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CO hydrogenation and methane activation over Pd–Co/SiO_2 catalysts prepared by sol/gel method

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Abstract

Silica supported cobalt, palladium and cobalt–palladium bimetallic catalysts were prepared by sol/gel technique and characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray absorption near edge structure (XANES). The CO hydrogenation and low temperature methane activation under non-oxidative condition were used as test reactions. It was established that, in contrast to other Pd–Co systems, bimetallic particles were not formed, only a part of cobalt was reduced in the presence of palladium and the cobalt was segregated to the catalyst surface. In the CO hydrogenation over a catalyst with the ratio of $Co/Pd = 2$, a synergism was observed, while over cobalt and palladium catalysts alone lower activities were measured. Over pure cobalt sample, which has a limited reducibility, only short chain hydrocarbons, mainly alkenes, are formed, whereas in the presence of palladium (sites for enhanced hydrogen activation), the amount of alkanes increased. The limited reducibility of the cobalt was explained by the small particle size due to the preparation technique. Palladium acts in the bimetallic system not only as a component, facilitating cobalt reduction, but as a source of hydrogen participating in the reaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pd–Co bimetallic particles; XANES studies on Co reduction (CO/H_2 reaction); CH_4 activation; Synergism

1. Introduction

Enhanced cobalt reduction has been observed in bimetallic systems regardless of whether the samples were supported on an inorganic carrier or inserted into NaY zeolite supercages [1–3]. Moreover, the cobalt was fully reduced in the presence of platinum when NaY zeolite was applied in place of alumina support [4]. Earlier work from this laboratory has shown [5] that the presence of palladium indeed increased the reducibility of cobalt ions in a Pd–Co/Al_2O_3 sample and separate cobalt and Co–Pd bimetallic surface phases were identified after the various pretreatments. Increasing the Co/Pd ratio decreased the formation of *n*-butane in the selective hydrogenation of 1,3-butadiene relative to the rate of butadiene conversion, although the improved selectivity was achieved at the expense of olefin isomerization. XPS and TPR measurements indicating a change in the surface concentration of cobalt and palladium and in the position of TPR peak on various treatments showed interaction between cobalt and palladium.

The situation is somewhat different if the two metals are deposited on graphite by incipient wetness method. Graphite is a less reactive support than alumina and certainly gives more freedom to surface metal atoms to move along the surface and form bimetallic parti-

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cles. Heterogeneous solid solution was present with the existence of cobalt- and palladium-rich phases as was proven by magnetic measurement [6]. Formation of solid solution decreased the adsorption strength of 1,3-butadiene on the palladium sites modified by cobalt.

Studies on the palladium–cobalt catalysts prepared on SiO_2 by incipient wetness method showed palladium enrichments at the surface after reduction in hydrogen indicated by XPS [7–10]. The particle size was rather small (about 3–4 nm) and XRD showed also an alloy formation in agreement with TPR data. The change in the selectivity in various hydrocarbon reactions also indicated palladium enrichment at the surface.

However, Pd–Co/Al_2O_3 showed a somewhat different picture [5,11]. First, a surface enrichment was found in cobalt or in palladium depending on the surface treatment by oxygen or by hydrogen, respectively. Alloy particles were also observed by TPR measurements, however, the hydrogen adsorption was found to be activated in contrast to what Juszczik et al. observed [9,10]. Nevertheless, the authors agreed that cobalt ions can be reduced in the presence of palladium. In selective hydrogenation a synergism was observed in the rate [11] and the selectivity in *trans*/*cis*-butene-2 ratio never reached the value characteristic of pure cobalt, even in the case of 0.1 wt.% Pd–5 wt.% Co composition.

Cobalt reduction was also experienced in other bimetallic combinations regardless of whether the samples were supported on inorganic support or encaged in NaY zeolite supercages [2,3,12–15]. Moreover, the cobalt was fully reduced in the presence of platinum when NaY zeolite was applied in place of alumina support [16].

From these works it appears that, while facilitating reduction of cobalt by palladium, platinum and ruthenium is a common feature for cobalt based bimetallic catalysts, there are several conflicting evidences and considerable disagreement in the further effect on the Pd–Co system. In the present work, the crucial problem is how the cobalt reduction is affected when sol/gel technique is applied for preparation. That is, when the support and the metal or bimetallic particles posses the same range of particle size. The samples are characterized by XPS, XRD technique and some of them by XANES methods. The CO hydrogenation and the methane low temperature conversion under non-oxidative condition will be used as test reactions.

2. Experimental

2.1. Catalyst preparation

Preparation of the palladium and cobalt samples using sol/gel method has fully been described in earlier paper [17,18]. The total metal loading is 5 wt.%. For preparation of Pd/SiO_2 dinitro-diamminepalladium, $Pd(NO_2)_2(NH_3)_2$, (0.002 mole) was dissolved in 22 g of ethyleneglycol containing acetylacetone, $CH_3COCH_2COCH_3$ (0.016 mole) at 80°C. After stirring for 10 min, 14.8 g of tetraethylorthosilicate, $Si(OC_2H_5)_4$, was added to the solution and mixed at 80°C for 2 h to give homogeneous reddish transparent solution. To the reddish transparent solution, 5.12 g of water was added and stirred at 80°C for 8 h to give transparent monolythic gel. The gel was dried at 80°C under reduced pressure, powdered and activated in a hydrogen stream of 6 l/h at 400°C for 4 h. For the preparation of Pd–Co/SiO_2 samples, before the addition of $Si(OC_2H_5)_4$, the ethanol solution of cobalt nitrate hexahydrate $Co(NO_3)_3{\cdot}6H_2O$ was added to the ethyleneglycol solution containing $Pd(NO_2)_2(NH_3)_2$ and $CH_3COCH_2COCH_3$. $Si(OC_2H_5)_4$ and $Co(NO_3)_3$ $6H_2O$ were used for preparation of Co/SiO_2 sample.

2.2. Sample characterizations

Characterization of the samples was carried out by means of X-ray diffraction (XRD). A Mac Science Model MPX 18 powder X-ray diffractometer collected the data. The palladium particle size were calculated on the bases of Pd(1 1 1) or Pd(2 0 0) faces. In Fig. 1, the XRD pictures are shown for the various samples. The particle size of Pd in 5 wt.% Pd/SiO_2 prepared was found to be 5 nm by TEM.

XPS studies were performed on the reduced catalyst samples using an XSAM-800 cpi photoelectron spectrometer manufactured by KRATOS. Al Kα and Mg Kα characteristic X-ray lines using a 80 eV pass energy were applied for measuring cobalt and palladium spectra, respectively, detailed elsewhere [17]. In situ cell was used for the post-treatment of the

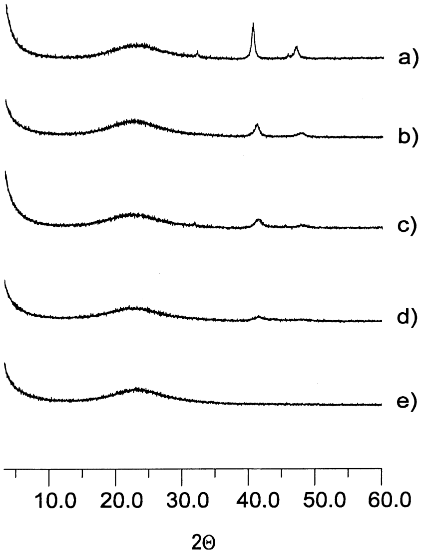

Fig. 1. X-ray diffraction data on Pd–Co/SiO_2 samples. The a–e are Pd/SiO_2, $Pd_{67}Co_{33}/SiO_2$, $Pd_{50}Co_{50}/SiO_2$, $Pd_{33}Co_{67}/SiO_2$, Co/SiO_2, respectively.

catalyst samples [19]. Thus, it was possible to measure surface composition of palladium and cobalt as well as valence states of the components.

XANES measurements on a Pd/Co sample with 1:1 atomic ratio were performed at LURE (Orsay) synchrotron radiation facility. Xanes spectra were collected at the Pd K-edge on the DCI beam line D44 using a Ge 400 double monochromator and ionisation chambers filled with argon. The catalysts were in powdered form meshed to a 100–200 μm range. A special furnace was used for in situ reduction treatment with entrance and exit windows of boron nitride transparent to the X-ray beam [20]. On-line data analysis was used in order to check that the chemical reaction was proceeding.

2.3. Catalytic reactions

CO hydrogenation was measured in a plug flow reactor at 1 bar pressure using a 2:1 H_2/CO mixture with a mass flow rate at 15 $cm^3 min^{-1}$ [17]. The catalysts were reduced for 2 h at 400°C before use. The catalyst samples were treated in the reaction mixture overnight to stabilize the activity and then the catalytic performance was measured. The effluent was analyzed by means of a Packard 9000 type gas chromatograph equipped with a FID detector and a 50 m long 0.53 mm i.d. wide bore CP–Al_2O_3/KCl plot fused silica plot column (type 7518). Only the hydrocarbon products were measured to calculate the rate and conversion.

The methane conversion was investigated in a flow system [18]. The 100 mg catalyst was placed into the reactor and one 0.5 cm^3 (22.3 μl) methane pulse was introduced into a stream of a mixture of H_2/He (1.3 vol.% hydrogen) with a total flow rate of 100 $cm^3 min^{-1}$ at various temperatures. The reaction products were collected in a trap cooled at liquid nitrogen temperature and after warming up the products were analyzed by means of a gas chromatograph type CHROMPACK CP 9002 using a 50 m long fused silica plot column (0.53 mm i.d.) as described above. After having the samples analyzed, the catalyst was heated in a stream of hydrogen/helium mixture at 250°C and the catalyst sample was hydrogenated for 1 h and the products were again collected in a cold trap and analyzed as previously. The unconverted methane was not trapped at liquid nitrogen temperature because no zeolite filling was used. The reaction was characterized by the amount of C_{2+} products in micro moles (in methane equivalents).

3. Results and discussion

The in situ XPS results presented in Table 1, undoubtedly show that cobalt ions in the absence of palladium cannot be reduced at 400°C (see row 1 in Table 1) and the binding energy is 781.3 eV, which corresponds to unreduced cobalt oxide. On the other hand, in the presence of palladium the cobalt ions can, at least partially, be reduced indicated by the binding energy around 778 eV, but the cobalt signal compared to palladium is very weak. Conclusions drawn from XPS measurements, are as follows: (i) the cobalt ions are not reducible without the presence of palladium; (ii) although addition of palladium facilitates the reduction of cobalt ions, full reduction cannot be reached (see column 5 in Table 1); (iii) after oxidation followed by repeated reduction metallic cobalt can be restored. We do not know at the present stage whether bimetallic particles are formed or not. On the oxidation of the bimetallic particles cobalt ions are enriched at the surface, while on the subsequent

Table 1
XPS data on Pd–Co/SiO_2 samples prepared by sol/gel technique after reduction

Treatment at 400°C	Co (%)	$(Co/Pd)_b$	Co 2p (eV)	$Co^0/(Co^0 + Co^{2+})$	Pd 3d (eV)	$(Co/Pd)_s$
H_2	100	–	781.5	0	–	–
H_2	67	2	778.1	0.5	334.2	2.3
O_2			780.0	0	336.3	3.4
H_2			777.7	0.7	334.2	2.6
H_2	50	1	777.6	0.5	334.8	2.7
H_2	33	0.5	777.8	0.8	334.8	2.0
H_2	0	–	–	–	333.2	–

reduction the metallic palladium is segregated to the surface (compare rows 2–4 in Table 1). Simultaneously, XPS results prove that cobalt enrichment occurs at the surface indicated by $(Co/Pd)_s > (Co/Pd)_b$ in all bimetallic samples. Nevertheless, interaction between cobalt and palladium at the surface of the samples can be suggested based on the Co 2p and Pd 3d binding energy values indicated in Table 1 (778.1 and 777.7 as well as 334.2 and 334.8 eV).

The scenario becomes more complicated when the XANES spectra are considered. In Figs. 2 and 3 the Pd K-edge and Co K-edge spectra, respectively, recorded during in situ reduction at various temperatures, are shown. Palladium is easily reduced even at low temperature, whereas the cobalt ions apparently cannot be reduced. This statement concerns only the $Pd_{50}Co_{50}/SiO_2$ sample (it was the only one we measured by means of XANES). Although in an oxidation/reduction cycle the cobalt ions in the $Pd_{67}Co_{33}/SiO_2$ sample behave in a reversible manner

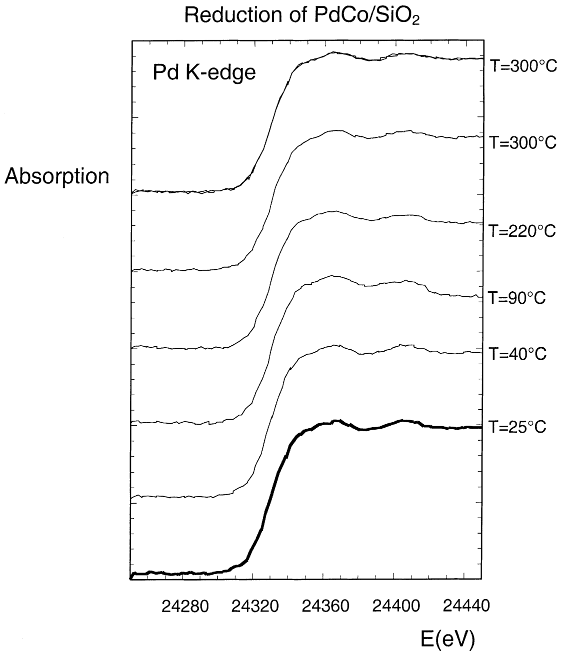

Fig. 2. XANES Spectra on Pd K-edge in $Pd_{50}Co_{50}/SiO_2$ sample during reduction at various temperatures.

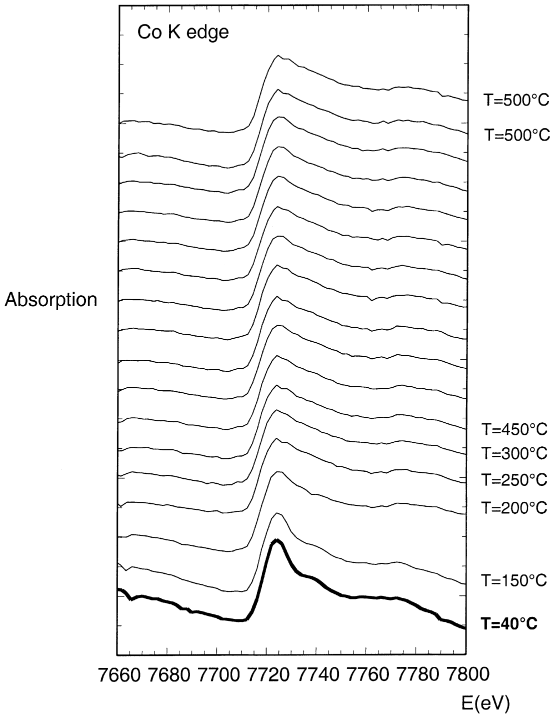

Fig. 3. XANES Spectra on Co K-edge in $Pd_{50}Co_{50}/SiO_2$ sample during reduction at various temperatures.

Table 2
Average particle size calculated from XRD (Pd(1 1 1) and (2 0 0) faces), and dispersion for various Pd–Co/SiO_2 samples

Co (%)	Pd particle size (nm) (by XRD)	Dispersion		
		XRD	H_2	CO
100	–	–	–	–
67	4.6	24.3	–	2.2
50	6.1	18.3	4.6	2.8
33	7.0	16.0	3.4	3.8
0	14.5	7.8	2.8	2.8

as indicated by XPS data, still a large part of the Co^{2+} ions cannot be converted into metallic cobalt by hydrogenation (the $Co^0/(Co^0+Co^{2+})$ ratio is approximately 0.7–0.8).

The above statement is further supported by the XRD and chemisorption data (see Fig. 1 and Table 2). As the amount of cobalt in the form cobalt oxide increases, the average size of the palladium particles being in metal form, becomes smaller (see Table 2 column 2). However, the discrepancy between XRD and chemisorption data concerning the dispersion is due to cobalt enrichment at the surface of the metal particles. Some of the Pd particles are encapsulated, thus, not exposed to H_2 and CO molecules. This behavior is in agreements with the special sol/gel preparation method in which the small support particles may partially cover a fraction of metallic particles unlike in a conventional support in which case the support grains are much larger than in our sol/gel prepared samples (Table 3).

In Fig. 4 the rate of CO hydrogenation is plotted as a function of cobalt content of the samples. The rate passes through a maximum as the nominal Co/Pd ratio increases. Similar synergism has also been demonstrated in the selective hydrogenation of 1,3-butadiene over Pd–Co/Al_2O_3 catalyst [5] and for CO hydrogenation over Ru–Co/NaY system [21]. It is not understood why the catalyst with similar Co/Pd ratio the activity is not the same (compare, e.g. Co_{67} and Co_{50}).

Table 3
Selectivity values in CO Hydrogenation over Pd–Co/SiO_2

Co (%)	S_{C_1}	$S_{C_{2+}}$	$C^=/(C^=+C^-)$	α
100	90.6	9.4	87	0.29
67	59.0	41	36	0.78
50	64.5	35.5	31	0.71
33	66	34	35	0.65
0	100	–	–	–

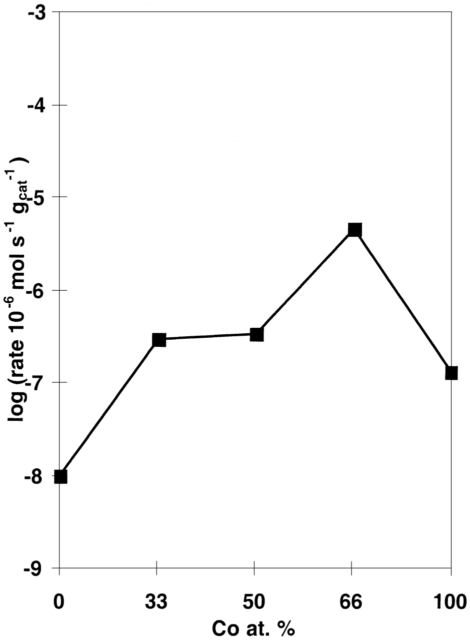

Fig. 4. Rate of CO hydrogenation vs. catalyst composition in the Pd–Co/SiO_2 samples.

In the low temperature methane conversion under non-oxidative condition the effect of composition of the same catalyst system is presented in Fig. 5. The

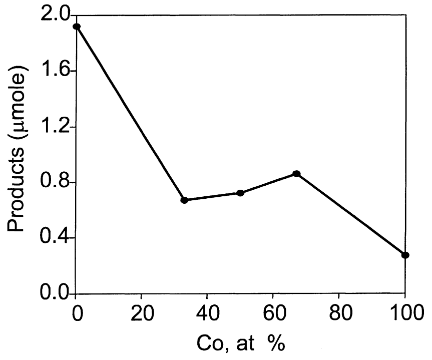

Fig. 5. The effect of cobalt concentration in the Co–Pd/SiO_2 samples in one-step methane conversion using one methane pulse (0.5 ml (22.3 μmole))

methane activation in 1.3% H_2/He as well as the hydrogenation of the CH_x species occurred at 250°C. The most striking results originated from the amount of products. The amounts of products formed in the one-step methane conversion are high on a pure Pd/SiO_2 sample, constant at the catalysts at intermediate Pd–Co/SiO_2 composition (Pd/Co ratios are 2, 1 and 0.5), while the pure Co/SiO_2 sample has the lowest activity. There are two processes: (i) alteration of the surface concentration of the metallic sites (Pd is fully reduced, whereas Pd–Co is partially reduced and the cobalt alone is poorly reduced): (ii) with decreasing the palladium content, the catalyst is starving in hydrogen, consequently, desorption of the hydrocarbon chains present at the surface, which needs hydrogen, is retarded. As we have shown earlier [18] at 250°C a fraction of the already polymerized hydrocarbons is still retained by the catalyst surface. Discarding the pure palladium containing catalyst a slight maximum can also be seen in the methane conversion.

As we pointed out earlier [21], the “one-step” process (when methane chemisorption occurs in the H_2/He mixture) has an advantage as compared to the “two-step” process. This is because hydrogen in a stream of helium prevents the total dehydrogenation of methane to form fully hydrogen deficient carbon species as carbonaceous deposits. Consequently, the surface hydrogen supplied by the palladium plays a decisive role in the product formation from methane. This may give explanation why the methane conversion gives such a high amount of products on Pd/SiO_2. Conversely, the low concentration of metallic cobalt sites in Co/SiO_2 sample is the explanation for low amount of product formation. In the bimetallic systems, however, both the metallic cobalt sites being responsible for chain growing and the hydrogen supply provided by palladium are present facilitating the product formation from methane.

Facilitating the cobalt reduction and synergism were also observed in the Ru–Co/NaY system [22] and on other inorganic oxides like Ru–Co/TiO_2 [23,24]. Significant promoter effect has been observed also on the Co/Al_2O_3 catalysts in the CO/H_2 reaction [25,26]. From these works it appeared that, while the enhanced reduction of the cobalt ions by palladium is a common feature regarding the platinum and ruthenium containing cobalt catalysts, considerable disagreements still exit in the further effect of the second metal.

In the present work we have only conflicting data to support the presence of Pd–Co bimetallic particles. Neither XPS, nor XANES data support the formation of bimetallic particles in the cobalt–palladium combination, nevertheless, the neighborhood of the two metals may not be excluded. The discrepancy concerning the valence state of the cobalt after reduction measured by these two techniques, gives indication that cobalt ions at the outermost surface can be reduced, whereas the bulk remains mainly in oxide form. This is a consequence of the new preparation method using sol/gel technique in which both the metal and support have small particle size and supposedly the small particles of metal and bimetallic system are stabilized.

In the CO hydrogenation the rate is low on pure Pd/SiO_2 and Co/SiO_2 in the latter case because of the lack of metallic cobalt. In the middle compositions the surface cobalt is reduced, thus, the rate increases causing synergism. Similar effect is valid in the methane conversion into higher hydrocarbons. The exceptionally high activity on Pd/SiO_2 is due to the higher rate of methane activation.

As far as the mechanism of synergism is concerned it is believed that palladium being inserted into the cobalt matrix, modifies the cobalt sites in a way that deactivation processes on the surface is retarded. Palladium itself is not a good catalyst in the CO hydrogenation and, thus, activity of the bimetallic sites shows an optimum performance.

Acknowledgements

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