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On the development of metallic particles and their initial catalytic properties in the $CO + H_2$ reaction over Co/Al_2O_3 catalyst

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Formation of Co^0 phases with different surface structure over 10 wt% Co/Al_2O_3 and their catalytic properties were induced by pretreatments in H_2 at 570 K for 1 h or 20 h. Electronic behaviour of the Co^0 phase, which consists of small (after 1 h reduction) or large bulk-like particles (after 20 h reduction), did not change during the CO hydrogenation after 5 h on stream as was determined by XPS. On the basis of the measured C_{2+} hydrocarbon selectivities the CO molecules are suggested to dissociate on small Co particles to a larger extent than on large cobalt particles. The slight decrease in the catalytic activity with increasing time on stream obtained for the long-term reduced sample is explained by the change in the surface Co^0 content detected by XPS. The increase in the catalytic activity along with the change in olefin selectivity, measured for the sample reduced for 1 h, is interpreted by the change of a reaction path involving the Co^0–support interface during the initial period of the reaction.

Keywords: surface structure of Co/Al_2O_3; catalytic activity and selectivity over Co/Al_2O_3 in CO/H_2 reaction

1. Introduction

Among transition metals cobalt is the best known for its high catalytic performance to produce medium chain length hydrocarbons in Fischer–Tropsch synthesis. Under certain conditions the chain growth probability over cobalt is superior to that measured for ruthenium [1]. However, in general practice high specific activity is demanded which is usually achieved by increasing the specific surface area of the active phase using supported catalysts.

Unfortunately, in the case of cobalt the conventional method to produce active metallic phase of high dispersion is of limited use. The primary cause is the exceptionally strong interactions between the cobalt ions in the precursor molecules and the oxide support. This interaction results in the formation of several different ionic cobalt phases on alumina [2–4] whose reducibilities are markedly different [5,6]. Their relative abundance depends mainly on the cobalt loading [2–4,6], pretreatment conditions [5], the nature of the precursor molecules [7,8], on the support used, its structural properties [9,10] and additives [11,12]. Cobalt reducibility is also influenced by these effects and no complete reduction was achieved below 1000 K, even though cobalt reduction is enhanced by addition of noble metals [13,14].

Most of the previous studies focused on the properties of catalysts after severe treatments, while little is known about the effect of the catalytic behavior of mildly treated supported cobalt. Over such samples formation of a small amount of metallic cobalt particles with high dispersion can be expected. In this work, properties of the alumina supported cobalt catalyst containing 10 m/m% of cobalt using short- and long-term reduction, are presented. The effects of different treatments are compared in terms of initial catalytic activity and selectivity revealed in the carbon monoxide hydrogenation and of the surface structure determined by X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. SAMPLE PREPARATION

The sample containing 10 m/m% cobalt was prepared by impregnating γ-alumina (Woelm) with the appropriate amount of the aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (Ipatieff method). After complete leaching of the solution the sample was dried in air at about 330 K for 8 h. The sample was then calcined in the atmosphere of a stream of oxygen at 573 K for 1 h. Reduction in H_2 was carried out in situ prior to the measurements either in the catalytic reactor or in a small reactor chamber attached to the ESCA apparatus.

2.2. CATALYTIC MEASUREMENTS

The calcined powder catalyst sample of 0.5 g was placed into a quartz reactor tube of about 1 cm i.d. Prior to the reaction the sample was in situ heated in a stream of H_2 (5 $cm^3\ min^{-1}$) at 15 K min^{-1} heating rate up to 573 K. Then it was held at this temperature for 1 h or 20 h (short-term or long-term reduction denoted, from here on, SR or LR, respectively). After reduction the sample was cooled in H_2 down to the reaction temperature of 523 K, then the gas flow was switched for an atmospheric mixture of CO/H_2 (2 : 1) with a mass flow rate of 30 $cm^3\ min^{-1}$. Periodically the effluent gas mixture was sampled and the composition was analyzed by a Girdel 300 gas chromatograph. The products were separated in a Hayesep R (2 m, 1/8″ i.d.) column. Conversions were always less than 10% in order to maintain the differential conditions. Catalytic activity was calculated on the basis of the amount of

CO converted into the products detected. Selectivity of a given product indicates its molar ratio in the product mixture as expressed in per cent. The olefin selectivity ($S_{C=}$) represents the molar percentage of unsaturated hydrocarbons in the C_2–C_5 products. The C_{2+} selectivity ($S_{C_{2+}}$) is expressed in molar percentage of the C_2–C_5 hydrocarbons among all products.

2.3. XPS MEASUREMENTS

XPS measurements were carried out in a Kratos ES-300 type ESCA apparatus. After calcination the catalyst powder was meshed (4 kN cm^{-2}) into a copper grid which was then placed onto the tip of the sample transfer rod. Prior to XPS measurements the samples were first reduced in a small pretreatment cell directly attached to the UHV chamber. The conditions of the H_2 pretreatments were the same as described above (flowing H_2). The procedure allowed the sample to be transferred to analysis position without being exposed to air. After spectra recording the samples were transferred again into the pretreatment chamber where they were treated in the reaction gas mixture under the same conditions as the reaction measurements were conducted. After 5 h on stream the samples were cooled to room temperature in the reactant mixture and the XPS spectra were again recorded.

During spectra recording the hemispherical analyzer worked in fixed retarding ratio (FRR) mode. In order to gain maximum resolution, the narrowest slits were applied. An Al K_α X-ray excitation source was applied with 150 W anode power. In the experiments the pressure in the UHV chamber did not exceed 10^{-6} Pa. The Al 2s line of 119.30 eV binding energy (BE) was used as an internal BE reference. The Co 2p XPS regions were evaluated with the help of a one-parameter peak synthesis method according to the following procedure: (i) first the XPS spectrum of pure CoO as the reference material was recorded at technical parameters identical to those of the sample measurements; the Co 2p region was then fitted with the smallest number of parameters (Gaussian peaks and their intrinsic parameters). (ii) Each parameter of all the Gaussian components was linked and fixed to those of the principal (highest) peak, whose intrinsic parameters were also fixed except its intensity (height). The parameter so obtained can be regarded and handled as a numerical peak of CoO having only one independent parameter (height). (iii) To determine the fraction of cobalt monoxide, the Co 2p regions of the samples were fitted with this *simulated numerical peak* in the regions where the ionic cobalt contribution is not disturbed (~ 780–790 eV and ~ 795–810 eV BE). (iv) The remaining intensity was fitted with a new doublet (Doniach–Sunjic type) at the low BE sides of the spin components for the reduced cobalt contribution. (v) Before each fitting a linear background was subtracted in a position proposed to eliminate the effect of underlying cobalt Auger transitions [15]. The procedure applied is similar to that used for unsupported cobalt oxide [16]. The estimated limit of error of the peak positions so obtained is about ± 0.15 eV.

3. Results and discussion

In table 1 the C_1–C_5 selectivities measured in CO hydrogenation over Co/Al_2O_3 catalysts reduced for short term (SR) and long term (LR), are shown. In figs. 1 and 3 the rate and $S_{C^=}$ and $S_{C_{2+}}$, respectively are presented as a function of reaction time on stream. The catalytic activity of LR sample always exceeds that of SR (fig. 1). This could have been expected because longer reduction should obviously result in the formation of more metallic cobalt sites. However, with increasing time on stream, the catalytic activity changes in opposite ways. It slightly decreases over the catalyst LR, while it increases over SR. Accordingly, with increasing time on stream, the relative difference decreases from more than one order of magnitude at the beginning to less than twice after 5 h.

It can also be established that steady state is reached after about 5 h. Such opposite changes may plausibly result from different effects. An increasing extent of cobalt reduction by the reaction mixture, as was suggested for silica supported cobalt catalysts [17], or a decrease (sintering) or deactivation (poisoning) of the active surface can explain the changes observed. Thus, the catalytically active [18,19] zerovalent cobalt phase must first be investigated.

In order to follow the structural changes, the LR and SR samples were measured by XPS before reaction (after reduction) and after the reaction carried out for 5 h on stream (steady state). In fig. 2 the Co $2p_{3/2}$ regions of the recorded XPS spectra

Table 1
C_1–C_5 selectivity measured for CO/H_2 (1 : 2) reaction carried out at 1 bar, 523 K over 10 wt% Co/Al_2O_3 catalysts after reduction in a stream of H_2 at 570 K

Time of reduction (h)	Time on stream (min)	Product selectivity				
		C_1	C_2	C_3	C_4	C_5
1	24	81.47	9.15	6.30	2.40	0.68
	48	80.56	9.16	6.58	2.73	0.98
	77	79.27	9.21	7.13	3.12	1.27
	104	79.07	9.17	7.32	3.18	1.27
	176	78.89	8.66	7.20	3.09	1.23
	207	80.34	8.49	7.06	2.95	1.16
	234	80.63	8.37	6.98	2.89	1.13
	301	80.80	8.08	6.77	2.79	1.05
	348	81.68	7.94	6.66	2.70	1.02
20	24	87.43	5.99	4.66	1.51	0.35
	48	87.43	6.00	4.60	1.57	0.40
	71	87.54	5.97	4.57	1.58	0.34
	95	87.60	5.93	4.51	1.63	0.33
	119	87.73	5.86	4.44	1.64	0.34
	306	88.42	5.66	4.22	1.41	0.28
	398	88.48	5.61	4.17	1.46	0.29

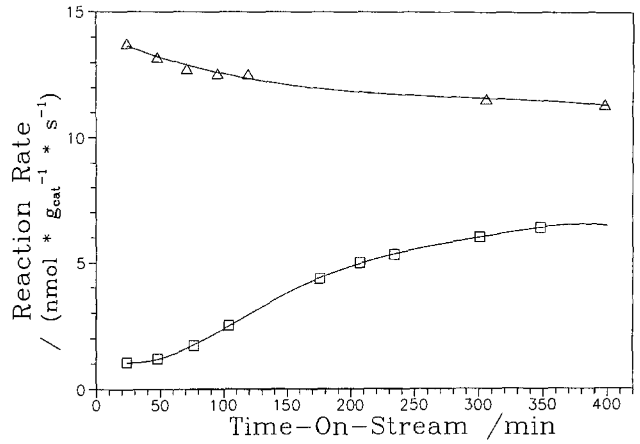

Fig. 1. Reaction rate of hydrocarbon formation (nmol g_{cat}^{-1} s^{-1}) versus time on stream for the samples treated in hydrogen for 1 h (□) and for 20 h (△).

and the curve fitting procedure are presented. As is seen, in addition to the presence of Co^{2+} ions in CoO, the low BE component in the spectra indicates the existence of zerovalent cobalt. Its position and relative intensity change within the series. The corresponding values are presented in table 2. The peak position obtained for sample LR indicates that after 20 h reduction a bulk-like metallic cobalt phase is formed [20]. Its electronic character does not change after 5 h of $CO + H_2$ reaction. For the SR sample the BE of the zerovalent component is significantly higher than that of a bulk metal. Such BE shift of a zerovalent species in an oxide supported system is characteristic of the metal phase which consists of small Co^0 particles (final state effect) [26]. Thus, the substantial difference between SR and LR samples is the structure of the zerovalent cobalt phase consisting of very small particles with unique electronic properties and of large bulk-like crystallites, respectively. It must also be noted that the electronic character of neither of these Co^0 phases is altered after 5 h reaction. Further XPS results listed in table 2 reveal the surface composition (ionic and zerovalent cobalt phases) of the SR sample which is maintained during the $CO + H_2$ reaction. Based upon these data, the possibility to explain the increasing catalytic activity of the SR sample by a modification of the surface composition during the reaction can unambiguously be excluded.

On the other hand, the CO/H_2 reaction itself caused a significant change in the surface composition of the LR sample. As is shown in table 2, the ratio of Co^{2+} ions significantly increased at the expense of Co^0, although the total surface content of cobalt remained unchanged.

This result cannot be rationalized by carbon deposition because in this case the total surface cobalt content was also decreased. Furthermore, significant carbon deposition over cobalt catalysts was detected at reaction temperatures above 550 K only [21]. This effect could be explained by oxidation of Co^0 with the oxygen resulting from the CO dissociation on the surface. Recent AES results, however, indicate

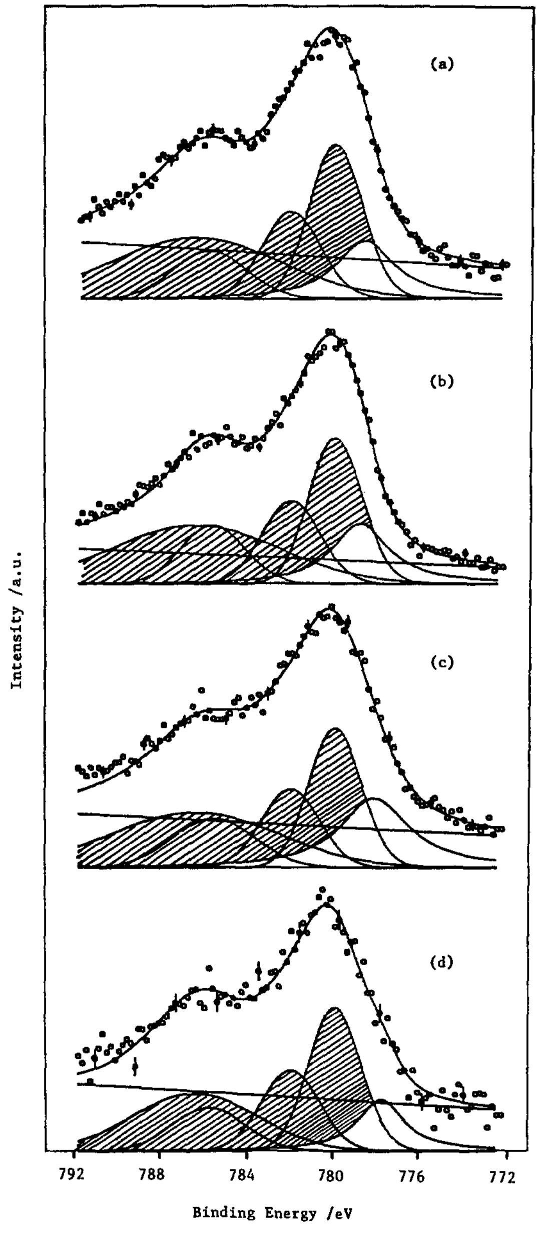

Fig. 2. XPS spectra of the samples treated in various ways.

that this effect is of minor importance (1–2% of oxygen per Co^0 surface) [21]. Therefore, to explain the observed decrease in the Co^0/Co^{2+} ratio, two possibilities can be suggested: (i) sintering or (ii) encapsulation of the Co^0 crystallites by the surrounding CoO matrix which can be postulated as a "self SMSI effect". Further sintering, however, can hardly occur to a significant extent at the temperature below that of the preceding reduction treatment. Therefore, we incline to explain the sur-

Table 2
XPS results obtained over 10 wt% Co/Al_2O_3 catalysts after different treatments

Treatment (h)	BE of Co^0 $2p_{3/2}$ (eV)	XPS intensity ratio		
		Co_{tot}/Al (2p/2s)	Co^{2+}/Al (2p/2s)	Co^0/Co^{2+} (%)
1	778.7	0.61	0.52	17
CO/H_2 [a]	778.9	0.64	0.54	18
20	778.2	0.68	0.55	26
CO/H_2 [a]	777.9	0.70	0.61	14

[a] After treatment in CO/H_2 at 1 bar at 523 K for 5 h.

face Co^0 decrease by covering the metallic particles with partially reduced cobalt oxide (CoO_{1-x}). In any case the decrease of the active surface detected by XPS can obviously cause a lowering of the catalytic activity of the LR sample during the 5 h on stream. No change in surface composition was found, however, for the SR sample and thus it is not operative for the increase of its catalytic activity.

According to the product selectivities (up to C_5 hydrocarbons) of the reaction shown in table 1, methane is the primary product in all cases, similarly to what was found for polycrystalline cobalt foil (80%) and evaporated cobalt film (90%) [24]. As is shown in fig. 3 the complementary C_{2+} hydrocarbon selectivity measured on the SR sample is always higher than that obtained on sample LR. They are scattered around distinctively different values (20 and 12%, respectively) regardless of the time on stream. Similar time-independence of the electronic character of the zerovalent cobalt phase was established for both samples by XPS. Therefore, it can be suggested that the relatively electron-rich, large cobalt crystallites promote

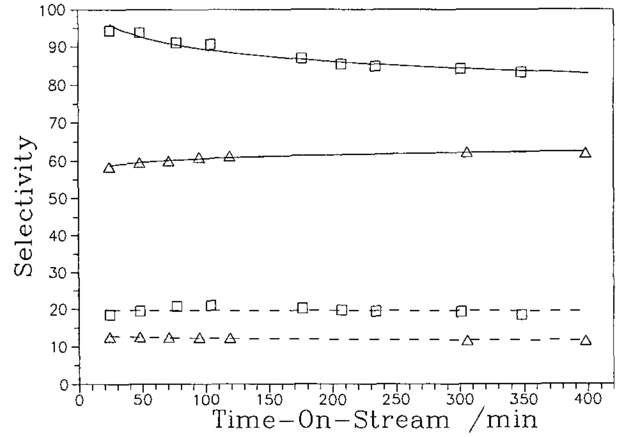

Fig. 3. Selectivities of $C^=$ and C_{2+} versus time on stream in the CO/H_2 reaction after treatment in hydrogen for 1 h (□) and for 20 h (△).

chain propagation less than the small particles of Co^0, which points to a higher efficiency of CO dissociation over the latter species of zerovalent cobalt.

By contrast, the olefin selectivities do change with increasing time on stream as shown in fig. 3. It definitely decreases for sample SR while a slight increase can only be observed in the case of the LR sample. In addition, the values of the former catalyst always exceed those of the latter one. The olefin selectivity curves which appear in the upper part of fig. 3, remarkably resemble those shown for the catalytic activities in fig. 1, but in an inverse correlation. It suggests that the catalytic activity is primarily connected with the available surface hydrogen, which also implies that the rate-limiting step may be hydrogenation. It can either be the hydrogenation of an intermediate C_nH_{2n+1} species, as was proposed for both cobalt single crystals [22,23] and polycrystalline foil [24], or, as was recently proposed [21], the hydrogenation of surface metal–oxygen bonds.

The problem of the catalytic activity and the olefin selectivity being changed over sample SR during the initial period of the reaction, is still unclear. The XPS data, according to which no change in the surface composition or in the electronic character of the active cobalt phase occurs during this time, suggest a change in the vicinity of small Co^0 particles, which results in an enhanced hydrogen supply and thereby an increase in catalytic activity. This is further supported by the fact that the highly dispersed Co^0 phase formed over sample SR consists of small particles which are intrinsically more influenced by the properties of the metal–oxide interface than the large crystallites of sample LR.

It was earlier observed using temperature programmed surface reaction (TPSR) that two different reaction states are active in the CO hydrogenation over supported cobalt catalysts [25]. The highly active path A produces hydrocarbons via hydrogenation of surface carbon over 3D metal crystallites, while the less active route B involves methoxy or formate species originally formed on the support via reaction between spilled-over hydrogen atoms and CO molecules. According to the results obtained by TPSR [25] at the beginning of the reaction both mechanisms are operative under our conditions. However, one might speculate that with increasing time on stream reaction path B becomes retarded either by direct blocking of the interface sites by carbonaceous deposits or by the modification of the surrounding oxide surface, which decreases the spillover. Assuming such an effect in the case of sample SR, the CO hydrogenation reaction proceeds at the beginning both via routes A and B simultaneously. With increasing time on stream, however, the more active mechanism A becomes prevailing and thus, an increase in the catalytic activity could be observed.

Our results, showing markedly different activities and selectivities for samples SR and LR, suggest that the CO hydrogenation reaction is structure sensitive over alumina supported cobalt catalysts. Its structure insensitivity was, however, reported by several authors [22,23,27,28] while structure sensitivity was stated in other cases [27,29,30]. The essential difference between the cobalt containing systems for which structure insensitivity or sensitivity of CO hydrogenation was established is the extent of cobalt reduction. The former applies if cobalt is nearly completely reduced, i.e. it is present in large metallic particles, and the latter if its reduction is incomplete. Therefore, the most likely origin of the structure sensitivity is a possible side reaction which is effective over the ionic cobalt phase surrounding the zerovalent cobalt particles in the incompletely reduced catalysts, as is represented above by route B.

4. Conclusion

With changing reduction time the zerovalent cobalt phases of two different structures could be obtained under mild conditions. Short-term reduction resulted in the formation of very small Co^0 particles, while long-term reduction lead to the formation of large bulk-like cobalt crystallites.

Neither of the different Co^0 phases changes its electronic character during CO hydrogenation carried out for 5 h on stream. Similarly, different but time independent C_{2+} hydrocarbon selectivities could be measured, which revealed a superior CO dissociation efficiency over small cobalt particles.

The decrease in the catalytic activity observed for the long-term reduced catalyst was mainly attributed to the decrease in the surface Co^0 content detected by XPS. In the case of the short-term reduced catalyst no effect of the catalytic reaction could be detected by XPS while the catalytic activity significantly increased during the reaction.

Changes in the catalytic behavior observed in the initial period of the reaction for the short-term reduced sample were interpreted by the shift in the ratio of the two parallel reaction states proposed earlier on the basis of TPSR results.

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