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Stability of Pt–Co bimetallic particles: effect of the support induced morphology on reactivity in CO hydrogenation

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The structure and the stability of bimetallic particles are controlled by their interaction with surface oxide species on support or by support geometry. Location and size of the bimetallic particles estimated by XRD and XPS, depends on the environment and treatment. Thus, the Pt–Co bimetallic particles entrapped in NaY zeolite cages become unstable upon mild oxidation by O_2 and/or reaction with surface protons causing the Co^{2+} ions formed to migrate irreversibly from the supercages into the sodalite cages as determined by TPR and TPD. Differences in the selectivity pattern observed for the CO hydrogenation over alumina and NaY zeolite supported Pt–Co catalysts, can be interpreted by the interaction between bimetallic particles with surface cobalt oxide species and the zeolite cage wall, respectively.

Keywords: Pt–Co in NaY; XPS on; CO hydrogenation on; decomposition of bimetallic on mild oxidation

1. Introduction

Interaction between metal particles and support plays an important role in determining the structure and surface properties of supported bimetallic catalysts. For Pt–Co/Al_2O_3 catalysts, the strong interaction between Co^{2+} and Al_2O_3 results in the formation of unreducible cobalt surface species which act as an interface between reduced Pt, Co or Pt–Co particles and the support surface [1–3]. In contrast, when Pt and Co are co-exchanged into NaY zeolite, Co cations, which are in the proximity with Pt, are reduced together with Pt, and bimetallic Pt–Co particles are formed in supercages, leaving unreduced Co in small cages [4,5]. In earlier

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experiments we have observed the presence of stable Pd–Fe particles in NaX during the CO hydrogenation reaction [6,7]. Recent results, however, showed that Ni and Cu in Pt–Ni/NaY [8] and Pd–Cu/NaY [9,10] can be leached out from the bimetallic particles into the sodalite or hexagonal cages by mild oxidation or by reaction with surface protons. Migration could be reversible, but for metals like Fe and Co with high negative chemical potentials, the reverse process is highly improbable. Several papers appeared in the literature for the migration of Pd in NaY zeolite upon CO adsorption [11–14] and hydrogenation [18,19]. Migration could also occur onto the external surface of the zeolite where large metallic or bimetallic particles can be formed.

In the present paper the effect of alumina and NaY zeolite supports on the formation and structure of Pt–Co bimetallic particles are illustrated. Particle size and the properties of the bimetallic catalysts induced by the support morphology are correlated with the activity and selectivity in CO hydrogenation reaction. XRD and XPS are used to determine the location of the metal particles.

2. Experimental

In this paper, three kinds of bimetallic catalyst have been used. The Pt–Co/NaY(IE) catalyst was prepared by successive ion exchange of NaY zeolite with $Pt(NH_3)_4(NO_3)_2$ and $Co(NH_3)_2$ solution introducing Pt^{2+} ions first as described elsewhere [4]. The Pt–Co/NaY(IM) catalyst was prepared by co-impregnation of NaY zeolite with the same Pt and Co precursors. Incipient wetness method was applied for Pt–Co/Al_2O_3 [1]. This latter catalyst was reduced either after calcination (CR) or directly after drying (DR). The metal contents and loadings are presented in table 1. The samples were calcined at 573 K for 2 h followed by reduction at 723 K for 2 h unless otherwise stated.

Temperature programmed reduction (TPR) and desorption (TPD) were carried out in a standard flow apparatus SORBSTAR. 0.03 g catalyst was first calcined in flowing O_2 (40 cm^3/min) at 573 K for 2 h. TPR was measured by using 1% H_2 in Ar (30 cm^3/min) to either 723 or 923 K with 10 K/min. The sample was then cooled

Table 1
Composition of the catalysts applied

Catalyst[a]	Co/(Pt + Co)	Pt (wt%)	Co (wt%)
Pt–Co/NaY(IE)	0.65	4.6	2.6
Pt–Co/NaY(IM)	0.7	4.8	3.4
Pt–Co/Al_2O_3(CR)	0.62	5.0	2.5
Pt–Co/Al_2O_3(DR)	0.65	6.2	3.8

[a] Notation: IE: ion exchange; IM: impregnation on NaY; CR: calcination and reduction; DR: direct reduction.

down to RT either in H_2 or in Ar followed by different TPD cycles in Ar (20 cm^3/min) with 20 K/min.

Oxidation of the reduced catalyst was carried out in flowing O_2 at 373 or 573 K for 2 h with 0.5 K/min ramp rate. TPR and TPD were then repeated on the oxidized sample.

XRD patterns were recorded by using Cu K_α radiation on a Philips X-ray diffractometer equipped with Guinier camera [4,5].

XPS measurements were carried out in a KRATOS ES-300 ESCA machine using an Al $K_\alpha = 1486.6$ eV source. The hemispherical analyzer worked in the fixed retarding ratio (FRR) mode. The samples were reduced in situ by flowing H_2 in a small reaction chamber attached directly to the vacuum chamber of the equipment. For data evaluation the Si 2p line of 102.75 eV binding energy was used as an internal reference.

CO hydrogenation was carried out in a standard flow through apparatus as described earlier [4].

3. Results and discussion

3.1. STRUCTURE OF CATALYST SAMPLES

XRD measurements indicate X-ray amorphous particles for Pt–Co/NaY(IE) samples, but for impregnated Pt–Co/NaY(IM) catalyst the size of Pt–Co particles amounts to 15 nm with about 30 at% Co. On Pt–Co/Al_2O_3 the particle diameter of Pt–Co bimetallics is about 70 nm (with 10 at% Co). Co oxide is proved to be X-ray amorphous in all samples.

XPS measurements were applied to estimate the difference between ion exchanged and impregnated zeolites. In table 2 the Na 1s/Si 2p ratio is taken as a measure of ion exchange. It is well illustrated that the Na 1s/Si 2p ratio considerably decreases when Pt and Co precursors are present (row 2), whereas in the impregnated Pt–Co/NaY sample no decrease is observed (row 4) indicating that for the latter sample the metal components are located at the external surface. Our studies [1,3,15] have indicated formation of bimetallic particles for alumina and NaY supported samples based on the Co^0 BE value being 0.5 eV higher than that

Table 2
Na 1s/Si 2p ratio for various samples

Sample	Treatment	Na 1s/Si 2p
NaY	no	0.43
Pt–Co/NaY(IE)	no	0.11
Pt–Co/NaY(IE)	reduced	0.08
Pt–Co/NaY(IM)	no	0.40
Pt–Co/NaY(IM)	reduced	0.43

for pure Co. The impregnated sample (IM) is reduced to larger extent than the exchanged one as shown by comparison of the XPS spectra of the reduced samples (figs. 1a and 1b). From these results it can be concluded that after calcination and reduction the bimetallic stays inside the NaY supercage for (IE) samples, whereas for (IM) samples it remains at the external surface.

Although according to XPS measurements the reduction of the cobalt component inside the zeolite cages is somewhat limited, TPR studies have indicated enhanced reduction [4]. In fig. 2 the TPR (curve a) is indicative of co-reduction of Co with Pt in Pt–Co/NaY(IE) bimetallic catalyst. However, after mild oxidation this peak disappears (curves b and c). The total H_2 uptake during TPR on the reoxidized sample is much lower than that on freshly calcined sample (fig. 2a) and the peak at around 350 K can be assigned to the Pt reduction alone. Our previous results [5] have also shown that calcination at 573 K leaves most of the Pt and Pt–Co mixed oxide particles in the supercages, thus, reoxidation under the same condition may result in complete separation of Pt and Co in the Pt–Co bimetallic particles and the isolated Co^{2+} ions are driven into sodalite or hexagonal cages leaving the Pt particles in the supercages.

In order to further elucidate the mechanism of Co to Co^{2+} transitions in Pt–Co/NaY(IE) samples, the effect of protons formed after reduction was studied at temperature higher than 723 K [4]. Different TPD cycles were carried out to monitor H_2 evolution at higher temperature (see fig. 3) and these experiments give further information about the stability of the Pt–Co bimetallic particles.

The reduced Pt–Co/NaY(IE) sample was first purged in Ar at 923 K and cooled

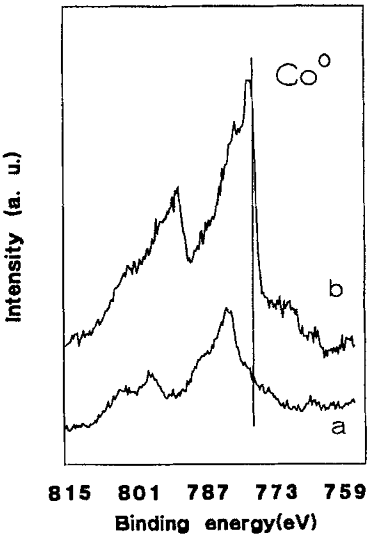

Fig. 1. XPS spectra of Co $2p_{3/2}$ bands on reduced bimetallic catalysts. (a) Pt–Co/NaY(IE); (b) Pt–Co/NaY(IM).

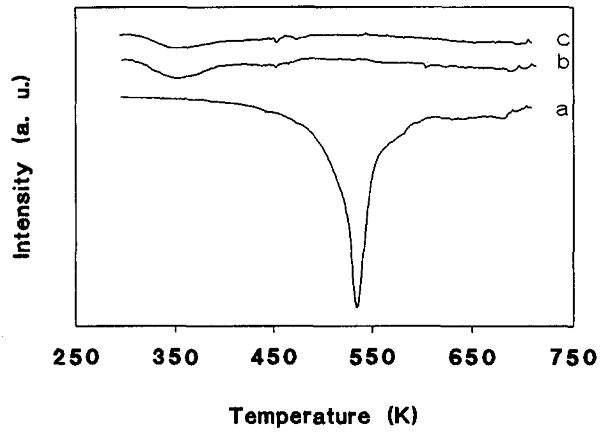

Fig. 2. TPR profiles for Pt–Co/NaY(IE) after different pretreatments. (a) After calcination at 573 K for 2 h; (b) reoxidation at 573 K for 2 h with 0.5 K/min after (a); (c) reoxidation at 573 K for 2 h with 10 K/min after (a).

down to RT. In fig. 3a the single TPD peak at about 360 K temperature corresponds to desorption of the H_2 adsorbed on the sample at RT. When the purging in Ar takes place only at 723 K, a second peak is present observed at around 850 K as shown in fig. 3c. This peak has been previously assigned to the oxidation of Co in Pt–Co bimetallic particles with surface hydroxyl groups [5]. When the reduced sample is cooled down first in H_2 to 523 K and then in Ar to RT, the second peak is shifted to 650 K (see fig. 3b). This peak can be assigned to activated H_2 which is chemisorbed on the sample at above 523 K.

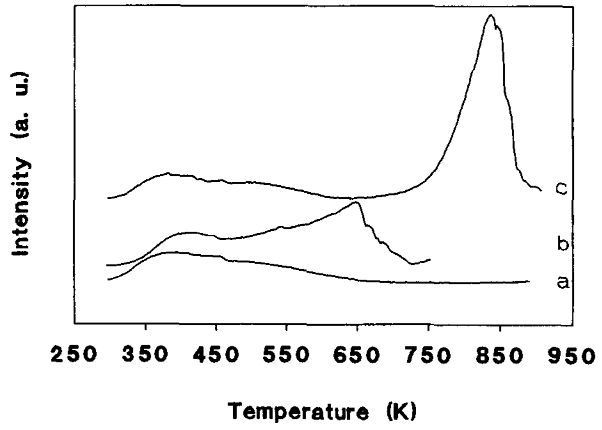

Fig. 3. TPD profiles of H_2 adsorbed on Pt–Co/NaY(IE) after calcination at 573 K for 2 h and reduction at 723 K for 2 h, followed by different treatments. (a) Purging with Ar at 923 K for 30 min; (b) cooled down in H_2 from 723 K to 523 K then in Ar to RT; (c) purging with Ar at 723 K for 30 min.

There are two explanations for the peak evolved at 850 K, i.e. this can be assigned either to partial oxidation of Co in Pt–Co bimetallic particles or to the desorption of the activated H_2 from the reduced Co in Pt–Co bimetallic samples. Since the high temperature peak appears even after hydrogen adsorption at RT, we incline to ascribe the second desorption peak in fig. 3c to the oxidation of Co(0) according to equation

$$Co^0 + 2H^+ \rightarrow Co^{2+} + H_2 .$$

The Co^{2+} ions migrate into small cages, because the subsequent TPR does not show any reduction peak for the sample as already indicated in fig. 2c.

3.2. CATALYTIC REACTION

Previously we showed the instability of the Pt–Co/NaY bimetallic particles under oxidative conditions. In table 3 the catalytic behavior of the different bimetallic samples is presented. It has been established [1–3] that on alumina an oxide layer is built up which increases the dispersion of Pt and forms Pt–Co bimetallic particles upon the reduction.

Comparing the (IE) and (IM) samples obviously both 1 and 10 bar pressure CH_4 and the C_{2+} selectivity is higher on (IM) and no oxygenates are formed. By comparing these results to the structure displayed by XRD and XPS the (IM) sample works as if Co particles were modified by large amount of Pt [17]. On the other hand, for oxygenate formation metal/oxide interface is needed like on alumina support, or on small metal particles which may interact with O^- or O^{2-} inside the supercage. Consequently, selectivity is an adequate indication to decide whether migration from the supercage to the external surface occurs or not. Nevertheless,

Table 3
CO/H_2 reaction on various samples

Catalyst[a]	T (°C)	Rate[b]	CH_4 (%)	C_{2+} (%)	Olef.[c] (%)	MeOH (%)	Oxy.[d] (%)
Pt–Co/NaY(IE)[e]	229	0.35	78.7	8.0	0	0	13.3
Pt–Co/NaY(IM)[e]	232	0.69	53.6	46.4	16.1	0	0
Pt–Co/Al_2O_3(DR)[e]	232	0.21	43.3	43.2	18.0	11.1	2.4
Pt–Co/NaY(IE)[f]	232	3.98	24.5	12.0	22.1	48.9	11.6
Pt–Co/NaY(IM)[f]	232	4.69	51.2	48.8	28.7	0	0
Pt–Co/Al_2O_3(CR)[f]	229	4.09	20.7	4.5	1.5	42.9	32.0
Pt–Co/Al_2O_3(DR)[f]	232	0.71	36.3	15.2	15.6	23.1	25.4

[a] IE = ion exchanged; IM = impregnated; DR = directly reduced without calcination; CR = calcination followed by reduction.

[b] $\times 10^{-4}$ mol s^{-1} (mol-metal)$^{-1}$.

[c] Olefin selectivity in C_{2+} hydrocarbons.

[d] Oxygenates other than methanol.

[e] At 1 bar pressure.

[f] At 10 bar pressure.

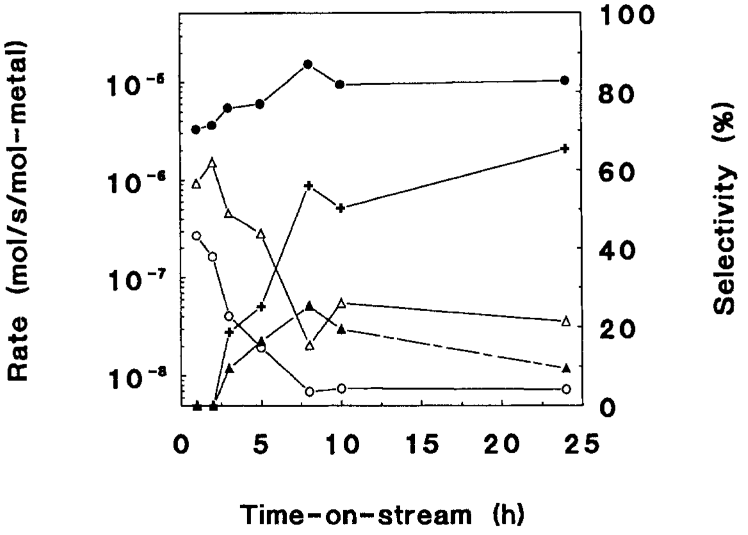

Fig. 4. Rate and selectivity of CO/H_2 reaction versus time-on-stream measured over Pt–Co/Al_2O_3(CR) catalyst at 505 K and at 1 bar pressure. Symbols: (●) rate; (△) CH_4; (○) C_{2+}; (+) CH_3OH; (▲) oxygenates.

on alumina the increase of reaction time changes its selectivity leaving the rate of reaction the same (see fig. 4) and this might be due to restructuring the active sites.

It can be concluded that the TPR and TPD indicate complete isolation of Pt and Co in Pt–Co bimetallic particles either by mild O_2 reoxidation or by reaction of Co with surface protons at higher temperature. The Pt–Co particles proved to be stable in the ion exchanged NaY indicated by a comparison of the selectivity values measured on (IE) and (IM) samples.

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