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Brass Formation in a Copper/Zinc Oxide CO Shift Catalyst

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It is shown that thermal treatment of a copper/zinc oxide CO-shift catalyst in a reducing gas causes a decrease in BET surface area as well as partial reduction of zinc oxide followed by the formation of α-brass. The presence of zinc in the copper-rich phase has a very strong negative effect on catalyst activity. The amount of brass formed is in agreement with concentrations predicted from thermodynamic calculations and the rate of diffusion of zinc in the copper crystallites.

INTRODUCTION

Since about 1960 copper/zinc oxide catalysts are used on a large scale for the second-stage CO-shift conversion in processes for the production of hydrogen and hydrogen-containing synthesis gases. Furthermore Cu/ZnO has been introduced in the manufacture of methanol by low pressure processes. Cu/ZnO is much more active for the CO-shift conversion than the older iron oxide/chromium oxide catalysts but also more sensitive to sulfur and chlorine compounds and to temperatures above 250°C, especially during the reductive activation (*1–3*).

Sulfur compounds deactivate by poisoning the active copper surface and the negative effect of chlorine is attributed to the formation of chlorides which promote sintering (*4*). Young and Clark (*5*) recently stated that even chlorine concentrations below 0.05% (w) on the catalyst cause deactivation by formation of zinc chloride, which accelerates sintering of ZnO by virtue of its low melting point. This reduces the ability of the carrier to stabilize the small copper crystallites, thus decreasing the copper surface area. The deactivation at temperatures above 250°C in the complete absence of poisons is also ascribed to sintering (*5*, *6*).

In this connection little attention has so far been paid to the solid-state chemistry of the ingredients of the low-temperature CO-shift catalyst under the reducing conditions prevailing during activation as well as processing. Results of work on this subject are reported below.

The first steps in the preparation of the catalysts are usually coprecipitation of the hydroxides, washing and drying. One obtains what may be considered as a very finely divided mixture of the oxides: the oxides of copper and zinc do not form compounds. ZnO may dissolve up to 5% (w) of cupric oxide (*16*). Activation is accomplished by reduction with 1–2% (v) hydrogen in an inert gas at about 200°C. Under these conditions CuO is reduced to copper:

$$CuO + H_2 \rightleftarrows Cu + H_2O \quad [\Delta G_r(200°C) = -25.6\ \text{kcal/mol}]. \quad (1)$$

Reduction of zinc oxide is not possible at 200°C:

$$ZnO + H_2 \rightleftarrows Zn + H_2O \quad [\Delta G_r(200°C) = +19.2\ \text{kcal/mol}]. \quad (2)$$

With intimate mixtures of the two oxides, however, dissolution of zinc in the copper phase may occur. Brass is formed, which results in a decrease of the free enthalpy of the system and compensates for the large positive ΔG-value of the zinc oxide reduction:

$$y\,\mathrm{Cu} + \mathrm{Zn} \rightleftarrows \mathrm{Cu}_y\mathrm{Zn}. \qquad (3)$$

This phenomenon has been observed and explained on a thermodynamic basis as early as 1930 (*7, 8*). Data published by Hultgren *et al.* (*9*) indicate that the free enthalpies of the two consecutive reactions balance at rather low concentrations of zinc, i.e., where the α-phase of brass is formed (Fig. 1). Therefore, we have carried out equilibrium calculations for this phase ($x_{\mathrm{Zn}} < 0.38$) for the reaction:

$$y\,\mathrm{Cu} + \mathrm{ZnO} + \mathrm{H_2} \rightleftarrows \alpha\text{-}\mathrm{Cu}_y\mathrm{Zn} + \mathrm{H_2O}. \quad (4)$$

In the calculations Lumsden's correlations (*10*) were applied because they were found to agree with the data mentioned above and are easier to handle. The free enthalpy of brass formation according to reaction (*3*) is given by:

$$\Delta G_0(y, T) = -7770 + \frac{3150}{y} - RT[(1 + y) \ln(1 + y) - y \ln y] + 1.69\,T \text{ (cal/mol)}. \qquad (5)$$

The states of reference are the solid elements at the same temperature. With the aid of this equation and the free enthalpies of formation of water and ZnO, taken from the correlations published by the Bureau of Mines (*11*), the equilibrium composition of reaction (*4*) can be found. The results in Fig. 2 show that the formation of brass is quite possible from a thermodynamic point of view when applying conditions similar to those prevailing during the reduction of the CO-shift catalyst, where values of up to 1000 for the pressure ratio, $p_{\mathrm{H_2}}/p_{\mathrm{H_2O}}$, can occur.

METHODS

Experiments were conducted to study the relation between catalyst activity and reduction conditions. A commercial catalyst consisting of 32% (w) CuO, 62% (w) ZnO and 2% (w) $\mathrm{Fe_2O_3}$ (G-66B supplied by Girdler-Südchemie, Munich) was crushed and a sieve fraction, 0.35–0.42 mm, prepared. About 0.5–3 g were used in each experiment; the reduction was carried out at atmospheric pressure in a microflow apparatus equipped with either a stainless steel or a glass reactor immersed in a thermostatically controlled bath containing a eutectic salt melt (*14*). After heating the reactor to the desired temperature in a nitrogen flow the reducing gas, hydrogen diluted with nitrogen, was admitted. Gases were dried over molecular sieves and oxygen was removed with BTS catalyst obtained from BASF, Ludwigshafen. Whenever necessary, water was introduced in concentrations of 1 or 100 ppmv by passing the gas over $\mathrm{P_2O_5}$ or 5A molecular sieves containing 13% (w) water, respectively. After activation and conditioning the samples were cooled to ambient temperature in a nitrogen flow. The cold reduced catalyst was never

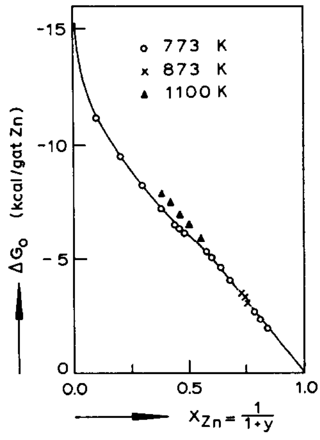

FIG. 1. Free enthalpy of brass formation as defined by reaction 3 [Ref. (*9*)].

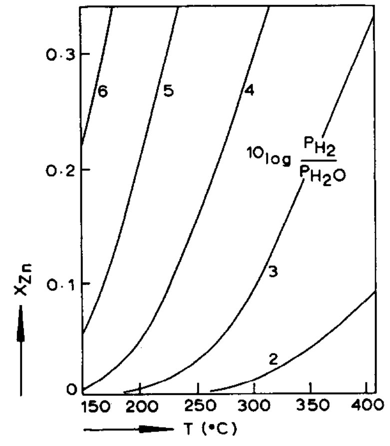

FIG. 2. Equilibrium composition for reaction 4.

pyrophoric; formation of copper oxides was also not observed on exposure to air.

BET surface areas were determined by nitrogen adsorption and crystallite sizes of copper and zinc oxide were calculated from broadening of X-ray diffraction lines (*12*). The amount of zinc present in the copper-rich phase was found from the lattice constant of copper, a_{Cu}, which depends almost linearly on the zinc molal fraction [(*13*), Fig. 3]. The lattice constant is determined from an X-ray powder diffraction diagram by extrapolation to zero of a plot of the value of a_{Cu} calculated from the appropriate reflections against the Nelson-Riley function (*14*).

Four reduced and conditioned samples were tested for their activity to catalyze the conversion of CO with water to CO_2 and hydrogen. This was done in a continuous microflow apparatus equipped with an on-line gas chromatograph for the analysis of the reaction products over a molecular sieve (5A) column using He as the carrier gas. The reaction rate measurements were performed at atmospheric pressure, 193°C and space velocities such as to give conversions between 5 and 15%. Previously the catalyst samples had been stabilized to essentially constant activity with a feed consisting of 10% (v) CO, 11% (v) N_2, 16% (v) H_2 and 63% (v) water.

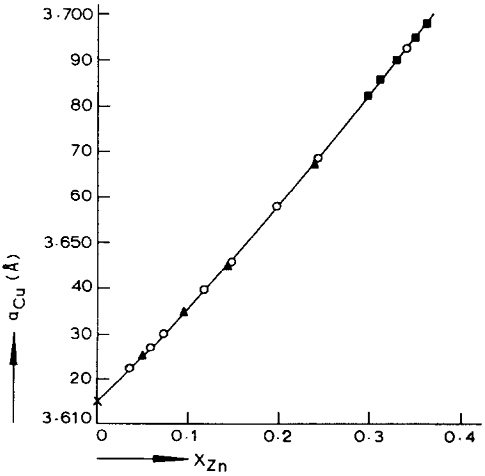

FIG. 3. Lattice constant of copper in brass [Ref. (*13*)].

RESULTS

In the first of the three series of reduction experiments made in the course of the work reported here variations were applied in hydrogen content of the gas phase, space velocity and reduction temperature. The results (Table 1) demonstrate that the variations in space velocity and hydrogen content have but little effect on the BET surface area of the reduced catalyst even for hydrogen contents far higher than the 2% (v) generally prescribed by catalyst manufacturers.

The second series of experiments consisted of a standard activation procedure with 5 vol% H_2 in nitrogen followed by conditioning with hydrogen containing 1 or 100 ppmv water for about 100 hr. The data shown in Table 2 indicate that a serious loss of surface area occurs only at 300°C. The samples conditioned at 300°C contain brass; the crystallite size of the copper and the zinc oxide remains virtually constant at the values observed after careful reduction, i.e., about 225 Å. Four other samples reduced by the standard method were subjected to aging about 120 hr at even more severe conditions (see Table 3); subsequently, the activity for catalysis of the reaction between CO and water was determined. Results are shown in Fig. 4; the activity is expressed per m^2 BET surface area. The reproducibility of the pretreatment procedure is not excellent—A_1 and A_2

TABLE 1
EFFECT OF REDUCTION CONDITIONS ON THE SPECIFIC SURFACE AREA

T (°C)	GHSV (hr^{-1})	x_{H_2} (mol%)	S (m^2/g)
200	750	1	22.2
		2	22.1
		5	21.6
		100	21.1
200	1500	2	22.7
		5	21.8
		50	22.1
		100	21.9
220	1500	5	21.9
		5	22.0

TABLE 2

EFFECT OF CONDITIONING ON CATALYST TEXTURE

T (°C)	x_{H_2O} (ppmv)	S (BET) (m²/g)	a_{Cu} (Å)	x_{Zn} —	$\bar{d}_{Cu}$ (Å)	$\bar{d}_{ZnO}$ (Å)
200	100	21.1	3.615	0.00	235	230
250	100	19.0	3.617	0.00	245	250
300	100	15.3	3.626	0.06	210	220
200	1	20.7	3.614	0.00	245	205
250	1	19.2	3.616	0.00	250	220
300	1	14.6	3.632	0.09	240	220

are duplicates—but it is nevertheless clear that a good correlation exists between the activity per m² BET surface area and the brass content, as is shown in Fig. 5. The structure and composition of the surface may differ somewhat among the samples but these differences are expected to be small.

DISCUSSION

It was confirmed experimentally that at temperatures above 250°C in a reducing gas brass can be formed in the Cu/ZnO catalyst, but the observed amount of zinc dissolved in the copper is much smaller than at thermodynamic equilibrium. This is most probably caused by the fact that the diffusion of zinc in the copper-rich phase is rate-determining. Calculation of the Fourier number for mass transfer, $Fo = Dt/R^2$, for spherical crystallites of 200 Å diameter using an extrapolated value of the diffusion coefficient of zinc in copper (*15*) confirms that below 250°C serious diffusional limitation occurs. Therefore the thermodynamic calculations overestimate the amount of ZnO that can be reduced in 100 hr at those temperatures. The small changes in BET surface area resulting from moderate heat treatment, i.e., at temperatures close to operating conditions, cannot account for the persistent decline in activity which is observed in completely poison-free operation. Furthermore, the fact that the crystallite sizes of the copper do not change during conditioning (Table 2) indicates that the copper surface area does not diminish selectively. Therefore, it seems likely that the strong negative effects on catalyst activity of thermal treatment under reducing conditions must be attributed to the formation of brass. It should be emphasized that the presence of CO causes industrial CO-shift feeds to be about equally "reductive" as the diluted hydrogen employed in reductive activation. However,

TABLE 3

RESULTS OF THE THIRD SERIES OF CONDITIONING EXPERIMENTS

Run	Conditioned with[a]	T_{cond} (°C)	S (m²/g)	x_{Zn}
A1	H_2	300	17.3	<0.001
A2	H_2	300	16.4	0.020
B	H_2	350	12.3	0.045
C	CO	300	17.9	0.085

[a] Dried with activated molecular sieves.

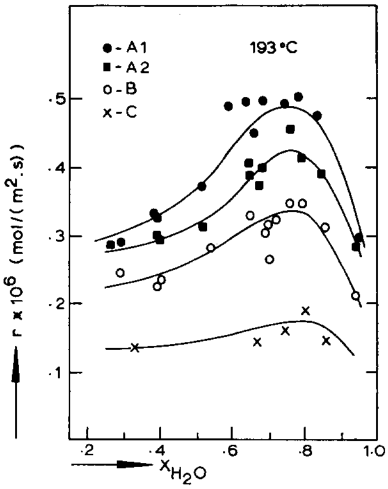

FIG. 4. Rate of CO-shift reaction on conditioned catalyst samples.

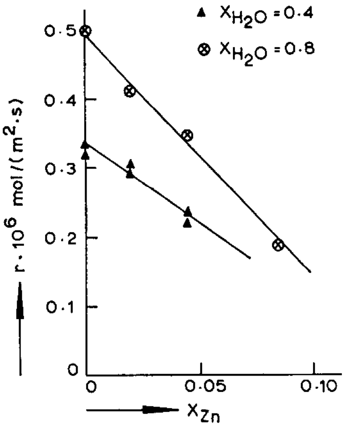

FIG. 5. Relation between the observed rate of reaction for the CO conversion and the zinc content of the copper-rich phase.

deactivation during the reduction is more likely because hot spots may occur during activation as a result of the large amount of heat evolved when copper oxide is reduced, and the relatively high rates of reduction, even at 200°C. Thus, both the equilibrium concentration of zinc in the copper and the rate of diffusion of zinc are higher in hot spots. Estimated equilibration times (Fo = 0.5) for the dissolution of zinc in copper crystallites of 200 Å under low temperature CO-shift reaction conditions are 1000 days at 200°C and 125 days at 225°C.

The following semiquantitative conclusions can be drawn by combining the results of the thermodynamic calculations (which indicate that under given conditions the equilibrium brass content increases markedly with increasing temperature) with the estimated rates of zinc diffusion in copper and the observed negative effect of brass on the activity for the CO-shift conversion:

At temperatures up to 200°C brass formation under reaction conditions is limited to a zinc molal fraction in the copper of at most 0.01. Moreover, since the diffusion of zinc is slow at these temperatures only a very slight deactivation results when the copper becomes saturated with zinc after about 1000 days.

At higher temperatures, say 250°C, concentrations of zinc of 5 at.% can and will be reached in process periods of a few months or even less. As a result, an appreciable rate of deactivation is observed. This picture roughly corresponds to data reported by Campbell (*6*) for the deactivation in 2000 hr when operating with poison-free water gas at varying temperature.

These calculations show that brass formation by reduction of ZnO may contribute appreciably to the deactivation of the copper/zinc oxide CO-shift catalyst, particularly at higher operation temperatures. It would be interesting to establish whether this mechanism of deactivation is also possible for methanol synthesis Cu/ZnO catalysts.

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