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ABOUT THE NATURE OF THE Co-Cu INTERACTION IN Co-BASED CATALYSTS FOR HIGHER ALCOHOLS SYNTHESIS

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As evidenced from magnetic measurements and FTIR spectroscopy of CO, the interaction of cobalt and copper in CoCu-based catalysts results in a surface CoCu alloy. It is proposed that this alloy is responsible for the orientation of the $CO + H_2$ reaction towards higher alcohols, probably via a dual-site mechanism which involves both Co and Cu of the alloy.

1. Introduction

Among the various routes of syngas conversion, the production of alcohols as motor fuels and octane boosters remains, despite the current low price of oil, an attractive goal for the near future. Cobalt-copper based catalysts are known in CO hydrogenation as selective towards alcohols [1–3]; however, the true nature of the active sites as well as the reaction mechanism remain unclear.

This paper presents some preliminary results concerning the nature of the interaction between cobalt and copper and proposes a tentative model for C_{2+} alcohol synthesis. These results were obtained on modelized solids deduced from industrial formulations patented by the French Institute of Petroleum [3].

2. Experimental

Catalysts were prepared using a coprecipitation method [2] by adding sodium carbonate to a solution of metal nitrates (Co + Al or Co + Cu + Al) under controlled and constant pH conditions. The precipitates were then dried and calcined at $T = 723$ K under air or oxygen leading to bulk mixed oxides; table 1 gives the composition of these oxide precursors.

Reduction was performed under flowing hydrogen at 773 or 973 K. The extent of reduction was determined by means of magnetic measurements using the

Weiss extraction method [4]. CoAl and CoCuAl denote the catalysts without and with copper respectively; number 773 or 973 indicate that the reduction is carried out at 773 or 973 K respectively.

Infrared spectroscopy studies of CO adsorption were carried out on a Brücker Fourier transform spectrometer. After outgassing the reduced sample at 673 K under vacuum, CO was admitted under ca 4 kPa and the IR spectrum recorded. The sample was then stepwise treated under vacuum at increasing temperatures and IR spectra recorded.

Catalytic properties were measured in a stainless steel reactor under dynamic conditions. Typical reaction conditions were $H_2/CO = 2$, 523 K, 5 MPa and HSV near 10^4 h^{-1}. Automatized on-line gas chromatography allowed hydrocarbon and alcohol analysis.

3. Results

The percentage of reduction of the samples studied is given in table 1. Complete reduction of the cobalt phase requires temperatures as high as 973 K.

Infrared spectra of CO adsorbed on $CoAl_{773}$ and $CoCuAl_{773}$ under CO atmosphere and after evacuation at room temperature are reported on fig. 1.

Table 1
Composition, degree of Co reduction and catalytic data for CoAl and CoCuAl samples.

Catalyst	$CoAl_{773}$	$CoAl_{973}$	$CoCuAl_{773}$	$CoCuAl_{973}$
Chemical (a) composition				
Co (%)	28.1	28.1	15.9	15.9
Cu (%)	–	–	14.3	14.3
Degree of cobalt reduction (%)	54	100	68	100
CO/H_2 activity at 523 K (gCO/gCo×h)	0.37	0.09	0.20	0.07
Selectivity (%):				
- CO_2	12	15	4	12
- alcohols	1	0	18	31
- hydrocarbons	87	85	78	57
α (b):				
- hydrocarbons	0.59	0.80	0.45	0.48
- alcohols	–	–	0.46	0.49

(a) determined by atomic absorption after calcination at 723 K.
(b) chain growth probability according Schulz-Flory distribution.

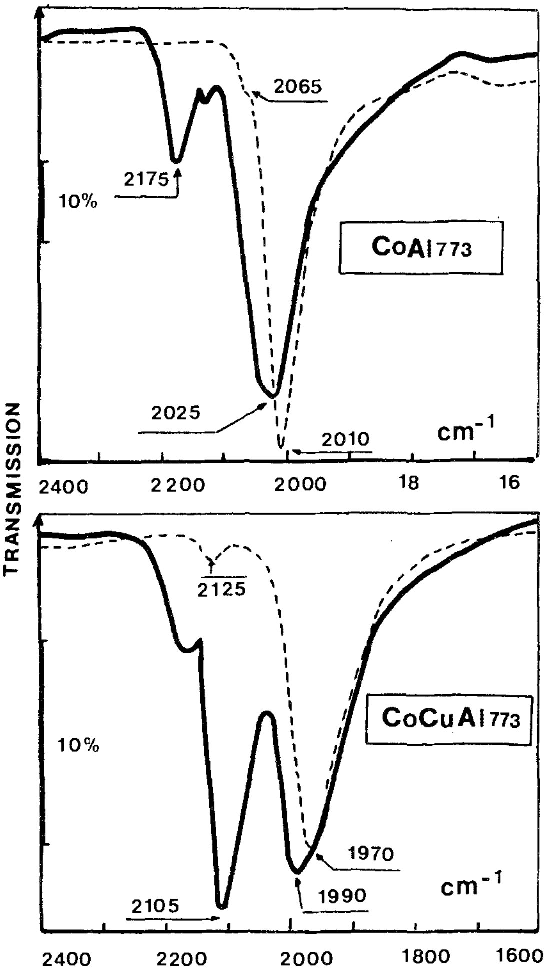

Fig. 1. Infrared spectra of CO adsorbed on $CoAl_{773}$ and $CoCuAl_{773}$: after adsorption of 4 kPa CO at 298 K (full line) and after desorption at 298 K (dotted line).

Catalytic data, conversion, selectivities and parameters of Schulz-Flory distributions (hydrocarbon and alcohol) are collected in table 1.

4. Discussion

4.1. THE NATURE OF THE Co-Cu INTERACTION

The infrared spectrum of carbon monoxide adsorbed on $CoAl_{773}$ presents under CO pressure two main bands which are assigned to CO adsorbed on unreduced Co species (2175 cm^{-1}) and on metallic cobalt (2025 cm^{-1}). The small band at 2140 cm^{-1} is due to gaseous CO. The remaining fraction of ionic cobalt after reduction at 773 K (table 1) is ascribable to the rather stable spinel structure $COAl_2O_4$ present in the catalyst precursor [5]. This low extent of reduction in similar conditions was already observed with alumina supported nickel catalysts [6].

After outgassing the CO adspecies weakly bound on unreduced cobalt disappear and the CO frequency on metallic cobalt is shifted towards 2020 cm^{-1}; moreover a small band at 2065 cm^{-1} is now visible and can be attributed to CO adsorbed on metallic cobalt interacting with unreduced Co species by analogy with Ni based catalysts [7]. Both 2175 and 2065 cm^{-1} bands disappear on sample $CoAl_{973}$ which is fully reduced (table 1).

In the case of $CoCuAl_{773}$ under CO pressure the band at 2105 cm^{-1} can be assigned to CO on metallic copper (a similar trend is observed for CO adsorbed on a CuAl sample prepared according the same coprecipitation procedure) and the one at 1990 cm^{-1} to metallic cobalt sites. Under vacuum at room temperature the large band due to copper disappears, in good agreement with what is reported for pure copper [8], and a small band at 2125 cm^{-1} is now visible and present up to 373 K; the ν CO band corresponding to cobalt sites is shifted to 1970 cm^{-1}. At variance with $CoAl_{773}$, no significant band corresponding to CO interacting with unreduced Co sites is observed on $CoCuAl_{773}$. This suggests that nearly no unreduced species remain on the metallic surface of $CoCuAl_{773}$, although a significant bulk ionic fraction still exists (table 1 [10]).

Thus, when adding copper to cobalt, two main effects are observed:

(i) the ν CO frequency on cobalt is shifted towards low values (i.e. 2010 to 1970 cm^{-1} under vacuum at room temperature)

(ii) a band at 2125 cm^{-1} appears which is likely due to CO adsorption on copper sites. As the 2105 cm^{-1} band is clearly ascribable to carbon monoxyde weakly bound to pure copper, the 2125 cm^{-1} band can be attributed to CO linked to modified copper sites.

These two effects of copper addition (i.e. shift of CO frequency towards low values for cobalt and appearance of a CO vibration above pure copper) are very similar with those reported when adding copper to nickel [9,10]. For the latter, they were attributed to an electronic interaction due to the NiCu alloy formation (electronic transfer from copper to nickel which modifies the back-donation in the π-antibonding orbitals of carbon and thus shifts the frequencies of CO adsorbed on alloyed nickel and copper atoms in an opposite way).

By analogy, we propose that the observed changes in the IR spectra when adding copper to cobalt could be related to the formation of a CoCu alloy inducing electronic effects of the very same type.

It has also been proposed [11] that a shift of the CO frequency can be accounted for by changes in the CO dipole-dipole interactions, due to alloy-induced modifications of the density of CO adspecies.

Figure 2 reports the wavenumbers of the CO bands for CO adsorbed on cobalt for $CoAl_{773}$ (a) and $CuCoAl_{773}$ (b) samples as a function of the temperature of

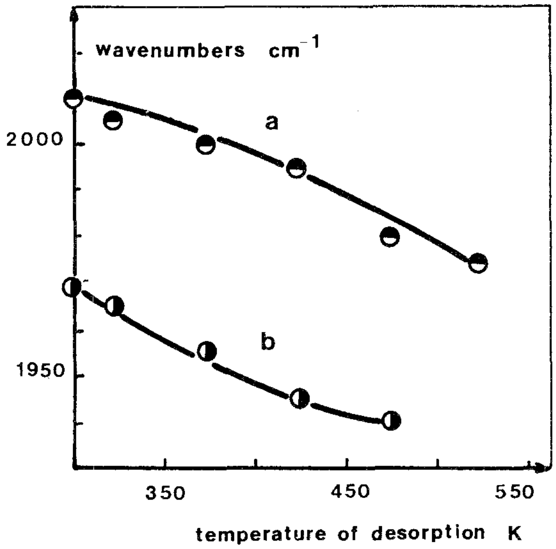

Fig. 2. Changes in the position of the νCO band of CO adsorbed on cobalt versus temperature of desorption after CO adsorption at 298 K onto $CoAl_{773}$ (a) and $CoCuAl_{273}$ (b) samples.

carbon monoxide desorption. The CO coverage of cobalt can be considered as monitored by the temperature of evacuation. At full coverage, the CO band (Co-CO species) is shifted down from 2010 to 1970 cm^{-1} following copper addition. At low coverages, i.e., vacuum treatments at temperatures higher than 450 K, a similar shift towards lower wavenumbers is still observed. Since at these coverage values the CO vibrator must be considered as a singleton, this result strengthens the idea that the shift of the CO band by adding copper to cobalt is not due to a dilution effect but to an electronic interaction between Co and Cu.

4.2. THE CoCu ALLOY

The phase diagram of the Co-Cu system indicates that the solubility of copper in cobalt is limited to about 10 at.% in all the temperature range used in this work. If bulk CoCu alloys were formed the saturation magnetization M_s (used in the determination of the extend of reduction, table 1) should reflect this formation, even with only 10% Cu [12]; as the M_s value obtained for $CoCuAl_{973}$ corresponds to a pure cobalt phase, one can conclude that only the surface of the cobalt particle interacts with copper (owing to the limited dispersion of the metallic particles [5], magnetic data are not accurate enough to detect this surface alloy). This picture, i.e. a pure cobalt core surrounded by a copper-cobalt shell, is in good keeping with the well-known segregation phenomena which predicts the segregation towards the surface of the metal with the lower heat of sublimation, in order to lower the surface tension.

4.3. CATALYTIC PERFORMANCES

Table 1 shows that the copper-free samples $CoAl_{773}$ and $CoAl_{973}$ produce almost only hydrocarbons with a classical Schulz-Flory distribution. When adding copper, the catalytic properties are deeply modified and display the following features;

(i) a significant decrease of the total activity. This difference in activity at 523 K on table 1 between CoAl and CoCuAl samples is actually minimized by a fast and important deactivation of copper-free samples due to extensive cobalt-sintering [5].

(ii) the appearance of a selectivity towards alcohol synthesis,

(iii) a decrease of the parameter of hydrocarbon chain growth reflecting a production of lighter alkanes. A similar chain growth parameter is observed for the C_{2+} alcohols distribution, the methanol production being far below the value expected from this Schulz-Flory distribution.

(iv) after activation at 973 K allowing complete reduction of cobalt (table 1), the overall activity is decreased but for the copper-containing sample, the selectivity towards alcohols is still improved.

Points (i) and (iii) are in good keeping with the above proposal of a CoCu alloy formation. It has been indeed reported [13,14] that alloying Cu with Ni results, in $CO + H_2$ reaction, in a decrease of the conversion and in an increase of the selectivity towards light hydrocarbons (as stated in the present case); these two effects were interpreted in terms of dilution of active Ni sites (ensembles of adjacent Ni atoms) in a matrix of inactive copper, which decreases the probability of existence of these active sites (C–C bond formation requires larger ensembles than CH_4 synthesis; Cu addition thus orientates the reaction towards methane). Alcohols (point (ii)) were not observed in our earlier work on NiCu [14], very probably because the reaction was performed under atmospheric pressure.

The selectivity towards alcohols is clearly related to the presence of Cu in table 1. Copper is known to be active in methanol synthesis as confirmed by the exclusive production of methanol which is observed on a cobalt free sample CuAl [5]. Therefore at least a part of the CH_3OH produced is generated on the pure copper metallic particles evidenced from IR spectroscopy (band at 2105 cm^{-1}). In numerous relevant mechanistic studies, the formation of C_{2+} alcohols have been assumed to proceed via the insertion of an undissociated CO adspecies in adsorbed alkyl group [15]. Point (iv) which underlines the improvement of alcohol selectivity on fully reduced CoCuAl samples tends to rule out any major participation of ionic cobalt species (like the cobalt-alumina spinel phase) in the higher alcohols synthesis. Therefore this reaction could quite occur on the CoCu alloyed particles since on this surface do exist:

- suitable (large enough) cobalt ensemble, able to open the C–O bond and to generate hydrocarbon precursors (as suggested by the activity of pure cobalt).

– copper atoms modified by cobalt, able to chemisorb CO species which are stable enough to undergo surface reaction without C–O rupture (these species display a stretching frequency at 2125 cm^{-1} higher than on pure copper and desorb only after heating, while evolved at room temperature on pure copper).

The vicinity, in the alloyed phase, of the two previous types of sites may facilitate the reaction between alkyl groups (Co site) and carbonyls (alloyed Cu site) leading to the $C_{2+}OH$ products. This dual-site model is in good agreement with a recent proposal from Courty and Chaumette [16]. These authors suggests that $C_{2+}OH$ synthesis on CoCu-based catalysts proceeds via a carbonaceous chain formation on one type of site followed by a reaction with a CO species coming from another type of site.

In the present model, the reaction of insertion of CO in the metal-alkyl bond could be promoted by the electrodeficient character of the copper atom in the CoCu alloy, according to a proposal on the promoting effect of positive ions reaction [15,17] and to theoretical calculations on the CO insertion [18].

5. Conclusion

In cobalt-copper catalysts for higher alcohols synthesis, copper, beside structural and textural effects [5], plays an important role on the viewpoint of the active surface. Its presence leads to the formation of a CoCu alloyed phase which is restricted to the surface of the metallic cobalt particle. It is proposed that C_{2+} alcohols could originate via a dual site mechanism involving copper and cobalt atoms of the alloy: the carbonaceous chain would be formed on large cobalt ensembles and the terminal OH group be provided by a CO species adsorbed on alloy-modified copper atoms.

Further studies are in progress to detail these mechanistic steps involving bimetallic active sites and leading to the higher alcohols formation.

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