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Investigation of Dispersion and Localization of Platinum Species in Mazzite Using EXAFS

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Dispersion and localization of Pt species in mazzite zeolites (0.3% Pt) were studied using an *in situ* EXAFS technique in the fluorescence mode and transmission electron microscopy. It was shown that an ion exchange with a $Pt(NH_3)_4Cl_2$ solution followed by calcination led to the formation of small clusters of PtO_2 located in the mazzite channels. Small metal particles ($N_{Pt-Pt} < 4$) were found in the zeolite after the reduction of Pt species with hydrogen. The comparison of the results gained with the TEM and EXAFS techniques showed that most of the Pt metal particles were located in the zeolite channels. Treatment of the Pt/mazzite with humid hydrogen at 823 K was found to result in the agglomeration of Pt metal particles up to the diameter of mazzite channels (7.4 Å).

Introduction

Mazzite zeolites modified by platinum are known as effective catalysts of paraffin isomerization.[1-3] The structure[3,4] of mazzites is characterized by unidimensional porosity with a diameter of the main channels of 7.4 Å. The catalytic properties of Pt mazzites[5,6] depend on dispersion and localization of metal particles in zeolites, which are affected by preparation conditions such as impregnation, calcination, and reduction.

Various physicochemical techniques are now currently used to study metal dispersion in zeolites: H_2 chemisorption, catalytic test reactions, extended X-ray absorption fine structure (EX-AFS), transmission electron microscopy (TEM), etc.

However, as the particles become very small, it is difficult to obtain precise data on the size, localization, and structure using traditional techniques. Moreover, it is known that an interaction with the support (mazzite, alumina) can modify dramatically the adsorption properties of small metal particles, and that is why data on metal dispersion obtained from hydrogen chemisorption can be misleading even in a qualitative sense.[7-9] For instance, Sachtler[7,8] et al. have shown that the interaction of acid OH-groups with metal atoms leads to electron transfer, rendering metal clusters electron-deficient. These adducts do not adsorb hydrogen at room temperature, and H_2 chemisorption gives a lower H/metal ratio for zeolites.

Using high-resolution transmission electron microscopy, one can obtain information on particle size greater than 6—8 Å. However, the diameter of channels and windows of mazzite zeolites is 7.4 Å, and consequently most of the Pt particles located in the mazzite channels cannot be seen by transmission electron microscopy.

EXAFS is nowadays one of the powerful methods of local order characterization in highly dispersed metal catalysts.[10,11]

This method is especially useful for investigation of the environment of very small metal particles, which are very difficult to study by other techniques. In many cases, information can be collected (*in situ*) during the different steps of preparation such as calcination, reduction, and different treatments, when the catalyst becomes inaccessible to traditional surface analysis. Usually it is very difficult to perform structural investigations in systems with concentrations of modifying components below 1%. It was shown in the literature,[12] however, that the fluorescence EXAFS method might be used successfully with very small concentrations of modifying components and could provide information about local geometry about the atoms in very diluted systems.

In this paper, dispersion and localization of Pt species in mazzite (0.3 wt %) were studied using an *in situ* EXAFS technique in the fluorescence mode and transmission electron microscopy. Special emphasis was placed on following the influence of treatment with humid hydrogen on the dispersion of the platinum clusters located in mazzite. EXAFS was employed to investigate the structural environment of Pt atoms in the oxidized samples and *in situ* during reduction with hydrogen. This technique was also used to estimate the Pt particle size. TEM allowed the sizes of relatively large Pt particles to be measured.

Experimental Section

1. Mazzite Zeolites. The samples were prepared from a parent mazzite synthesized using a standard method[1] activated by steaming and acid leaching. After these treatments the Si/Al ratio in the framework was about 20 and the Si/Al total ratio was about 12. Ion exchange with a $Pt(NH_3)_4Cl_2$ solution was carried out to introduce Pt (0.3 wt %) into the structure of the zeolite. Then the mazzite was calcined in dry air at 723 K (3 L g^{-1} h^{-1}). The initial 1PtMaz sample was obtained after this treatment.

To prepare the 2PtMAz and 3PtMaz samples, 1PtMaz was reduced under dry hydrogen at 823 K. Then the sample was

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TABLE 1: Pt Content, Preparation Conditions, and Average Particle Size by TEM in Mazzites

sample	Pt content, wt %	preparation conditions	state of Pt after preparation	average particle size (TEM) after reduction, Å
1PtMaz	0.3	calcined under air after ion exchange at 800 K	oxidized	12.4
2PtMaz	0.3	1PtMaz after treatment 2 h at 823 K with hydrogen saturated with H_2O at 298 K, exposed to air	reduced	17.4
3PTMaz	0.3	1PtMaz after treatment 2 h at 823 K with hydrogen saturated with H_2O at 298 K, exposed to air	reduced	20.0

treated in a flow of humid hydrogen at 823 K for 2 (2PtMaz) and 4 h (3PtMaz). The hydrogen was saturated with water at room temperature ($P_{H_2O} \approx 32$ mbar). The preparation conditions of the samples are also presented in Table 1. The dispersion of Pt in all the samples after reduction at 720 K was checked by TEM.

2. EXAFS Experiments. EXAFS experiments were carried out at the Laboratoire pour l'Utilisation de Rayonnement Electromagnetique (Orsay) at the EXAFS4 beam line using synchrotron radiation from the DCI storage ring running at 1.85 GeV with an average current of 250 mA. Because of low Pt content (0.3%) in the samples, X-ray detection was performed in the mode of fluorescence using a double-crystal (Si_{III}) monochromator at the L_{III} edge of platinum (11563 eV). At the Pt L_{III} edge the estimated energy resolution of the monochromator was approximately 3 eV. The apparatus was identical to that designed by Lytle.[13] Two ion chambers were employed for X-ray detection. The first one, filled with He, was placed in front of the EXAFS experimental cell and was used to measure the intensity of the beam before the contact with the sample. The second chamber, filled with Ar, situated at ~90° from the X-ray beam, was used to measure the fluorescence arising from a zeolite sample (count rate ~5000–10 000/s).

The EXAFS experimental cell, equipped with a heater unit, water cooling system, thermocouples, and a system of gas circulation, allowed *in situ* treatment of the samples at temperatures 298–773 K. The experimental unit prior to the experiments was checked for gas leakage. The gases used for the experiments (He, H_2; Air Liquide) had a purity of 99.995%. The mazzite samples were reduced *in situ* using a temperature ramping of 5 deg/min. The recording time of measuring an EXAFS fluorescence spectrum (11 400–12 100 eV) was about 15 min. An example of an X-ray fluorescence spectrum near the L_{III} edge of Pt and an EXAFS spectrum measured in this work are shown in Figure 1.

3. Analysis of Data. Information on the local order of Pt atoms was extracted from both the L_{III} edge and the EXAFS part of the spectra. Qualitative data in that case were provided by the L_{III} edge area evolution as its intensity increases with the 5d band unoccupancy.[14,15] Quantitative information was given by the EXAFS spectra, which were analyzed in a conventional manner with a Victoreen fit for the preedge region and a k^3-weighted Fourier transform with Hanning's windows beyond the edge. To obtain a better signal to noise ratio, two or three spectra were averaged. The amplitude and phase shift parameters associated with the backscattering process were extracted from the reference compounds (PtO_2 powder, solution of H_2PtCl_6, and foil of platinum). The fitting of experimental and calculated EXAFS was carried out using the SIMPLEX software package.[16]

Results

1. Transmission Electron Microscopy. The particle size distribution histograms (Figure 2) calculated from TEM micrographs show that in the reduced Pt/zeolites detectable particles are in the range 6–30 Å. Smaller particles were found in the initial 1PtMaz sample. Treatment of mazzite with humid
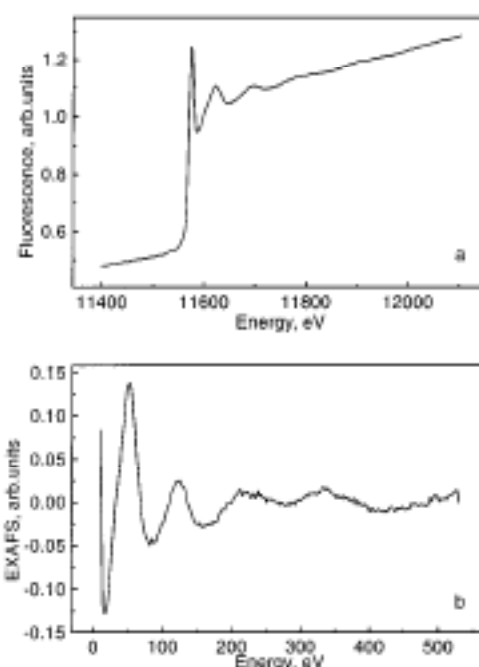

Figure 1. X-ray fluorescence spectrum (a) and EXAFS (b) of calcined 1PtMaz under He at 298 K.

hydrogen (2PtMaz, 3PtMaz) results in an increase in the diameter of Pt particles.

The average particle size was evaluated from the histograms (Figure 2) using the expression

$$d_{av} = \sum N_i d_i / \sum N_i$$

where d_i is the particle diameter measured from TEM photographs, N_i is the number of particles with diameter d_i. The diameters of more than 350 particles were measured to obtain each histogram. As could be seen from Table 1, d_{av} values found for the 2PtMaz and 3PtMaz samples are reasonably rather close and markedly exceed the average size of Pt particles detected in the initial 1PtMaz sample. The Pt–Pt coordination number for the first coordination sphere was calculated from the average particle diameter using a model of cuboctahedrons.[17] The coordination numbers obtained from TEM observations are compared with those coming from EXAFS analysis (Table 3). The differences are discussed later.

2. EXAFS Results. First, reduction of Pt species in calcined mazzite (1PtMaz) under dry hydrogen was studied.

Data on the reduction of platinum oxide clusters in 1PtMaz were obtained from EXAFS measured under flowing hydrogen at temperatures from ambient to 723 K. Within these conditions it was observed that the Pt–O coordination number did not change after treatment of the sample under hydrogen at temperatures lower than 473 K. The formation of Pt–Pt bonds in mazzite starts at 473 K and is completed at 573 K. Further increase in temperature up to 723 K did not lead to any remarkable changes in Pt–Pt and Pt–O coordination number or interatomic distances.
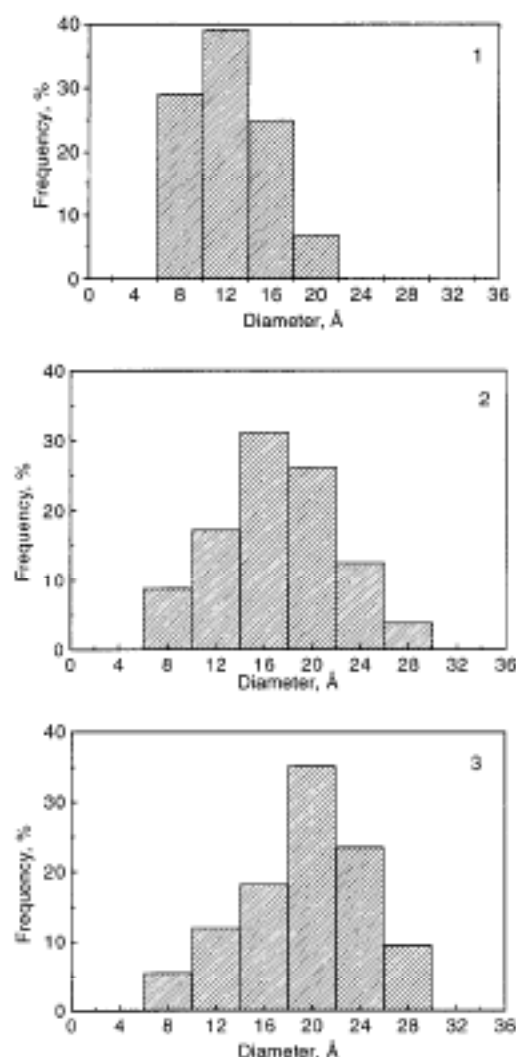
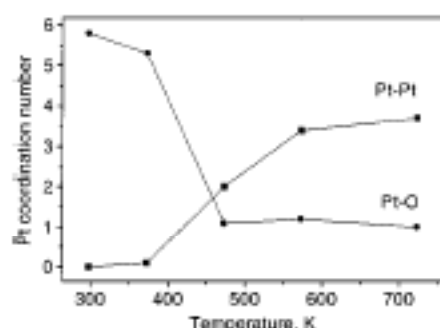**Figure 2.** Histograms of Pt particle size: (1) 1PtMaz, (2) 2PtMaz, (3) 3PtMaz.

Figure 3. Dependencies of Pt–Pt and Pt–O coordination number in the 1PtMaz sample on the temperature of treatment under hydrogen.

TABLE 2: EXAFS Results for the 1PtMaz Sample ($\Delta R = 0.05$ Å, $\Delta N = 20\%$)

conditions	N_{Pt-Pt}	R_{Pt-Pt}, Å	N_{Pt-O}	R_{Pt-O}, Å
He or H_2, $T = 298$ K	0		5.8	2.03
H_2, $T = 373$ K	0.1	2.73	5.3	2.07
H_2, $T = 473$ K	2.0	2.70	1.1	2.04
H_2, $T = 573$ K	3.4	2.70	1.2	2.07
H_2, $T = 723$ K	3.7	2.71	1.0	2.03

The structural parameters including coordination number and interatomic distances of the 1PtMaz sample are presented in Table 2. In Figure 3, the evolution of the coordination number in terms of platinum and oxygen neighboring is presented as a
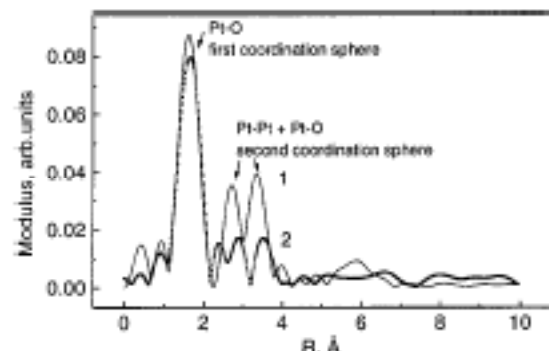

Figure 4. Moduli of Fourier transform (k^3, Hanning's windows 30, 60, 300, 400 eV): (1) PtO$_2$; (2) 1PtMaz, calcined under air at 800 K.
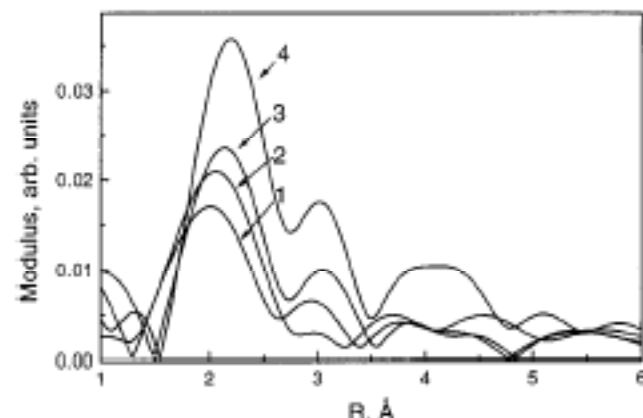

Figure 5. Moduli of Fourier transform (k^3, Hanning's windows 30, 60, 240, 300 eV) for reduced mazzites at 723 K: (1) 1 PtMaz, (2) 2PtMaz, (3) 3PtMaz, (4) bulk Pt.

TABLE 3: Diameter of Pt Particles and Pt–Pt Coordination Numbers Calculated from TEM and EXAFS Data

	TEM		EXAFS
sample	average Pt particle size, Å	N_{Pt-Pt} cuboctahedron	N_{Pt-Pt}
1PtMaz	12.4	7.4	3.7
2PtMaz	17.4	8.6	5.1
3PtMaz	20.0	9.3	6.4

function of temperature. Fourier transform moduli for 1PtMaz, calcined in air at 800 K and PtO$_2$, are shown in Figure 4.

The Fourier transform moduli of the starting 1PtMaz sample and 2PtMaz and 3PtMaz zeolites treated with humid hydrogen for 2 and 4 h as well as the modulus of bulk metal are presented in Figure 5. It is clear that such a treatment of the initial Pt/mazzite leads to an increase in the intensity of the moduli corresponding to the occurrence of PtPt bondings in the first coordination sphere of Pt atoms. Treatment of the initial 1PtMaz with humid hydrogen longer than 4 h (3PtMaz) did not give any further changes in EXAFS spectra. The N_{Pt-Pt} coordination numbers for the samples treated with humid hydrogen obtained from EXAFS analysis are presented in Table 3. An example of the quality of adjustment between experimental and calculated data for 3PtMaz is shown in Figure 6.

Exposure of the reduced Pt/mazzite zeolite to air at room temperature results in considerable changes in EXAFS spectra. As can be noticed from Figure 7, exposure of the reduced sample to air results in a shift of the Fourier transform modulus to lower interatomic distances. The subsequent treatment of the sample with hydrogen at room temperature was found to restore the initial EXAFS spectrum.
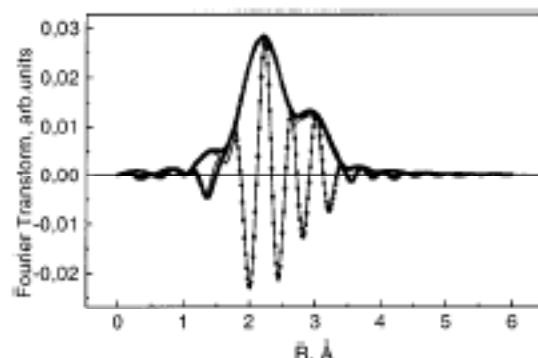
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Figure 6. Results of fitting for the 3PtMaz sample (723 K, in H_2), FT modulus and imaginary part: (—), experimental curve, (—■—) calculated curve.
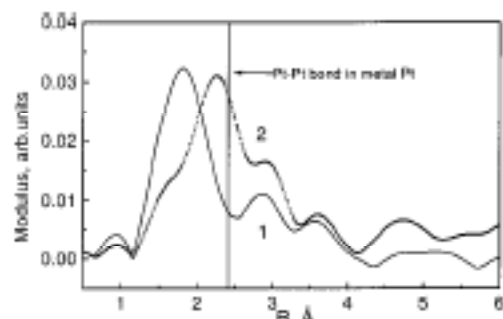

Figure 7. Moduli of Fourier transform (k^3, Hanning's windows 30, 60, 300, 400 eV) for the 3PtMaz sample. The sample was prereduced under hydrogen and then exposed subsequently to air (1) and to hydrogen (2) at 298 K.

Discussion

Let us first discuss the local order of Pt species that are the precursors of metal clusters in the calcined 1PtMaz sample. As can be seen from Table 2, Pt atoms in the calcined sample are surrounded in the first coordination sphere like in PtO_2 by six atoms of oxygen. However, comparison of Fourier transform moduli for the 1PtMaz sample and PtO_2 gives evidence to suggest that Pt atoms in mazzite have a different type of coordination in the second coordination sphere from that existing in oxide (Figure 4). The intensities of the peaks corresponding to the second coordination sphere were much lower for oxidized clusters located in the zeolite than in bulk oxide. According to the literature data of Joyner[18-21] et al., the temperature of calcination has significant influence on the metal particle size in zeolites. That is why it seems to be reasonable to propose that agglomeration of Pt ions into clusters of platinum oxide starts at the stage of calcination. In our case, according to EXAFS data, it seems to be reasonable to suggest that after calcination mainly small clusters of PtO_2 with considerably fewer Pt atoms in the second coordination sphere can be found in the 1PtMaz sample. These very small platinum oxide clusters seem to be the precursors of highly dispersed metal Pt species after reduction.

As already mentioned, reduction of Pt in mazzites starts from 473 K and is completed at 573 K (Figure 3). Reduction results in a formation of very small metal particles with Pt—Pt coordination number 3.8 (Tables 2, 3). The Pt—Pt distances in these small Pt particles were found to be shorter (2.70—2.73 Å) than in the bulk metal (2.77 Å). Although very weak, coordination of Pt atoms with oxygen ($N_{Pt-O} \approx 1$) was still detected. Exclusion of the platinum—oxygen bond from EXAFS fitting was found to lead to considerably worse agreement with experiment. Such Pt—O bonding in fully reduced samples

is in good agreement with the previous works[18-23] in which it was shown that this bonding arises not from incomplete reduction of Pt oxide in the catalysts but from platinum interaction with oxygen from the zeolite framework. Joyner and Shpiro, for instance, saw the Pt—O bonding in the reduced Pt/HZSM-5 zeolites at 1.94—1.98 Å with a Pt—O coordination number of about 0.5—2. The value of N_{Pt-O} close to 1, which we measured in our case (Table 2), indicates that at least most of the Pt atoms are bonded to the zeolite and, as a result, strong metal support interaction should be considered.

Another type of interaction that may affect the small Pt particles in mazzites is related to a formation of a O—H···Pt bridged structure. Due to the polarization by positively charged protons of the hydroxyl groups, the small Pt particles change their properties, for example, their ability to adsorb hydrogen.[7-9] It should be mentioned here that the EXAFS technique is not able to follow coordination of Pt atoms by protons. However, in our case, this interaction cannot be excluded.

A suggestion for strong chemical bonding between small metal particles and the support is confirmed by the data on methane deuterium exchange on zeolites studied on a series of Pt/Al_2O_3 and Pt/mazzite catalysts.[6] It was found that catalysts with high metal dispersion had higher activity in methane deuterium exchange. For mazzite, the activity per atom was found to be considerably higher for smaller metal particles than for larger ones. This effect was explained by positive charging of small metal particles in zeolites due to an interaction with oxygen atoms of the support and protons of the superacid hydroxyl groups. This interaction seems to stabilize Pt—CH_3 species, whose formation limits the rate of the exchange reaction. It was also suggested that the interaction between protons of zeolite groups and Pt species would be more noticeable for smaller particles than for the larger ones.

The N_{Pt-Pt} coordination numbers for the first coordination sphere calculated from electron microscopy data using a model of cuboctahedrons and from EXAFS analysis are presented in Table 3. The highest Pt—Pt coordination was found in the 3PtMaz sample both by TEM and by EXAFS techniques, whereas the smaller N_{Pt-Pt} was observed for the initial 1PtMaz sample. This means that treatment with water vapor used to obtain the 2PtMaz and 3PtMaz samples results in some sintering of the Pt particles. The low Pt—Pt coordination number ($N_{Pt-Pt} < 4$) found for the 1PtMaz sample indicates a very small size of Pt particles. A value of Pt—O coordination close to 1 gives evidence to suggest that due to a strong interaction of Pt with zeolites, the structure of clusters is affected by the zeolite. The shorter Pt—Pt distance (Table 2) found in the small Pt clusters relative to that in the bulk metal ($d_{Pt-Pt} = 2.77$ Å) seems to be another argument in favor of the suggestion that the structure of small Pt clusters is different from the bulk metal.

The structure of small Pt clusters located in the zeolite channels is likely to be strongly dependent on the structure of mazzite, and models assuming coordination of Pt atoms similar to that in bulk metal are far from being correct. For example, possible models for these Pt clusters based on Pt_4 tetrahedrons with an effective diameter 5.5 Å or bidimensional rafts cannot be excluded.

As has been stated previously, the limit of detection of TEM (6—8 Å) is about of the diameter of the main channels in mazzite (7.4 Å). So, most of the particles seen by TEM are, therefore, probably localized on the external surface of the zeolite but not in the channels. The N_{Pt-Pt} coordination number deduced from TEM data using a model of cuboctahedrons[17] is consequently significantly larger than that measured by EXAFS, which takes

into account all the Pt particles (Table 5). This indicates that a large number of Pt particles are too small to be detected by TEM.

An attempt was made to estimate the relative Pt concentrations inside and outside the zeolite microcrystallites A model of Pt_4 tetrahedrons ($N_{Pt-Pt} = 3$) was adopted for Pt clusters located in 1PtMaz, and a model of Pt_{13} cuboctahedrons ($N_{Pt-Pt} = 5.5$), whose size (8.3 Å) is compatible with the diameter of mazzite channels, was taken for metal particles in the volume of the 3PtMaz zeolite, which has been treated using water sintering. The PtPt coordination numbers for the particles on the external surface of the zeolite were calculated from the TEM data (Table 3). The calculations of the metal distribution showed that in 1PtMaz 85% of Pt should be located in the mazzite channels and 15% of Pt are at the external surface. For 3PtMaz the corresponding values are 75 and 25%. It should be noted, however, that this estimation is only qualitative because of the lack of more accurate information about the structure of small Pt particles located in the zeolite channels.

Thus, in this discussion we will assume that small Pt particles are predominantly localized in the channels of zeolites. The first argument in favor of this assumption is the low Pt–Pt coordination number ($N_{Pt-Pt} < 7$). The second argument in favor of this assumption comes from the sintering phenomenon in the presence of water vapor. The treatment with humid hydrogen results in an increase in the N_{Pt-Pt} coordination number due to growth of metal particles in the zeolite. However, as mentioned above, the coordination number N_{Pt-Pt} measured by EXAFS reaches a limit (< 6.4) as a function of the duration of the sintering treatment (4 h). This is a good indication that the size of most of the Pt particles is limited by the diameter of the mazzite channels in which they would be preferentially localized.

Pt particles in mazzites were found to present unusual properties regarding their interaction with oxygen at room temperature. The Fourier transform moduli for the 3PtMaz sample submitted successively to air and under H_2 at 298 K are presented in Figure 7. As one can see, submission of hydrogen to the Pt mazzite zeolite shifts the position of the 3PtMaz modulus from the oxidized state to the reduced metal. This effect can be explained by easy reoxidation of small metal particles containing very few Pt atoms under air and then their reduction to the metal state under hydrogen.

These data are in agreement with the earlier work of Gallezot and Boudart.[24] These authors showed by using a radial distribution function calculated from the X-ray scattering data that the structures of small Pt particles located in the supercages of Y-type zeolites were completely disrupted if they were exposed to O_2 at 773 K. However, normal platinum structure can be restored by treatment with H_2 at room temperature.

In our opinion, easy reducibility of small Pt particles after admission to hydrogen shows that the structure of Pt particles does not completely break down during exposure to air. This seems to be additional evidence for the strong interaction between metal and support that might be realized by a direct chemical bonding of Pt atoms with oxygen of the zeolite framework.

Conclusions

Impregnation of mazzite with Pt followed by calcination results in the formation of small PtO_2 particles located presumably within zeolite channels.

Treatment of calcined mazzites with hydrogen leads to the reduction of Pt species, which starts at 473 K and is completed at 573 K. After the reduction, small metal clusters with low Pt–Pt coordination and a chemical bonding with oxygen atoms of the zeolite lattice were found. Treatment of Pt mazzite with humid hydrogen causes agglomeration of Pt particles up to the diameter of mazzite channels (7.4 Å).

Metal particles can be reoxidized under air and reduced again under hydrogen at room temperature.

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