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Reduction and State of Co in Co/ZnO Catalysts: Evidence of a Metal–Support Interaction

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The extent of reduction of Co^{2+} to Co^0 in Co/ZnO and Co/SiO_2 catalysts has been ascertained by temperature-programmed reduction, chemisorption, magnetic susceptibility, and activity in propane hydrogenolysis. The results indicate that Co^{2+} is not fully reduced at 573 K on either ZnO or silica, but that there is a strong Co^0–Co^{2+} interaction with ZnO which depresses hydrogen chemisorption and hydrogenolysis activity towards propane; the causes of this are considered. The metal–support interaction causes propane hydrogenolysis to occur at a rate on each hydrogen adsorption site on Co^0–Co_x/ZnO almost 100 times more slowly than on such sites on silica-supported Co. © 1992 Academic Press, Inc.

INTRODUCTION

Co- and Cu-containing catalysts (e.g., potassium-promoted Cu–Co/ZnO/Al_2O_3, Cu–Co/MO (where MO = MgO, CeO_2, or ZrO_2), and Cu–Co–Cr, Cu–Co–Al mixed oxides) are active in conversion of CO/H_2 to higher alcohols (*1*). Various methods have revealed the extent of Cu^{2+} reduction in such catalysts (*2*), but in the present paper attention is given to the nature of Co in such catalysts and the types of Co site of relevance to CO hydrogenation (*3*). Supported cobalt tends to produce alkanes in CO/CO_2 hydrogenation and hence its use in combination with other active metals (such as Cu) which selectively produce methanol (*4*), since together they may facilitate the synthesis of higher alcohols.

The hydrogenolysis of alkanes (*5*) involving C–C scission is catalysed by many zero-valent metals, but especially Co which exhibits the lowest activation energy of the Group VIII metals (*6, 7*). It was therefore judged that these reactions might be useful probes for the fraction of zero-valent Co^0 produced in CoO/ZnO catalysts after reduction. Here hydrogenolysis of propane has been selected to probe the nature of cobalt in reduced catalysts upon silica and ZnO supports.

Incomplete reduction of alumina-supported Co suppressed hydrogen chemisorption capacity (*8*), and this adsorption method has also been used here to probe the Co surface sites in preference to CO chemisorption, which at higher temperatures might produce carbidic and graphitic carbon (*9*).

EXPERIMENTAL

Materials

Catalysts were prepared by coprecipitation from an aqueous solution of

$Co(NO_3)_2 \cdot 6H_2O$ (BDH; Analar; 99.0%)

$Zn(CH_3COO)_2 \cdot 2H_2O$ (BDH; Analar; 99.5%)

with 1 *M* NaOH–$NaHCO_3$ at pH 10.5 ± 0.02, followed by filtering, washing well with deionised water, drying at 403 K (16 h), and finally calcining at 523 K (3 h). The fully reduced catalyst contained 8(wt.%)Co/ZnO. A further sample containing 8(wt.%)Cu–8(wt.%)Co/ZnO was also prepared. In addition 8(wt.%)Co/silica was obtained by impregnating the pre-dried sup-

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port (Shell; 2.5 mm particle size; 211 m^2g^{-1}) with the cobalt nitrate solution. In the text catalysts are denoted in terms of their reduced compositions.

Characterisation Methods

The *in-situ* X-ray diffraction (XRD), temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS) methods used here are described elsewhere (*10*), as also is a full characterisation of the calcined precursors (*11*). The extent of chemisorption of CO and H_2 at 298 K was measured volumetrically. Magnetic susceptibilities of reduced samples were measured after reduction at increasing temperatures (up to 973 K) and further passivation in nitrogen, in a Johnson Matthey magnetic susceptibility balance at 298 K.

Catalytic Methods

Samples (0.2 g) of the catalysts were tested in propane hydrogenolysis (after prereduction for 30 min at 573 K) in a propane (10 cm^3/min), hydrogen (100 cm^3/min), and nitrogen (30 cm^3/min) stream at 101 kPa as the catalyst temperature was increased in steps from 523 K or 548 K to 573 K, at which intervals isothermal catalytic measurements were carried out. Kempling–Anderson selectivity parameters (*12*) S_1 and S_2 to methane and ethane were deduced. No measurable yield of iso-butane was noted. The temperature of catalytic testing was selected so that no additional reduction occurred after the pretreatment (i.e., the temperature was identical to that used in CO hydrogenation (*11*)).

RESULTS AND DISCUSSION

Co Catalysts

TPR profiles in Fig. 1 for CoO_x on ZnO and on silica showed that its reduction on both supports occurred in two stages, with that on the former support occurring over a wider temperature range and thus ultimately requiring higher temperatures (i.e., up to 1119 K) for complete reduction. The amount of hydrogen consumed in each was about the same (1.72 mmol/g for Co/ZnO and 1.77 mmol/g for Co/silica). However, hydrogen reduction prior to adsorption and catalytic measurements was carried out at only 573 K for 30 min and this essentially only involves the first reduction process (although it remains uncertain whether this is reduction of one Co species to the zero-valent state to be followed later by a more resistant species or whether it is reduction of some Co^{3+} to Co^{2+} and that the later step is that of Co^{2+} to the zero-valent state). In both samples reduction to 573 K involves consumption of a similar amount of hydrogen (0.41 mmol/g for Co/ZnO and 0.49 for Co/silica). Hence the extent of Co reduction *after* this pretreatment on either oxide support is *not* complete (i.e., is 24–28% of the maximum seen for both samples); con-

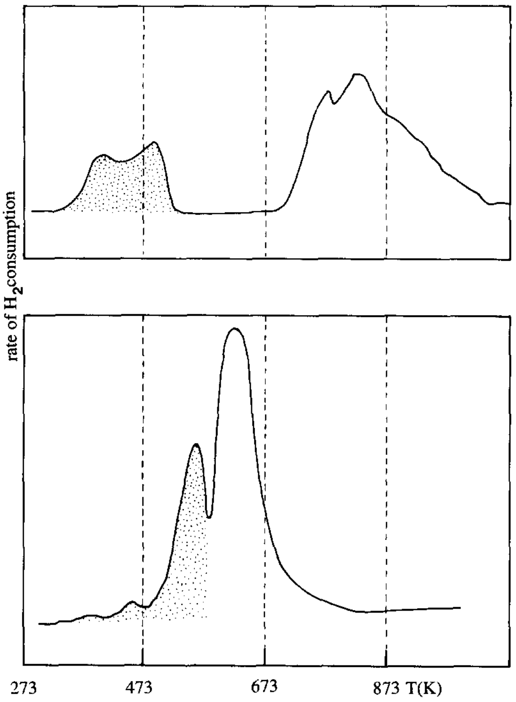

FIG. 1. TPR profiles (on different scales) plotted as rates of H_2 consumption (arbitrary units) versus temperature for reduction of CoO (in an 8% metal loading) upon ZnO (top) and silica (bottom). Reduction to 573 K prior to catalysis and adsorption gives hydrogen consumptions which correspond to the shaded areas.

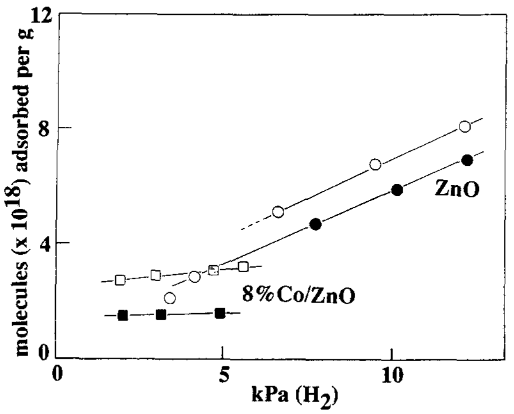

FIG. 2. Adsorption isotherms of hydrogen at 298 K on ZnO (○, ●) and 8%Co/ZnO (□, ■), where open symbols are the total extent of adsorption and black symbols are the reversibly adsorbed hydrogen.

versely then ZnO does *not* stabilise the Co in a higher oxidation state than with Co/SiO_2, unless in CoO_x/ZnO (where TPR indicates that $0.72 < x < 0.76$ at 573 K) the support is reduced sacrificially to give CoO_x/ZnO_y ($x > 0.76$, $y > 0.92$). Certainly slight ZnO reduction is possible (*13*) and could be accelerated by CoO_x, but probably not to the extent needed for the above hypothesis.

In-situ XPS during reduction has been carried out and results will be published separately; they show that some Co^0 is formed in both samples on reduction as described above, but that cobalt conversion to the zero-valent state on ZnO is only about 50% complete (*14*).

XRD revealed no detectable CoO_x or Co^0 in the Co/SiO_2 or Co/ZnO catalysts, although others (*15*) have detected them previously in Co/SiO_2 catalysts by this method and so it is presumed that the Co on the two supports here is quite highly dispersed.

Figures 2 and 3 show adsorption isotherms for H_2 and CO on ZnO and on 8%Co/ZnO; in one case the isotherm Langmuirian in form. On ZnO the adsorption of CO is essentially entirely reversible. It is interesting that Co *diminishes* the extent of H_2 adsorption (but enhances that of CO) on ZnO at 298 K. Specifically, at 11 kPa 8%Co/ZnO adsorbs only 47% of the amount of hydrogen adsorbed by ZnO alone, but as much as 164% of the amount of carbon monoxide adsorbed by ZnO alone. The results for CO adsorption therefore suggest that cobalt addition increases the ZnO surface area and/or that the Co is at the ZnO surface and able to adsorb additional CO to that taken up by the support. However, the more important result is the one for H_2 adsorption, which indicates a clear Co–ZnO interaction, with the effect that not only does the supported Co produced not adsorb dihydrogen extensively but it modifies the ZnO surface, diminishing *its* own extent of hydrogen adsorption. Metal–support interactions often suppress hydrogen chemisorption on the metal, but here it appears that adsorption on the support is also decreased. This seems noteworthy.

Figure 4 shows that the magnetic susceptibility of Co/ZnO and Co/SiO_2 both increase with increasing temperature of hydrogen reduction (at least up to 773 K). This cannot occur by partial reduction to lower Co oxides (i.e., results for CoO, Co_3O_4, and Co_2O_3 are similar) but only due to the formation of pre-ferromagnetic domains of metallic Co^0. That both Co/SiO_2 and Co/ZnO show the same characteristics

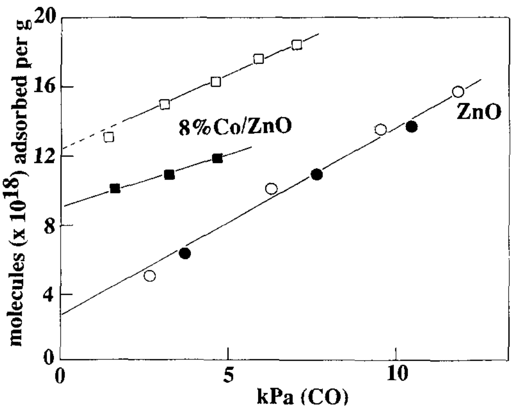

FIG. 3. Adsorption isotherms at 298 K of CO on ZnO (○, ●) and 8%Co/ZnO (□, ■) where the symbols are the same as in Fig. 2.

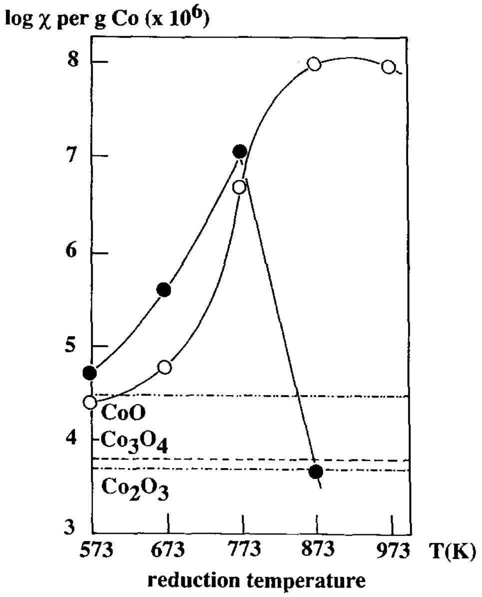

FIG. 4. Magnetic susceptibilities of 8%Co/ZnO (○) and 8%Co/SiO_2 (●) with increasing temperatures of reduction: –··–, –––, and –·–·– relate to magnetic susceptibilities seen for unit weights of CoO, Co_3O_4, and Co_2O_3, respectively. Susceptibilities per g Co for supported Co rise above those for these oxides but not to the values expected for ferromagnetic Co^0. It is presumed therefore that at these temperatures only a very small fraction of Co is really reduced entirely. This agrees with the 26% Co reduction deduced from the TPR profiles in Fig. 1.

up to 773 K suggests that Co is in the same reduced state and produced to the same extent on each support. Again this modest rise in magnetic susceptibility with increase in reduction temperature agrees with TPR evidence of meagre extents of reduction at 500–700 K.

It is believed that the catalyst was not significantly reduced further *during* catalysis. In Table 1 it is seen that Co on silica *is* active in propane hydrogenolysis after prereduction at the standard temperature of 573 K, producing methane almost selectively at the temperatures studied. The activation energy for this propane conversion was deduced from the temperature dependence of conversions (9.25% at 523 K, 20.3% at 548 K, and 26.9% at 573 K) to be 53.5 kJ/mol. However, surprisingly, Co^0–Co_x/ZnO which was also prereduced at the same temperature (573 K) to about the same extent as on silica did *not* catalyse propane hydrogenolysis to anything like the same extent: thus it converted 0.13% at 573 K (and under conditions not relevant to the analysis here this only rose to 2.22% at 673 K and 8.15% at 773 K). The relevant activation energy was 77.2 kJ/mol. However, within this meagre activity it did produce methane with an S_1 selectivity of 3.

Cu–Co Catalyst

Others (*16*) have studied the effect of Co addition to Cu catalysts on various supports. It is likely that the extent of Co reduction in these systems will vary from

TABLE 1

Adsorption Capacities and Rates of Hydrogenolysis on Co Catalysts

Sample	Hydrogenolysis[a]			Adsorption[b] (mmol/g)	TON (s^{-1})[c]
	S_1	S_2	rate (mmol/g/min)		
8%Co/silica	2.96	0.02	33.50	8.3	0.0336
8%Co/ZnO	3.00	0.00	0.16	3.9	0.0003

[a] Measured for propane at 573 K after pre-reduction at the same temperature.

[b] Measured for total adsorption capacity towards hydrogen at 298 K volumetrically (by extrapolation of adsorption data to the zero-pressure intercept) after pre-reduction at 573 K and desorption; it is useful to compare this uptake with that for ZnO alone (*12*) (i.e., 3.17 nmol H_2/g).

[c] Propane molecules converted per second per hydrogen adsorption site.

those seen here for Co alone on ZnO, since the addition of Cu may *promote* Co reduction just as Co addition retards Cu reduction on ZnO (*10*); certainly Mouaddib *et al.* (*1e*) have seen 9% Co reduction in Co/MgO which was increased to 22% when Cu was present. Nevertheless, the present results are relevant to Co-modified Cu/ZnO catalysts which are useful for alcohol synthesis (*16*). On this point it has been found that when 8% Cu is coprecipitated into the 8% Co/ZnO catalyst the amount of propane converted by hydrogenolysis at 568 K (0.104%) remains as low as that seen for Co/ZnO alone (i.e., 0.129% at 573 K). Either it is presumed that a similar Co–ZnO interaction will prevail in Cu–Co/ZnO catalysts or Cu encapsulates the Co phase. Although Cu/SiO_2 and Cu/ZnO catalysts alone not unexpectedly showed no measurable hydrogenolysis activity under the present conditions (*17*), the catalytic method of investigation did not allow the alternative descriptions to be differentiated.

CONCLUSIONS

It is clear that a profound mutual effect has been observed between ZnO and Co in terms of their adsorption capacity and the hydrogenolysis activity of the latter. This is despite the fact that Co reduced on silica to the same extent (in terms of TPR and magnetic susceptibility data) at 573 K exhibited the same high selectivity to methane (S_1 = 2.96 – 3.00). However, Figs. 1 and 4 indicate that not all Co is reduced on ZnO or SiO_2 supports under present catalytic and chemisorption experiments. It may of course be that samples were reduced *more* during these isothermal catalytic measurements than was seen in dynamic TPR, but in choosing conditions every attempt was made to avoid this situation arising.

The turnover numbers per hydrogen adsorption site per second for propane hydrogenolysis at 573 K were on silica-supported Co about 100 times those seen for Co/ZnO. Naturally both adsorption and catalysis could be affected by a strong metal–support interaction in Co/ZnO as a result of electronic or decorative effects. Alternatively, ZnO may induce different crystallographic planes on the surface of the Co crystallites from those seen on silica, since these do affect activity (*18*).

How the ZnO interacts so specifically with Co and where the Co is located in the Co/ZnO catalysts remains the subject of further study. It may for example involve Co^{2+} entering into the interstitial sites otherwise occupied by Zn^{2+}. $2e^-$ pairs in nonstoichiometric ZnO_y (*12*).

The work has also highlighted a strange interaction between Co and silica at above 773 K in a reducing atmosphere which requires further study. It is interesting that the magnetic susceptibility for Co/SiO_2 only decreased abruptly at the temperatures at which TPR suggests bulk cobalt reduction. For the moment the use of chemisorption and alkane hydrogenolysis to probe the extent of reduction and nature of Co in CO hydrogenation catalysts upon ZnO have at the very least thrown light upon an interesting metal-support interaction (*19*) of relevance to Cu–Co-type catalysts considered by many, including Courty *et al.* (*1a*), for this important reaction.

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