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Preparation of Metal/Zeolite Catalysts: Formation of Palladium Aquocomplexes in the Precursor of Palladium–Mordenite Catalysts

Previous research has revealed that the catalytic performance of metal/zeolite catalysts can be significantly modified by exposing the catalyst precursor to H_2O vapor during the period after calcination, but before reduction. For bimetallic PdCo/NaY catalysts used for CO hydrogenation, the selectivity was changed from predominant production of oxygenates to predominant production of higher hydrocarbons (*1*). For Pt/H-mordenite catalysts, this water treatment has been reported to improve the alkane isomerization activity (*2, 3*). Although it is certain that Lewis sites are transformed to Brønsted sites by reaction with H_2O (*4, 5*), the activity of the catalyst is affected most when the water is added after calcination, when the noble metal is present as ligand-free ions (*6*). This observation led to the hypothesis that complexation of transition metal ions with water might be instrumental for the observed effects.

In zeolites containing cages, such as Y, the formation of metal–ligand complex ions appears to incite their migration from small to large cages (*7*). In cageless zeolites such as mordenite, however, it is not clear a priori, whether hydration of transition metal ions will increase or decrease their reducibility and whether it will ultimately result in higher or lower metal dispersion. We have therefore undertaken research to clarify these issues. Palladium supported in H-mordenite (Pd/HMor) or Na-mordenite (Pd/NaMor) has been tested using methylcyclopentane as a probe reaction; temperature-programmed reduction (TPR), desorption (TPD), and extended X-ray absorption fine structure (EXAFS) spectroscopy have been used to characterize the effects of water treatment on the samples.

The catalysts were prepared by ion-exchange of $Pd(NH_3)_4^{2+}$ ions into either NH_4Mor (UOP, LZ-M-8, Si/Al = 9.3) or NaMor (UOP, LZ-M-5, Si/Al = 5.4) as described previously (*8*). Catalysts with two different weight loadings were prepared: 3% Pd for characterization and 0.3% Pd for the reaction studies. All samples were calcined in a high flow of UHP O_2 (1000 ml/min/g-cat) from RT to 510°C at 0.5°C/min. This calcination decomposes the ammine complexes and transforms the NH_4Mor into HMor. Water treatment, if desired, was accomplished by flowing UHP He (100 ml/min) through a water saturator maintained at 11.4°C (~10 Torr). All water was assumed to be absorbed by the catalyst bed, and the length of the water treatment was calculated to add 12 wt% water to the catalyst sample. TPR, TPD, and EXAFS experiments were performed following the procedure in Refs. (*8*) and (*9*), respectively. For the reaction studies, ~100 mg of either 0.3% Pd/HMor or 0.3% Pd/NaMor was used. All catalysts were first calcined to 510°C and reduced to 350°C. The H_2 flow rate was 20 ml/min, the vapor pressure of MCP in the reactor was 40 Torr, the total pressure was 1 atm, and the reaction temperature was 240°C.

Figure 1 shows the reduction profiles for wet and dry Pd/HMor and Pd/NaMor (1a–d). The differences are rather dramatic. A much higher temperature (~80°C for Pd/NaMor and ~120°C for Pd/HMor) is required to reduce the samples that were exposed to H_2O. Also shown in Fig. 1 are reduction profiles for Pd/HMor that had been reduced to 250°C and subsequently exposed to O_2 at 100 or 500°C. From previous experience, it is known that PdO is formed at 100°C; at 500°C, the oxide reacts with

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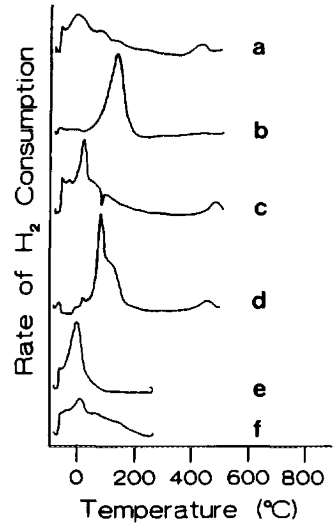

FIG. 1. TPR Profiles of (a) 3% Pd/HMor-dry, (b) 3% Pd/HMor-wet, (c) 3% Pd/NaMor-dry, (d) 3% Pd/NaMor-wet, (e) 3% Pd/HMor after reduction to 250°C and oxidation to 100°C, and (f) 3% Pd/HMor after reduction to 250°C and oxidation to 500°C.

protons to form Pd^{2+} ions and H_2O. Accordingly, the TPR profile after reoxidation to 500°C resembles the one obtained directly after calcination.

Because all treatments were performed in quartz reactors, it was possible to monitor the color changes of the samples. These color changes are summarized in Fig. 2. The pink color of the samples after calcination is assumed to be that of mordenite supported Pd^{2+} ions (*10, 11*). The samples turn yellow if exposed to H_2O, indicating the formation of an aquo-complex (*12*). These color changes are consistent with changes in the TPR profiles in Fig. 1, and they confirm that the PdO formed at low temperatures reacts with zeolite protons at higher temperatures to form Pd^{2+} and H_2O.

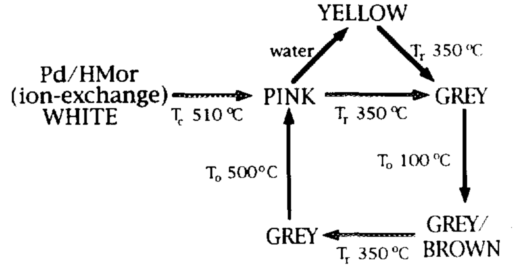

FIG. 2. Color changes of Pd/HMor after various treatments (T_c = calcination temperature, T_r = reduction temperature, and T_o = oxidation temperature).

The crucial point with respect to the issue motivating the research is that exposure of the calcined sample to H_2O changes both the reduction profile and the color. The fact that H_2O is able to ligate to Pd^{2+}, but not to PdO, justifies the conclusion that Pd^{2+} are present in the sample after calcination. It is noteworthy that formation of an aquo-complex stabilizes the Pd^{2+} ions significantly, so that a much higher temperature is required for their reduction. Apparently, the $Pd(H_2O)_n^{2+}$ coordination shell is more favourable than the coordination provided by the walls of the zeolite.

The area under the TPR profiles can be integrated and used to calculate the change in Pd valence, ΔV, during reduction. The values in Table 1, were obtained by integrating the profiles between -40 and 500°C. With the exception of dry Pd/HMor, all ΔV values agree, within experimental error (5%), with the expected value of 2.0. It is notable that the Pd^{2+} ions in dry Pd/HMor cannot be fully reduced to Pd^0 even at 500°C. Apparently, in the absence of H_2O, some Pd^{2+} are highly stabilized in the zeolite; the side pockets are likely candidates. As the HMor used in this study contains ca. four Al^{3+} per unit cell, it is reasonable that some of the side pockets will carry two negative charges; in these positions the Pd^{2+} ion would be coordinated by zeolite oxygens in a distorted octahedron (*13*).

The metal dispersions measured by H_2-TPD as (H/Pd ratio) and EXAFS (as coordination number) are shown in Table 1 for samples that have been calcined to 510°C and reduced to 250°C. Both sets of data consistently show that the Pd particle size is larger in samples that have been exposed to H_2O prior to reduction. In addition, the EXAFS data confirm that the protons in the HMor sample have an anchoring effect, i.e.,

TABLE 1

TPR, TPD, and EXAFS Data for Pd/HMor and Pd/NaMor

Catalyst		ΔV	H/Pd	CN_{Pd-Pd}	r_{Pd-Pd} (Å)	σ^2
3% Pd/HMor	Dry	1.78	1.1	2.11	2.70	0.0050
	Wet	2.00	0.81	6.19	2.73	0.0015
3% Pd/NaMor	Dry	1.98	1.2	4.58	2.74	0.0043
	Wet	1.96	0.87	6.15	2.74	0.0005

the Pd particles are smaller in HMor than in NaMor. The increase in particle size for the wet samples can most easily be explained by accepting that the mobility of the $Pd(H_2O)_n^{2+}$ ion is larger than that of the bare Pd^{2+} ion due to less interaction with the zeolite framework. A similar increase in mobility has been observed for $Pd(NH_3)_4^{2+}$ in Y zeolite (*7*). As a consequence of the higher mobility, the aquocomplex can more easily travel to a reduced Pd particle covered by chemisorbed H atoms. As always, the ultimate particle size is determined by the ratio of two rates: nucleation and growth. The growth rate of Pd nuclei is determined by the mobility of the Pd^{2+} ions. Formation of the aquocomplex thus leads to larger Pd particles.

Results of the catalytic MCP reaction study are shown in Table 2. Pd/NaMor (wet or dry) is hardly active for this reaction. This is in line with the very large size of the metal particles. The only chemical anchors in these samples are the protons that are produced by metal reduction. As was shown previously, interaction of MCP with these protons induces growth of the Pd particles (*14*). For the Pd/HMor samples, the water treatment has a slight negative effect on the total activity of the sample, but also leads to an increased selectivity and yield towards ring enlargement products. As ring enlargement occurs via a bifunctional mechanism (*15*), this selectivity correlates with the ability of the catalyst to isomerize paraffins. The increase in ring enlargement could be due to an increase in the acidity of the sample after water treatment, or a larger concentration of Pd-proton adducts, which might act as "collapsed sites" in the bifunctional mechanism (*16, 17*).

TABLE 2

Catalytic Properties of Pd/Mor

Catalyst	$X(\%)^a$	$S_{CR}(\%)^b$	$S_{RO}(\%)^c$	$S_{RE}(\%)^d$
0.3% Pd/HMor-dry	3.13	9.37	6.82	83.83
0.3% Pd/HMor-wet	2.73	7.2	5.3	87.49
0.3% Pd/NaMor-dry	0.08	0	51.3	48.7
0.3% Pd/NaMor-wet	0.08	0	54.3	45.69

[a] Conversion at 190 min TOS.
[b] Cracking selectivity.
[c] Ring opening selectivity.
[d] Ring enlargement selectivity.

In conclusion, water treatment of Pd/HMor and Pd/NaMor after calcination, but before reduction results in several changes in the sample. Metal reduction requires a higher temperature due to the formation of aquocomplexes. The higher mobility of these complexes leads to larger metal particles. Although the water treatment has a slight negative effect on the catalytic activity of Pd/HMor (in stark contrast to Pt/HMor), the yield of ring enlargement products increases. As observed previously for Pd in Y zeolite, no autoreduction of $Pd(NH_3)_4^{2+}$ occurs during programmed calcination, and redispersion of PdO by zeolite protons is effective. The reduced Pd particles are smaller in the H form of the zeolite than in the Na form. Finally, color changes during calcination and reduction provide detailed information about the chemical processes that occur.

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