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Selective synthesis of alcohols from syngas and hydroformylation of ethylene over supported cluster-derived cobalt catalysts

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Hydroformylation of ethylene and CO hydrogenation were studied over cobalt-based catalysts derived from reaction of $Co_2(CO)_8$ with ZnO, MgO and La_2O_3 supports. At 433 K a similar activity sequence was reached for both reactions: Co/ZnO > Co/La_2O_3 > Co/MgO. This confirms the deep analogy between hydroformylation and CO hydrogenation into alcohols. In the CO hydrogenation the selectivity towards alcohol mixture (C_1–C_3) was found to be near 100% at 433 K for a conversion of 6% over the Co/ZnO catalyst; this catalyst showed oxo selectivity higher than 98% in the hydroformylation of ethylene. Magnetic experiments showed that no metallic cobalt particles were formed at 433 K. It is suggested that the active site for the step that is common to both reactions is related to the surface homonuclear $Co^{2+}/[Co(CO)_4]^-$ ion-pairing species.

Keywords: higher alcohol synthesis; vapor phase hydroformylation; supported cluster-derived cobalt catalysts

1. Introduction

The formation of alcohol from syngas over heterogeneous catalysts is believed to proceed via CO insertion into an alkyl–metal bond, a path which is shared by the hydroformylation reaction. Attempts to compare both reactions over heterogeneous nickel-based catalysts have confirmed this view [1,2]. This work was primarily aimed at extending the comparison of both reactions to cobalt catalysts, which are widely used in the synthesis of alcohol mixtures from syngas [3–7] and the hydroformylation reaction either in homogeneous phase or as supported heterogeneous catalysts [8]. This work was also intended to assess the extent to which these similarities may help us to design new catalysts with improved performances.

This paper reports on ethylene hydroformylation and CO hydrogenation reactions over different supported cobalt catalysts prepared from the reaction of $Co_2(CO)_8$ with MgO, ZnO, and La_2O_3 surfaces which leads to new surface carbonyl species [9–11]. One of these novel catalysts demonstrates an unprecedented high selectivity towards alcohol mixture in the CO hydrogenation reaction at a surprisingly low temperature.

2. Experimental

2.1. Preparation of catalysts

The three catalysts were prepared by placing a hexane solution of $Co_2(CO)_8$ in contact with MgO (obtained by adding ammonia to $MgCl_2$ solution, surface area 110 m^2/g), ZnO (Kadox, 15 m^2/g) and La_2O_3 (prepared from the citric complex, 18 m^2/g). Prior to use, the supports were partially dehydrated by high-vacuum treatment at 473 K for 16 h. The impregnation was carried out under argon atmosphere (0.1 MPa) at room temperature using vacuum-gas-line techniques. After solvent evaporation, the catalysts were treated under high vacuum at room temperature for 16 h and kept under argon. No other calcination or reduction step was carried out prior to catalytic or characterization studies. Chemical analysis revealed that the cobalt contents were 0.96 (Co/MgO), 0.84 (Co/ZnO) and 0.75 wt% (Co/La_2O_3).

2.2. Catalytic activity

The hydroformylation reaction was carried out in an 80 ml magnetically stirred stainless-steel autoclave at a total pressure of 8 MPa and 433 K for 4 h with a $C_2H_4 : CO : H_2 = 1 : 1 : 1$ molar ratio and a catalyst charge of 0.5–0.6 g. The reaction products were collected by bubbling the gases through toluene kept at 194.5 K and analyzed by GC-MS. No other hydrocarbons apart from ethylene were detected in any case. The carbon monoxide hydrogenation reaction was performed under continuous flow (1.8 ℓ/h NTP) and differential conditions at a total pressure of 5 MPa between 433 and 513 K with a $H_2 : CO = 2 : 1$ molar ratio. The reaction products were analyzed by on-line gas chromatography. The weight of catalyst was 0.2–0.3 g. The reaction temperature was increased stepwise from 433 to 453, 473, 493 and 513 K, then decreased to 433 K. The catalyst was held at each temperature for 2 h. This time was chosen

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after a study carried out at 433 K over the Co/ZnO catalyst, which did not show any change in the selectivity or activity with time on stream from 0.5 to 7 h.

2.3. *Magnetic measurements*

Magnetic measurements are suitable to detect minute amounts of ferromagnetic materials: as a matter of fact, they give rise to signals several orders of magnitude higher than dia, para or antiferromagnetic compounds, and are characterized by a saturation which is reached at moderate field strength. Thus, this technique provides significant information on the characterization of supported catalysts with less than 1 wt% Co.

In this work, the magnetization, M, was measured in an electromagnet (fields up to 2 T) at 300 K using the Weiss extraction method [12,13]. Saturation magnetization measurements were achieved by plotting M against the reciprocal field strength, H, after proper correction for a diamagnetic contribution arising from the support, and extrapolation at $1/H = 0$.

Samples were introduced without contact with air into a stainless steel non-magnetic sample-holder allowing in situ catalyst treatments under controlled atmosphere at various temperatures under 5 MPa. The sample-holder, which is described elsewhere [13], consists of two sections (separated by a valve) designed for magnetic measurements and heat treatments respectively. The sample was inserted in a shuttle which could move rapidly from the treatment section to the measurement section under gravity. It was thus possible to quench the sample under controlled atmosphere from reaction temperature to room temperature, at which magnetic measurements were carried out.

After sample introduction in the sample-holder, the inert gas was replaced by a $CO + 2H_2$ gas mixture flow at 5 MPa. The catalyst was then heated to reaction temperature T for 1 h, quenched at room temperature and the magnetic measurement was performed.

3. Results and discussion

3.1. *Hydroformylation*

The results obtained in the hydroformylation of ethylene at 433 K for all catalysts prepared are presented in table 1. The Co/ZnO catalyst demonstrated the highest activity. The Co/MgO catalyst showed the highest hydrogenating capability as revealed by the ratio C_3-ol/C_3-al.

The activity sequence was the following:

$$Co/ZnO > Co/La_2O_3 > Co/MgO\,. \qquad (1)$$

Although only oxo-products were detected in the toluene solution through which reaction gases were bubbled, the direct analysis by mass spectrometry of the gas-phase mixture after reaction was carried out for the most active catalyst. This analysis did not reveal hydrocarbon formation either. Since the detection limit of hydrocarbons was estimated to be less than 2%, the oxo selectivity was therefore, at least for the Co/ZnO catalyst, better than 98%. This high value contrasts with that obtained under dynamic conditions over Co/SiO_2, by Takeuchi et al., who report a selectivity of about 36%. This catalyst was prepared from $Co_2(CO)_8$ and H_2-reduced at 673 K before use [8].

3.2. *CO hydrogenation*

Fig. 1 shows the CO conversion at 5 MPa as a function of temperature. The conversions measured at 433 K (the hydroformylation temperature) were 5.7, 1.6 and 0.7% for Co/ZnO, Co/La_2O_3 and Co/MgO, respectively. The activity sequence was:

$$Co/ZnO > Co/La_2O_3 > Co/MgO\,. \qquad (2)$$

This is similar to sequence (1). As the temperature increases, the behaviour of the Co/ZnO catalysts was very unusual since its conversion decreased, in contrast with the trend observed for the other catalysts. After reaction at 513 K, the conversion measured subsequently at 433 K was larger than the corresponding initial conversion. It increased from 5.7 to 6.3, 1.6 to 2.3 and 0.7 to 2.0 for Co/ZnO, Co/La_2O_3 and Co/MgO, respectively. This in situ activation under reaction conditions (5 MPa CO/H_2, $T = 433$–513 K) suggests some beneficial transformations of the cobalt active phase over the support surface. It is noteworthy that this temperature cycle does not alter the activity sequence (2).

Fig. 2 shows the variation of selectivity with temperature for Co/ZnO. At 433 K, only alcohols

Table 1
Catalytic activity in the C_2H_4 hydroformylation of cobalt catalysts prepared from $Co_2(CO)_8$ on different supports [a]

Catalyst	CO conversion (%)	Selectivity (%)		
		C_3-al	C_3-ol	Et_2CO
Co/ZnO	2.6	95	1	4
Co/La_2O_3	0.25	99	0.8	0.2
Co/MgO	0.02	87	13	0

[a] Reaction conditions: $CO : H_2 : C_2H_4 = 1 : 1 : 1$, $T = 433$ K, $P = 8$ MPa, reaction time = 4 h.

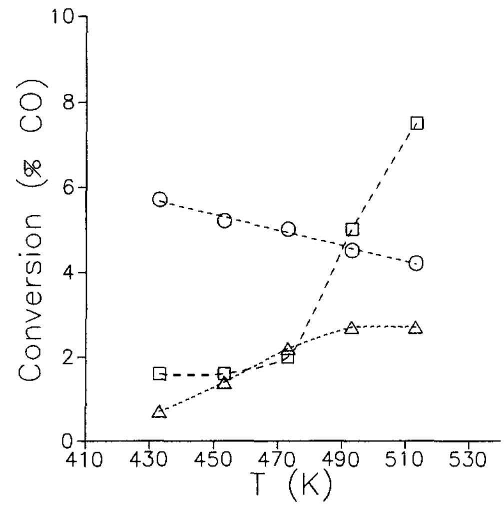

Fig. 1. CO conversion in the CO hydrogenation reaction as a function of temperature. Reaction conditions: CO : H_2 = 1 : 2, 5 MPa total pressure. (○) ZnO; (□) La_2O_3; (△) MgO.

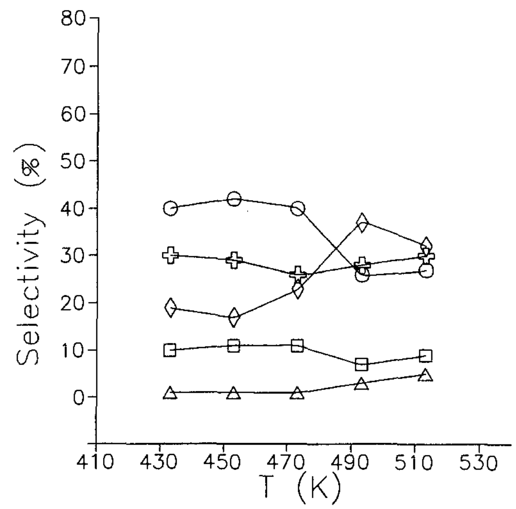

Fig. 3. Selectivity values for the CO hydrogenation reaction over Co/La_2O_3 catalyst. Reaction conditions: 5 MPa total pressure, CO : H_2 = 1 : 2. (○) MeOH; (□) EtOH; (△) PrOH + BuOH; (✚) CH_4; (◇) C_{2+}.

(methanol + ethanol) were observed. At 470 K, minor amounts of hydrocarbons were formed. Above 470 K the hydrocarbon production increased rapidly. After reaction at 513 K and subsequent lowering of temperature to 433 K, the selectivity towards alcohols was almost restored (67, 21, 7 and 4% for C_1, C_2, C_3 and C_4 alcohols, respectively). To our knowledge, this is the first report of a heterogeneous catalyst achieving such a high selectivity towards an alcohol mixture.

Selectivity values observed over the Co/La_2O_3 catalyst as a function of temperature are shown in fig. 3. Over the range 433–473 K the selectivity towards alcohol mixture was found to be constant (52%). At temperature in excess of 473 K, it decreased substantially and reached 42% at 513 K. When the temperature was subsequently lowered to 433 K, the selectivity towards alcohols was improved: it was 71% (53, 13, 4 and 1% for C_1, C_2, C_3 and C_4 alcohols respectively). This shows that surface rearrangements, induced by the temperature cycle under the reacting mixture, which were shown to be beneficial to conversion, were also beneficial to selectivity towards alcohols. The behaviour of Co/MgO catalysts is shown in fig. 4. The conversion at 433 K was not large enough to enable accurate selectivity measurements; however, it can be established that the selectivity towards hydrocarbons is large. At higher temperatures, the general trends are similar to those observed over Co/La_2O_3; the selectivity towards alcohols was found to be 50% at 513 K. When the reaction temperature was lowered to 433 K, the selectivity was found to be 83% (63, 15, 4 and 1% for C_1, C_2, C_3 and C_4 alcohols respectively).

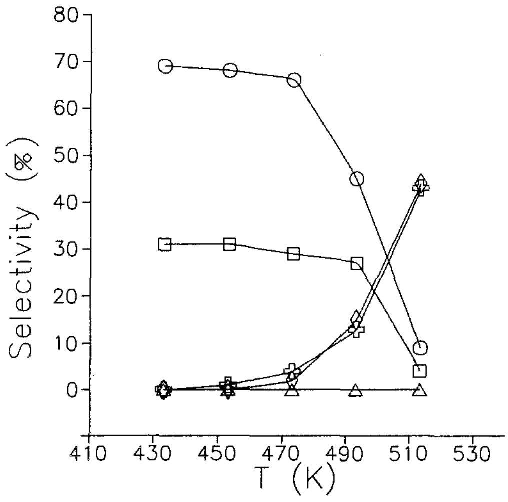

Fig. 2. Selectivity values for the CO hydrogenation reaction over Co/ZnO catalyst. Reaction conditions: 5 MPa total pressure, CO : H_2 = 1 : 2. (○) MeOH; (□) EtOH; (△) PrOH + BuOH; (✚) CH_4; (◇) C_{2+}.

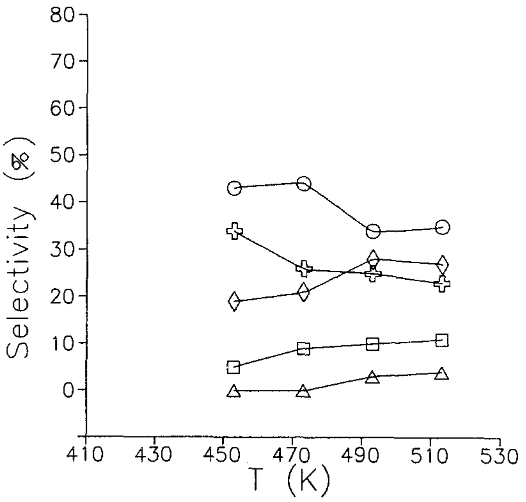

Fig. 4. Selectivity values for the CO hydrogenation reaction over Co/MgO catalyst. Reaction conditions: 5 MPa total pressure, CO : H_2 = 1 : 2. (○) MeOH; (□) EtOH; (△) PrOH + BuOH; (✚) CH_4; (◇) C_{2+}.

When comparing selectivities towards alcohols at 433 K (the hydroformylation temperature) the following sequence was thus obtained:

$$Co/ZnO > Co/La_2O_3 > Co/MgO . \qquad (3)$$

As can be seen, sequences (1), (2) and (3) are similar, confirming the deep analogy between the hydroformylation reaction and the alcohol synthesis from syngas in good keeping with conclusions drawn for similar studies over Ni catalysts [1,2].

3.3. Preliminary characterization of catalysts and active sites

In order to relate the catalytic behaviour of different samples with the different species on the catalysts, the samples were characterized by magnetic measurements after in situ treatments under reaction conditions. Fig. 5 shows the variations of magnetization of the Co/ZnO catalyst with field strength, measured after reaction at given temperature T. As can be seen, contact with syngas at 433 K, which leads selectively to alcohol mixtures, did not result in the formation of a ferromagnetic phase. From this observation it can be assessed that no metal cobalt particles (of significant size) are formed under these conditions. It should be noted that the presence of very small cobalt particles cannot be excluded: as a matter of fact cobalt particles of size lower than a certain critical diameter, D_c, behave, as a first approximation, as a paramagnetic compound and are not detected. D_c, calculated from the Langevin function at 2 T and 300 K is found to be ca. 1.5 nm. This shows that the active phase which leads to alcohols does not consist of Co particles of size larger than 1.5 nm. When the reaction temperature was increased to 513 K, magnetic measurements revealed the presence of a ferromagnetic phase which is likely to be assigned to metallic cobalt, the most plausible candidate for ferromagnetism. The amount of ferromagnetic cobalt was calculated by comparing the saturation magnetization of the ferromagnetic phase with the specific saturation magnetization of bulk cobalt. It was found to be 0.09 wt% which is equivalent to ca. 10% of the total amount of cobalt. Catalytic measurements have shown that the catalytic pattern at 433 K was almost unchanged after treatment at 513 K. These observations strongly suggest that the active phase for alcohol formation has nothing to do with the ferromagnetic phase detected by magnetic measurements. This result is also in agreement with the hypothesis, already proposed for alcohol formation over cobalt-based catalysts deposited on basic support according to which $[Co(CO)_4]^-$ anions, which are not ferromagnetic, could be the active site [7].

We have speculated that Co particles might be redispersed into surface carbonyls by a subsequent treatment at 433 K under the syngas atmosphere at 5 MPa. The results of fig. 5 show that this is not the case. Cobalt particles seem to be irreversibly formed. Treatment at higher temperatures (i.e. 623 and 723 K) resulted in the formation of further amounts of cobalt particles (0.295 wt%). It is noteworthy that increasing the reaction temperature from 623 to 723 K did not result in an increase in the amount of Co particles, suggesting a stabilization of the extent of reduction, and that a subsequent treatment at 433 K did not give rise to a redispersion of Co particles, confirming the irreversibility of their formation.

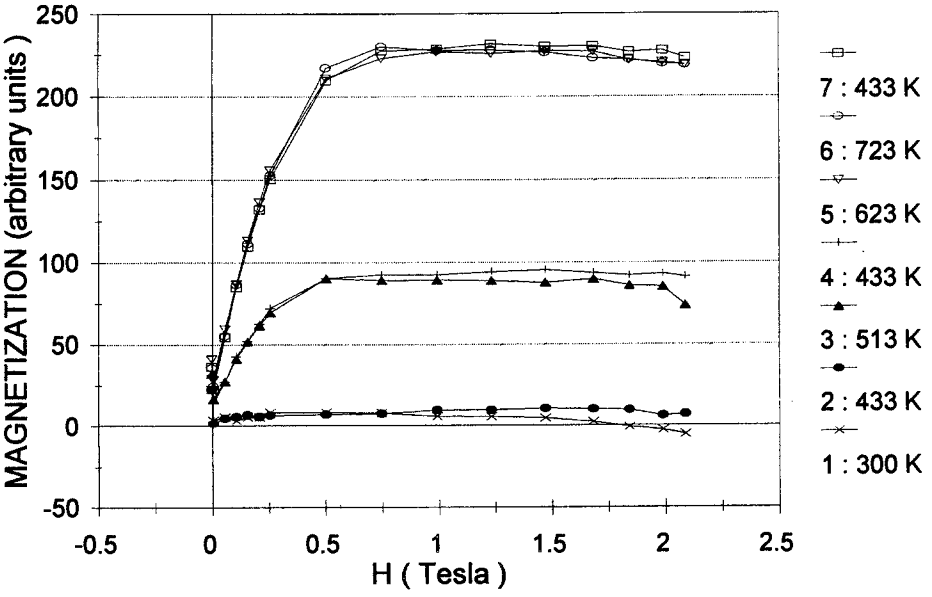

Fig. 5. Magnetization at 300 K as a function of field strength of 252 mg of Co/ZnO catalysts after different treatments: curve 1, initial under He; curves 2, 3, 4, 5, 6 and 7, treated in sequence for 1 h under $CO + 2H_2$ at 5 MPa at 433, 513, 433, 623, 723 K, and then 433 K, respectively.

When $Co_2(CO)_8$ reacts with partially hydroxylated MgO its disproportionation to $[Co(CO)_4]^-$ and Co^{2+} has been established and the formation of a heteronuclear $Mg^{2+}/[Co(CO)_4]^-$ ion-pairing species has been proposed [10]. With respect to the reaction between ZnO and $Co_2(CO)_8$ the existence of a homonuclear $Co^{2+}/[Co(CO)_4]^-$ ion-pairing surface species has been related to catalytic activity in ethylene hydroformylation [9].

Based on the sequence similarity, it is suggested that the active site involved in the CO insertion occurring during alcohol synthesis from syngas is analogous to that postulated for the hydroformylation reaction, i.e. species related to the homonuclear ion pairing $Co^{2+}/[Co(CO)_4]^-$. This species would be stable over ZnO support at 433 K, thus explaining the high selectivity towards alcohol achieved at this temperature by this catalyst. In contrast, $Mg^{2+}/[Co(CO)_4]^-$ species spontaneously formed over magnesia, results in the formation of active species towards alcohol synthesis only after a thermal cycle under syngas.

4. Conclusions

From comparison of the sequences of activity and selectivity it can be concluded that the hydroformylation reaction and the CO hydrogenation into alcohols are closely related: both reactions proceed via a migratory insertion into a metal–alkyl bond, confirming preliminary studies on heterogeneous nickel-based catalysts. The active site for the common step to both reactions is understood to be related to the homonuclear $Co^{2+}/[Co(CO)_4]^-$ ion-pairing species. This hypothesis is substantiated by preliminary characterization using magnetic methods which strongly suggests that the active phase does not demonstrate ferromagnetic properties, as it would be the case for metallic cobalt particles of size larger than 1.5 nm. Further characterizations particularly using in situ infrared spectroscopy are underway to ascertain this hypothesis. This study has also shown that the cross study of both reactions proves to be useful from the viewpoint of catalyst design: it has led to the preparation of heterogeneous catalysts, Co/ZnO, highly chemoselective for the hydroformylation reaction and highly selective (100%) towards alcohol mixture at a surprising low temperature for the CO hydrogenation.

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