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MÖSSBAUER SPECTROSCOPY STUDIES OF PtFe/NaY ZEOLITE

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PtFe/NaY was characterized by Mössbauer spectroscopy after pretreatments in O_2 and H_2 at 700 K. Comparison of room-temperature spectra with those for standard Fe/NaY gave evidence for interaction between Pt and Fe. This result is discussed with respect to the phenomenon of chemical anchoring of Pt in zeolites.

1. Introduction

Numerous cases are documented, where the performance of bimetallic catalysts is superior to that of their monometallic counterparts. For example, significant modifications of catalyst selectivities can be attained by adding a reducible but catalytically inactive metal, such as gold, to an active metal, such as platinum [1]. The activity maintenance of $PtRe(S)/Al_2O_3$-Cl is distinctly superior to that of $Pt(S)/Al_2O_3$-Cl and this has been responsible for the worldwide displacement of the latter "reforming catalyst" by the former [2]. Such improvements are not limited to metals which are reducible and can thus form an "alloy" or "mixed metal cluster" with the prime catalyst metal. Rather, metal elements which are non-reducible under the conditions of the catalytic process have also been reported to improve catalytic performance. For example, Schulz and Weitkamp [3] report that the conversion of n-dodecane for C_{12}-isomerization at 573 K was 3% for Pd/H-Y, but 31% for PdMn/H-Y. The effects of non-reducible metal additives on supported-metal catalysts have been the subject of recent research.

Briefly, the following three causes have been identified as to how such an additive can affect the catalytic performance of the reduced metal: (1) a catalyst promoter effect, i.e., direct or indirect electronic interaction with adsorbed molecules [4–6]; (2) site blocking in zeolites, i.e., the escape of ions such as Pt^{2+} or Ni^{2+} into small zeolite cages is prevented, and after reduction, small Pt- or Ni-particles are formed in larger cases [7–9]; and, (3) chemical anchoring, i.e.,

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transition metal ions in the support surface interact with reduced metal particles, thus impeding their migration and sintering [10,11].

The latter phenomenon of chemical anchoring motivates the present research. In particular, it has been shown that the metal dispersion of Pt/NaY in hydrogen flow at 773 K decreases with time; this decrease is much smaller for PtFe/NaY [10]. Furthermore, the Rh dispersion in RhCr/NaY is much higher than in Rh/NaY; for this system, EXAFS has proved the existence of distances which can reasonably be ascribed to Rh-Cr^{3+} bonds [11]. Finally, the existence of positive Pt or Rh ions at the metal-support interface in silica-supported Pt or Rh catalysts, even after extensive reduction in hydrogen, has been demonstrated using ESR [12].

Mössbauer spectroscopy has proved to be a useful tool for investigating the nature of supported-metal catalysts, especially when these contain Fe, a commonly encountered Mössbauer isotope. In the present work, PtFe/NaY was characterized by this technique. The spectra were collected at room temperature, after treatments in O_2 and H_2 at 700 K, and compared with those for standard Fe/NaY. It was hoped that this would provide additional insight into the phenomenon of chemical anchoring of Pt in zeolites.

2. Experimental

PtFe/NaY (having metal loadings of 3.1 wt.% Fe and 10.8 wt.% Pt) was prepared by ion exchange, using first $FeSO_4 \cdot 7H_2O$ and then $Pt(NH_3)_4Cl_2$. The details of the preparation procedure are given elsewhere [10]. The sample was subjected to the following successive treatments, all for 5 h and at 700 K: (1) in O_2; (2) in H_2; (3) in O_2 (second oxidation); and (4) in H_2 (second reduction). The experimental details of these treatments are given elsewhere [13].

Mössbauer spectra were recorded with an Austin Science Associates Model S-600 Mössbauer Spectrometer Controller and a Tracor-Northern Model NS-900 multichannel analyzer. A 50-mCi single-line ^{57}Co source in a Pd matrix was used. The velocity scale of the spectrometer was calibrated with a sodium nitroprusside standard absorber. Isomer shifts are reported relative to metallic iron at room temperature. The spectra were fit using the program MFIT [14].

3. Results and discussion

The spectra for an oxidized and reduced, standard Fe/NaY sample are shown in figures 1(a) and 2(a), respectively. The data for these were taken from Aparicio et al. [13]. The corresponding spectra for the PtFe/NaY sample are shown in figs. 1(b) and 2(b), respectively. The spectra for the re-oxidized and re-reduced PtFe/NaY sample are shown in figs. 1(c) and 2(c), respectively. Tables 1 and 2

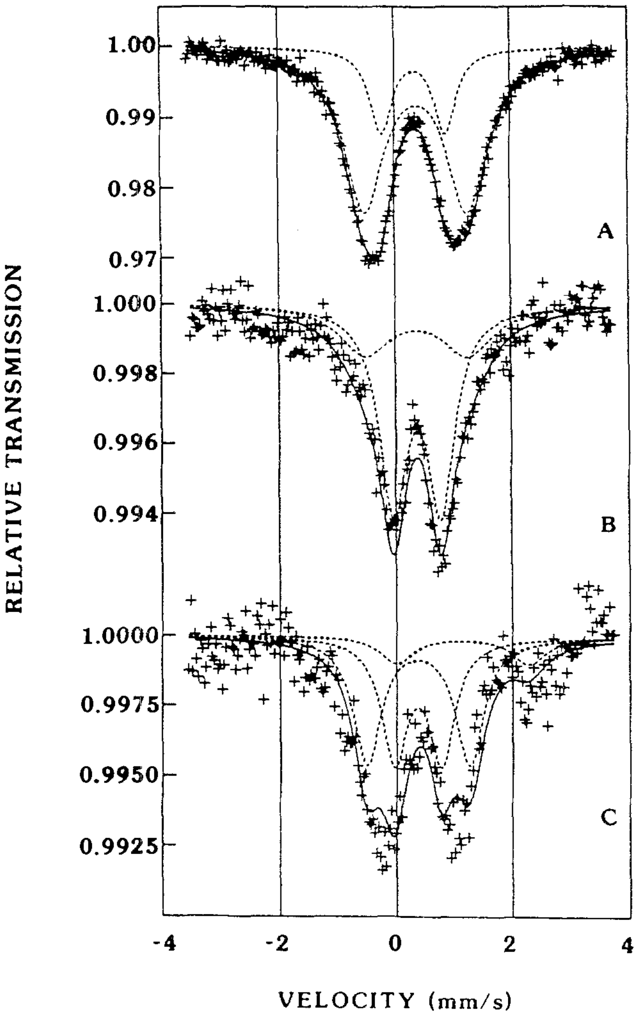

Fig. 1. Room temperature Mössbauer spectra of oxidized samples: (A) Fe/NaY, (B) PtFe/NaY, (C) PtFe/NaY (second oxidation).

Table 1
Mössbauer spectroscopy parameters of oxidized samples

Sample	Figure	IS (mm/s)	QS (mm/s)	Relative area (%)	Species
Fe/NaY	1A	0.38	1.77	77.8	Fe^{3+} outer doublet
		0.33	1.10	22.2	Fe^{3+} inner doublet
PtFe/NaY	1B	0.38	1.77	32.4	Fe^{3+} outer doublet
		0.37	0.83	67.6	Fe^{3+} inner doublet
PtFe/NaY	1C	0.38	1.77	46.6	Fe^{3+} outer doublet
(second		0.37	0.83	40.6	Fe^{3+} inner doublet
oxidation)		1.15	2.28	12.8	Fe^{2+} outer doublet

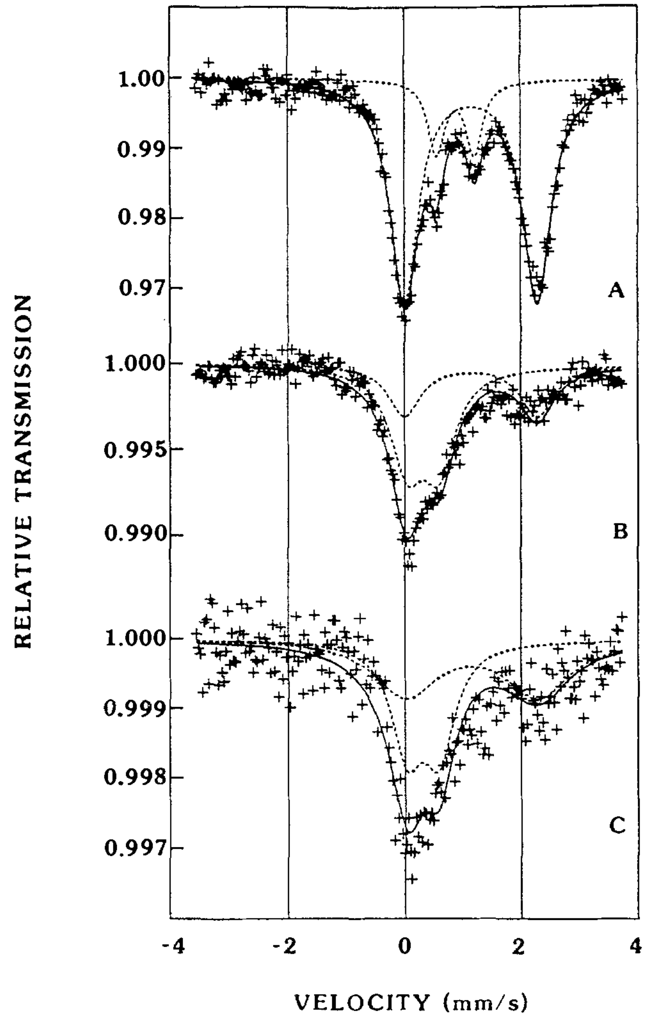

Fig. 2. Room temperature Mössbauer spectra of reduced samples: (A) Fe/NaY, (B) PtFe/NaY, (C) PtFe/NaY (second reduction).

Table 2
Mössbauer spectroscopy parameters of reduced samples

Sample	Figure	IS (mm/s)	QS (mm/s)	Relative area (%)	Species
Fe/NaY	2A	1.15	2.28	83.8	Fe^{2+} outer doublet
		0.89	0.66	16.2	Fe^{2+} inner doublet
PtFe/NaY	2B	1.15	2.28	34.6	Fe^{2+} outer doublet
		0.31	0.55	65.4	$(Pt_x - Fe)^{n+}$
PtFe/NaY	2C	1.15	2.28	52.6	Fe^{2+} outer doublet
(second reduction)		0.31	0.55	47.4	$(Pt_x - Fe)^{n+}$

list the Mössbauer parameters for the fitted spectra. The locations of the doublets in figs. 1(c) and 2(c) were constrained to be the same as for those in figs. 1(b) and 2(b), respectively.

The spectrum of the oxidized standard Fe/NaY sample shows two doublets that can be assigned to Fe^{3+} in the sample. The doublet with the smaller quadrupole splitting has been denoted as the inner doublet, while the doublet with the larger quadrupole splitting is called the outer doublet. The spectrum of the PtFe/NaY sample also shows two Fe^{3+} doublets.

It is clear from these spectra that the PtFe/NaY sample contains a larger relative amount of the inner doublet species. In general, the inner doublet is due to ferric cations in sites of higher symmetry than those for ferric cations that contribute to the outer doublet [15]. While it is not possible, from this information, to unambiguously determine how the presence of Pt has altered the environment of the ferric cations, it can be inferred that the presence of Pt, in fact, changes the local environment of the ferric cations.

The spectrum of the reduced standard Fe/NaY sample exhibits two characteristic Fe^{2+} doublets, also denoted as the inner and outer doublets. The generally accepted interpretation of these ferrous doublets in Mössbauer spectroscopy is that the inner doublet is due to iron cations in sites of lower symmetry and lower coordination than the ferrous cations that contribute to the outer doublet [15]. For the particular case of zeolite samples, the outer doublet in the reduced standard Fe/NaY has been assigned to ferrous cations in site I and the inner doublet to cations in sites I′, II′, and/or site II [16]. Most of the Fe^{2+} in standard Fe/NaY is present in the relatively inaccessible site I.

The spectrum of the reduced PtFe/NaY sample is quite different, exhibiting one doublet having the same characteristics as the outer doublet of the standard Fe/NaY sample, and another doublet having low isomer shift. The characteristic inner doublet of the standard sample is absent. The PtFe/NaY clearly contains some cations in site I. However, from the Mössbauer spectrum, it is evident that most of the iron apparently interacts with Pt.

Bartholomew and Boudart [17], Garten [18,19], Niemantsverdriet et al. [20], and Garten and Ollis [21], among others, have used Mössbauer spectroscopy to carry out extensive studies of alloys of Fe with group VIII elements, such as Pt, Ru, Pd, on a variety of supports. They obtained spectra which exhibit peaks similar to the low isomer shift doublet obtained in the case of the PtFe/NaY sample. This suggests that the interaction of Fe with Pt in the PtFe/NaY zeolite may result in the formation of an alloy, with iron being zerovalent.

However, in studies of PtFe/NaY, PtCr/NaY, RhCr/NaY, and PtLa/NaY [10,11], it has been proposed that Fe, Cr, and La are not zerovalent, but remain electropositive when Pt is reduced. It was suggested that the multivalent irreducible transition metal ions (Fe^{2+}, Cr^{3+}, and La^{3+}), which are electrostatically bound to the zeolite matrix, interact chemically with the Pt metal particles, and thus act as “chemical anchors”.

The two aforementioned phenomena of Pt-Fe alloy formation and chemical anchoring of Pt by Fe^{2+} are, in fact, both consistent with the Mössbauer spectra. In particular, the isomer shift, IS, of iron is related to the s-electron density at the ^{57}Fe nucleus, and an increase in IS may be due to either a decrease in the number of s-electrons or an increase in the d-electron density (since the d-electrons partially shield the s-electrons from the nucleus). Accordingly, the IS is not a unique measure of the oxidation state of iron, as illustrated by the fact that Fe^{3+} and iron in Pt-Fe alloys both show values of IS close to 0.3 mm/s (with respect to metallic iron).

In view of the chemical evidence for anchoring of Pt by Fe, Cr, and La in Y-zeolite [10,11], we favor an interpretation of the Mössbauer spectra in terms of $(Pt_x - Fe)^{n+}$. Since the work function of platinum is lower than the second ionization potential of iron, electrons would be transferred from Pt particles to adjoining Fe^{2+} cations, thereby forming $(Pt_x - Fe)^{n+}$ species, in which the positive charge is smeared over several atoms. The positively charged particle would show a coulombic interaction with the electrostatic field within the zeolite framework, and this would lead to the stability of the particle against migration and agglomeration, i.e., chemical anchoring. Finally, it should be noted that although it is not possible, using Mössbauer spectroscopy, to distinguish between neutral alloy particles and those of the form $(Pt_x - Fe)^{n+}$, the present work shows conclusively that Pt-Fe interactions do exist in PtFe/NaY zeolite.

The additional doublet in the case of the re-oxidized PtFe/NaY sample is apparently due to some remaining Fe^{2+} having outer doublet characteristics. Its location was constrained to be the same as that for the doublet in the reduced PtFe/NaY sample. The Mössbauer spectrum of the PtFe/NaY sample after the second reduction is essentially the same as that after the initial reduction. This indicates the reversibility of the Pt-Fe interaction upon carrying out oxidation/reduction cycles.

4. Conclusion

The Mössbauer spectra for the PtFe/NaY sample are different from those for the standard Fe/NaY sample. The differences can be explained in terms of interaction between Pt and Fe, consistent with the observed chemical anchoring of Pt by Fe.

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