increased slightly from its minimum at the higher concentration level, probably as a consequence of the catalytic action of ruthenium (*3*). This behavior is similar to that observed with cobalt (*1*). As with cobalt, at low additive concentration there was an exponential relationship between the amount of Ru or Re added and the catalyst deactivation. This suggests that deactivation of the catalyst occurs through specific interaction of the metals with methanol synthesis sites.

TABLE 2

Effects of Promoter Concentration on Methanol Yield for Ru and Re at 523 K

| Promoter | M : Cu atom ratio | Methanol yield (g/g cat/h) | Surface area ($m^2/g$) |
|---|---|---|---|
| None | — | 1.23 | 39 |
| 0.51% Ru | 0.010 | 0.54 | 36 |
| 1.0% Ru | 0.019 | 0.22 | 35 |
| 2.0% Ru | 0.038 | 0.066 | 24 |
| 5.0% Ru | 0.095 | 0.096 | 21 |
| 0.10% Re | 0.001 | 1.02 | 43 |
| 0.18% Re | 0.002 | 0.54 | 34 |
| 0.28% Re | 0.003 | 0.53 | 42 |
| 0.90% Re | 0.009 | 0.021 | 53 |
| 1.85% Re | 0.019 | 0.004 | 34 |

The BET surface areas determined after the synthesis tests are listed in Table 1. No relationship was found between catalyst deactivation and changes in surface area. Also, the addition to the Cu/ZnO of the metals at the concentration levels given in Table 1 caused no significant changes in the average crystallite sizes of copper and of zinc oxide determined by XRD analysis after the synthesis test. At higher concentrations of Ru (Table 2), the crystallite size of the zinc oxide increased and the surface area decreased, analogously to what was observed for cobalt (*1*).

Samples of the base catalyst and of a catalyst impregnated with 1% cobalt were examined by Auger spectroscopy to determine whether the cobalt caused changes in the relative surface concentration of Cu and Zn. The samples were reduced in flowing hydrogen at 523 K for 1 h in the pretreatment cell of the spectrophotometer before the Auger spectra were recorded. In contrast to what has been reported for poisoning of the catalyst by sulfur, for which a significant surface enrichment with Cu relative to Zn was observed (*4*), the Zn/Cu ratio was not affected by the addition of cobalt in sufficient amount, 1%, to cause almost complete deactivation of the catalyst (*1*). Metallic copper was the only copper species observed by ESCA/Auger analysis in the reduced catalyst with or without cobalt.

Hydrogen and carbon monoxide adsorption isotherms of the base catalyst and of the catalysts containing 0.28% Re, 0.29% Co, and 0.24% V, were measured at 298 K. Each catalyst sample was reduced in a flowing stream of hydrogen at 423–473 K for 2 h, then at 523 K for 3 h, and was evacuated at 523 K for 15–17 h before the adsorption measurements. After the isotherm was determined the sample was evacuated for 10 min and a second isotherm was obtained to measure the weakly adsorbed gas. The difference between the first and second isotherm corresponds to the strongly adsorbed gas. The total, weak, and strong adsorption capacities for CO and for $H_2$ at 298 K and at a pressure of 100 Torr are listed in Table 3. Contrary to what was previously reported for cobalt (*1*), no reduction in the adsorption of CO was observed in the presence of the additives; the CO isotherms were nearly identical for all four catalysts. Both the weak and the strong hydrogen adsorption capacities of the catalyst containing 0.29% Re were slightly higher than those of the base catalyst, while for the catalyst containing 0.29% Co the weak adsorption capacity was higher and the strong adsorption capacity lower than for the base catalyst. No correlation was found between the adsorption properties of the catalysts for the individual reactants at 298 K and their activity for methanol synthesis at 523 K.

TABLE 3

Hydrogen and Carbon Monoxide Chemisorption on Cu/ZnO at 298 K and 100 Torr

| Additive | None | None | 0.24% V | 0.29% Co | 0.28% Re |
|---|---|---|---|---|---|
| Activity[a] | 1.0 | 1.0 | 0.96 | 0.29 | 0.43 |
| CO adsorption ($\mu$mol CO/g cat) | | | | | |
| Total | 88 | 85 | 88 | 88 | 90 |
| Weak | 67 | 62 | 62 | 64 | 68 |
| Strong | 21 | 23 | 26 | 24 | 22 |
| $H_2$ adsorption ($\mu$mol $H_2$/g cat) | | | | | |
| Total | 55 | 53 | 57 | 56 | 64 |
| Weak | 32 | 33 | 33 | 39 | 37 |
| Strong | 23 | 20 | 24 | 17 | 27 |

[a] Relative methanol synthesis activities from the data in Tables 1 and 2.

## CONCLUSIONS

The purpose of this work was to determine the effects on the catalytic activity and selectivity of Cu/ZnO produced by the addition to the catalyst of small amounts of the transition metals listed in Table 1. The selectivity of the catalyst was not altered by any of the metals. Some of the additives (Ti, Zr, V, W, Rh, and Pd) also had little or no effect on the methanol synthesis activity; others (Mo, Ru, and Pt) were moderate inhibitors; rhenium and cobalt were strong poisons. The inhibition of the methanol synthesis was not accompanied by observable changes in either the bulk or the surface properties of the catalyst, or by significant changes in the adsorption by the catalyst of $H_2$ and CO. We conclude that the poisoning of the catalyst is related to specific interactions of the metal with the active sites. The nature of these interactions remains to be clarified.

## REFERENCES

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