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The influence of oxide–oxide interaction on the catalytic properties of Co/Al_2O_3 in CO hydrogenation

P.A. Chernavskii, G.V. Pankina and V.V. Lunin

Department of Chemistry, Moscow State University, Moscow 119899, Russia

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The influence of oxide–oxide interaction on the catalytic properties of cobalt in CO hydrogenation is investigated on the example of a Co/Al_2O_3 catalyst. Oxide–oxide interaction was prevented by modification of the alumina surface with magnesia. It has been shown that oxide–oxide interaction affects catalytic activity and the amount of carbon deposited on the catalyst surface.

Keywords: cobalt/alumina, CO hydrogenation, *in situ* magnetization, oxide–oxide interaction, modification, catalytic activity, carbon

1. Introduction

As a rule, in the process of supported metal catalysts preparation oxide–oxide interaction occurs between the supported metal oxide and the support, particularly, when Al_2O_3 or MgO is used as the support. As a result, mixed oxide systems such as aluminates, spinels or solid solutions appear on the surface layer of the support [1]. Subsequent reduction of the supported oxide in the catalyst leaves the products of oxide–oxide interaction on the metal–support interface partially intact. At small concentrations of supported metal the oxide–oxide interaction does not allow high degrees of metal reduction to be reached, and in some cases, complete reduction to pure metal is impossible.

Modification of the support surface allows the oxide–oxide interaction to be suppressed by the formation of crystal structures with more compact elementary cells than that of alumina in the Al_2O_3 surface layer [2].

The question of oxide–oxide interaction influence on the catalytic activity of supported metal catalysts remains open in many aspects. The influence of oxide–oxide interaction on the catalytic activity of Co/Al_2O_3 and $Co/MgAl_2O_4/Al_2O_3$ in CO hydrogenation is described in this paper.

2. Procedures

2.1. Materials

Catalysts were prepared by impregnation of alumina (Rhone-Poulenc, surface area 300 m^2/g, average pore volume 0.44 ml/g) with aqueous solutions of $Co(NO_3)_2$ and $Mg(NO_3)_2$. In addition, the support was synthesized in which the layer of $MgAl_2O_4$ spinel was formed by means of Al_2O_3 surface modification with magnesia [3]. After impregnation the samples were dried in air at 100 °C for 5 h. Cobalt content was found to be about 15% in all cases.

All gases were purified from oxygen in columns filled with Ni/Cr_2O_3 and MnO/Al_2O_3. To avoid contamination by iron carbonyls an active carbon column was kept at 200 °C.

Before the experiments, the catalysts were either calcined at 400 °C in Ar flow for 1 h or used without such calcination.

2.2. Magnetic measurements

The magnetic measurements were carried out on a vibrational magnetometer [4] in the temperature range from 20 to 600 °C in controlled gas medium of specified composition.

2.3. Measurements of catalytic activity in CO/H_2 synthesis

Catalytic activity was investigated in a continuous-flow quartz microreactor serving simultaneously as magnetometer cell. In the experiments CO conversion to hydrocarbons did not exceed 1% and the main reaction product was methane. The rate of methane formation was measured by a flame ionization detector. After each experiment the detector was calibrated on high-purity methane.

2.4. Thermodesorption and temperature-programmed reduction

Thermodesorption (TPD) and temperature-programmed reduction (TPR) were carried out in a KL-1 installation. Temperature-programmed surface reaction (TPSR) of preadsorbed CO with hydrogen was carried out after the TPR experiment. Hydrogen was desorbed from the freshly reduced catalyst in Ar flow at 300 °C, then CO was adsorbed at 20 °C in order to study the hydrogenation of adsorbed CO in the temperature-programmed surface reaction (TPSR).

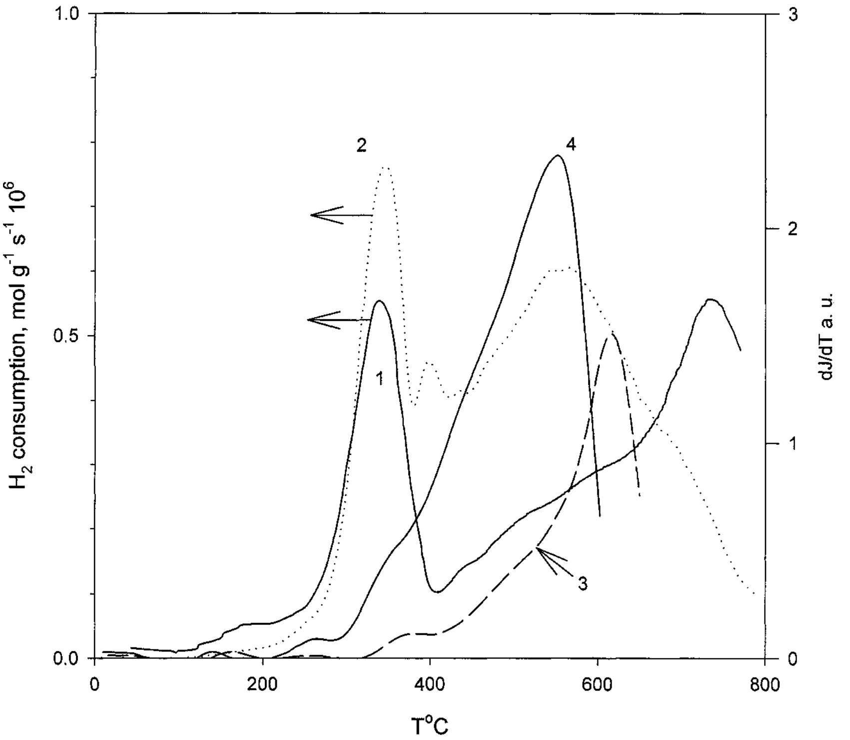

Figure 1. TPR spectra of calcined Co/Al_2O_3 (I) and $Co/0.2\%\ MgO/Al_2O_3$ (II) catalysts (curves 1 and 2) and the temperature dependence of magnetization change rate (dJ/dT) for these catalysts (curves 3 (I) and 4 (II)).

3. Results and discussion

Figure 1 shows TPR spectra of the calcined Co/Al_2O_3 (I) and $Co/0.2\%\ MgO/Al_2O_3$ (II) catalysts (curves 1 and 2). It is clearly seen that the temperatures of the first maximum of reduction rate for both catalysts are equal (340 °C). It will be shown below, that the first maximum of the TPR spectrum corresponds to the reaction $Co_3O_4 + H_2 \rightleftharpoons 3CoO + H_2O$. The peak intensities for both catalysts are different, the reduction rate of catalyst I is lower in the first stage. The second peak, corresponding to the reaction $CoO \rightarrow Co$, has the maximum temperature 550 °C for catalyst II and 750 °C for catalyst I.

Figure 1 also illustrates the temperature dependence of magnetization change rate (dJ/dT) for these catalysts (curves: 3 for catalyst I and 4 for catalyst II, respectively). Considering that in the studied systems only Co is ferromagnetic, curves 3 and 4 show the rate of Co formation. The position of maxima in curves 3 and 4 proves the above peak positions in the TPR spectrum and also points to the fact that the rate of reduction to metal is significantly higher for catalyst II than for catalyst I.

The smaller area of the first maximum (curve 1) in the TPR spectrum of catalyst I as compared to that of catalyst II indicates that at the first stage of calcination interaction of Co_3O_4 with the support takes place, reducing the amount of Co_3O_4 on the Al_2O_3 surface. The position of rate maxima for process $CoO \rightarrow Co$ permits one to suggest that during reduction the interaction $CoO–Al_2O_3$ also takes place.

From the TPR spectra, the modification of the alumina surface markedly decreases the interaction between cobalt oxides and support both in the stage of precalcination and in the stage of reduction.

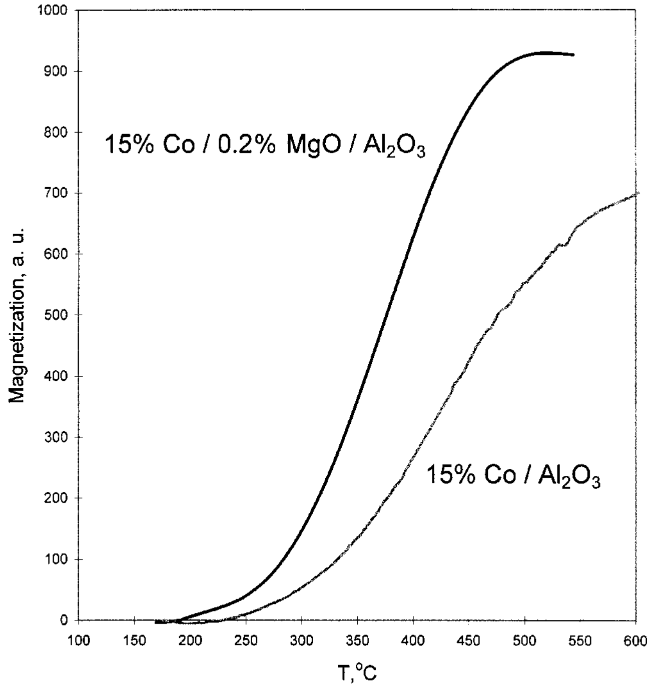

Figure 2. Temperature dependence of magnetization in the process of catalyst reduction without precalcination.

Figure 2 illustrates the temperature dependence of magnetization in the process of reduction without precalcination. It represents the kinetics of metallic cobalt formation.

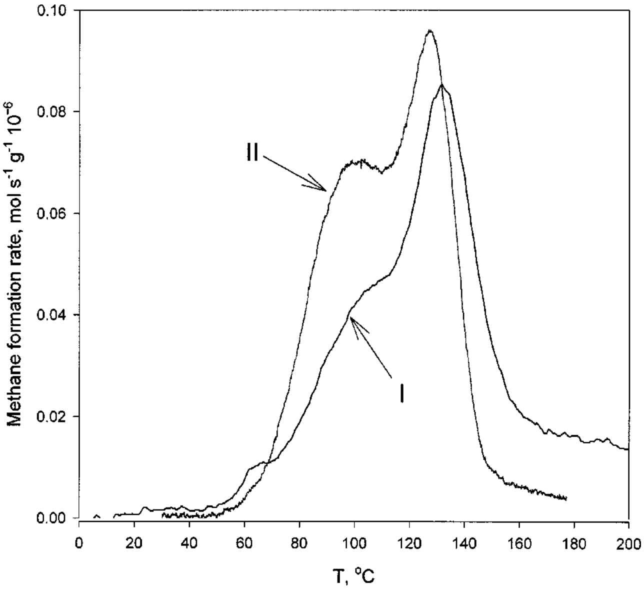

Figure 3. TPSR spectra of calcined Co/Al_2O_3 (I) and Co/0.2% MgO/Al_2O_3 (II) catalysts, reduced up to the state of constant magnetization at 600 °C.

The enhancement of rate and degree of reduction is exhibited for catalyst II.

To characterize the catalytic properties of catalysts I and II the temperature-programmed surface reaction (TPSR) of pre-adsorbed CO with hydrogen at 20 °C was used [5]. The reaction was carried out both on preliminary calcined and reduced catalysts and on catalysts reduced without calcination.

Figure 3 shows TPSR spectra of catalysts I and II, calcined and reduced to the state of constant magnetization at 600 °C. The presence of at least two peaks of methane in the TPSR spectrum demonstrates the availability of CO hydrogenation centers of different nature. Lee and Bartholomew [6] believe that the first peak corresponds to the process of CO hydrogenation on metallic Co, and the peak with higher temperature maximum of CH_3O intermediate from the support surface to surface metallic Co is related to a reverse spillover. To prove this interpretation we have reproduced the experiment from [6]. After CO pre-adsorption, oxygen was adsorbed at room temperature on the catalyst surface. Oxygen adsorption leads to disappearance of the first peak in the TPSR spectrum (figure 4), which is probably related to interlocking of CO hydrogenation centers on Co. However, increase of temperature causes reduction of Co surface hydrogenation of the CH_3O intermediate (formed as a result of partial hydrogenation of adsorbed CO on the support and reverse spillover of the CH_3O intermediate onto the metallic Co surface) becomes possible. This is responsible for the formation of the second peak in the TPR spectrum.

The peaks in the spectra overlap and make further analysis difficult. However, the spectrum may be approximated at a high degree of accuracy by the sum of two Gaussian peaks. It allows one to take into consideration the ratio of peak areas. As has been previously shown [6], the ratio of the first peak area to the sum of areas $(\mathrm{A}/(\mathrm{A}+\mathrm{B}))$ rises along with the increase of reduction degree. Similar patterns were observed in this study. Precalcination leads to the decrease of the ratio for the given catalyst samples. For samples I and II, precalcined, this ratio significantly differs, as illustrated in figure 3. Moreover, the peak shape analysis [5] permits one to evaluate the activation energy (E^*) for the processes responsible for appearance of peaks “A” and “B”. The analysis has shown that E^* of peaks of type “A” for systems I and II is approximately the same and equals 70–80 kJ/mol, whereas for peak “B” an appreciable increase is observed in the case of system II as compared to system I, 121 and 70 kJ/mol, respectively. We believe that such increase of activation energy may be connected with the increase of activation energy of surface radical CH_3O diffusion on the surface of the $MgAl_2O_4/Al_2O_3$ support, as compared to the same value for the diffusion process on the Al_2O_3 surface.

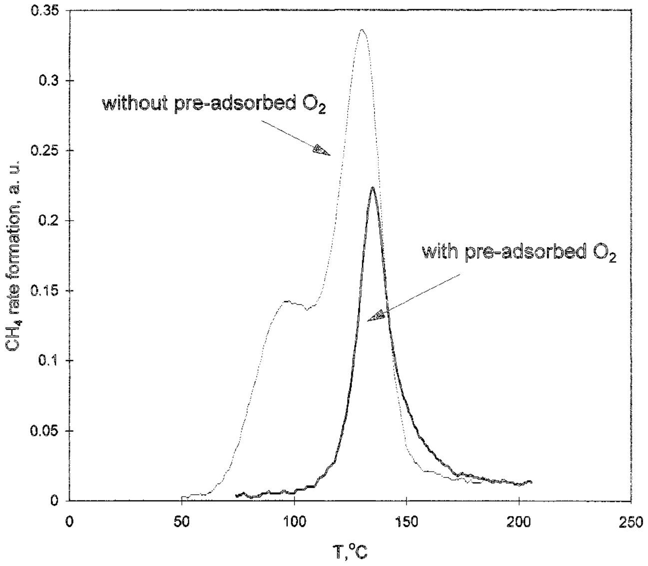

Figure 4. TPSR spectra of calcined Co/Al_2O_3 (II) with oxygen pre-adsorption.

Thus, it can be suggested that the decrease of oxide–oxide interaction in the Co/Al_2O_3 system results in the decrease of support participation in CO hydrogenation.

For correct comparison of catalytic activity of the obtained catalysts the specific area of surface supported Co was measured considering the results of hydrogen TPD, as well as the amount of metallic Co was measured considering the results of Co oxidation by oxygen.

Data on specific surface area of supported metal, degree of reduction and specific catalytic activity are given in table 1.

As a criterion of catalytic activity under isothermal conditions the specific rate of methane formation was used. It was measured at the 10th minute from the start of catalytic reaction at 200 °C.

As it is seen from table 1, the modification of support surface by MgO usually increases not only the degree of

Table 1
Catalytic properties of Co/Al_2O_3 (I) and $Co/0.2\%\ MgO/Al_2O_3$ (II) catalysts.

Catalyst	S (m^2/g)	Degree of red.[a] (%)	E^{*b} (kcal/mol)	$W_{CH_4}{}^{c}\ 10^6$ ($mol/(m^2\ s)$)
I calcined	6 ± 0.2	60	30 ± 1	0.11 ± 0.05
I not calcined	5 ± 0.5	51	30 ± 1	0.15 ± 0.05
II calcined	4 ± 0.5	77	28 ± 1	0.8 ± 0.05
II not calcined	3 ± 0.5	80	30 ± 1	1.1 ± 0.05

[a] Degree of reduction for metallic cobalt.
[b] Effective activation energy of CO hydrogenation.
[c] Methane formation rate at 200 °C.

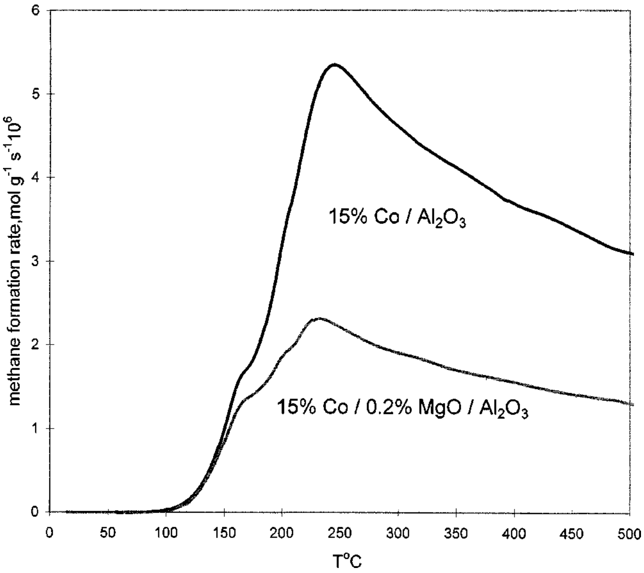

Figure 5. Temperature dependence of methane formation rate in the process of exposition of used catalysts in hydrogen flow.

Co reduction into metal, but also significantly increases the catalytic activity in CO hydrogenation. From comparison of data on specific surface area and degree of reduction it is evident that the decrease in oxide–oxide interaction leads to the decrease in Co dispersity. The latter might be connected with the decrease in a fraction of highly disperse metallic Co, formed in reduction of cobalt aluminate.

Concluding the catalytic activity experiment, the catalyst was abruptly cooled in the flow of reaction mixture to room temperature and the flow was switched to that of hydrogen. After that the programmed heating of the catalyst in hydrogen flow was carried out and the hydrogenation rate of the remaining carbon surface deposits was recorded.

Figure 5 presents the temperature dependence of CH_4 formation rate for catalysts I and II. As seen from figure 5, the amount of formed methane or the formation rate of carbon deposits is significantly less for catalyst II than for catalyst I. The same phenomenon was observed for supported iron catalysts for CO hydrogenation [3]. Most likely, the explanation of this fact may be attributed to the properties of support rather than that of the supported metal. Indeed, as it was noted above, the analysis of TPR spectra reveals that spillover of CH_3O is hindered on the surface of catalyst II.

As was previously shown, Co/Al_2O_3 specific activity in CO hydrogenation increases along with the decrease in dispersity and with the increase of Co content [7]. The authors consider the increase in the fraction of planar sites on the surface of Co particles to result from the increase of the dimensions of these particles as the reason of this phenomenon. But later results indicate the independence of CO hydrogenation rate from the structure of Co surface [8]. It was suggested that the specific activity depends on the degree of Co reduction. Our studies support this suggestion and justify that the nature of support affects Co specific activity in CO hydrogenation. The mechanism of this effect may be connected with the spillover of surface intermediates and demands further investigation.

Nevertheless, it can be suggested that the greater the degree of reduction, the smaller is the alumina contamination degree for the Co surface. Alumina particles are present on the Co surface as a result of spinel reduction. A decrease in oxide–oxide interaction leads to a decrease in $CoAl_2O_4$ concentration on the catalytic surface and, consequently, to a decrease of decoration by support the degree for the particles of cobalt.

It has been shown previously that oxide–oxide interaction does not influence the specific catalytic activity of Al_2O_3-supported Fe and Ni CO hydrogenation catalysts [3,9]. It gives us grounds for thinking that the CO hydrogenation mechanism on Co is different from that on Ni and Fe.

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