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Non-acidic Pd/Y Zeolite Catalysts from Organopalladium Precursors: Preparation and Catalytic Activity in MCP Reforming

Carlo Dossi,* Rinaldo Psaro,* Renato Ugo,* Z. Conrad Zhang,†,[1]
and Wolfgang M. H. Sachtler†

*CNR Center and Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy; and †V. N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208

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Pd/NaY and Pd/NaHY catalysts have been obtained by chemical vapor deposition of allylcyclopentadienylpalladium and characterized by temperature-programmed reductive decomposition and by EXAFS. In the conversion of methylcyclopentane at 300°C, the non-acidic catalyst shows a constant 100% selectivity towards ring-opening without significant coke deposition. In particular, the deactivation rate is lower than with the non-acidic system prepared by a conventional method. With the bifunctional Pd/NaHY catalyst ring enlargement is predominant, and significant coke deposition occurs as confirmed by temperature-programmed oxidation measurements. © 1994 Academic Press, Inc.

INTRODUCTION

Since the early introduction of Pt/KL catalysts for the selective aromatization of linear alkanes (1), much work has been devoted to the preparation and characterization of non-acidic Pd and Pt catalysts as a possible alternative to the classical bifunctional systems for hydrocarbon reforming (2–4).

Acidic sites on reforming catalysts are known to initiate deposition of "coke," which is a major cause of catalyst deactivation (5). In the case of zeolites, the ion-exchange methodology that is conventionally used for Pd and Pt, starting from $[\mathrm{Pd(NH_3)_4}]^{2+}$ and $[\mathrm{Pt(NH_3)_4}]^{2+}$, respectively (6, 7), inherently leads to the stoichiometric formation of acid sites (protons) upon reduction of the exchanged cation:

$$M^{2+}(\mathrm{Pd, Pt}) + \mathrm{H_2} \rightarrow 1/n\, M_n^0 + 2\,\mathrm{H}^+.$$

Where protons are not desired, they have to be re-exchanged against Na^+ ions in aqueous solution or by reaction with sodium azide (8).

The development of a "one-step" preparation of non-acidic Pd/zeolite catalysts would instead rely upon the use of neutral metal precursors of suitable size and reactivity, which can be introduced inside cages without altering the original distribution of positive charges. The use of organopalladium complexes is particularly promising in this sense, since zerovalent metal particles can be obtained through the reductive elimination of volatile ligands:

$$\mathrm{PdL}_x/\text{zeolite} + x/2\,\mathrm{H_2} \rightarrow 1/n\,\mathrm{Pd}_n^0 + x\,\text{L–H}.$$

In addition, incipient wetness solvent deposition, as well as chemical vapor deposition, can be used for sample preparation.

In this paper, the applicability of suitable organopalladium complexes for the preparation of non-acidic Pd/Y catalysts will be investigated and critically discussed, using the methylcyclopentane ring-opening reaction for probing the nature of the active sites.

EXPERIMENTAL

Catalyst Preparation

$[\mathrm{Pd}(^3\eta\text{-}\mathrm{C_3H_5})(^5\eta\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Pd}(^3\eta\text{-}\mathrm{C_3H_5})_2]$($^3\eta$-$\mathrm{C_3H_5}$, allyl; $^5\eta$-$\mathrm{C_5H_5}$, cyclopentadienyl) were synthesized according to literature methods (9, 10). $[\mathrm{Pd(CH_3CN)_2Cl_2}]$ was purchased from Strem Chemicals, and used as received. NaY (LZY-52) and NaHY (LZY-72) were commercial zeolites obtained from U.O.P., Linde Division.

For incipient wetness impregnation, the organopalladium precursors were dissolved in a suitable solvent, *n*-pentane for $[\mathrm{Pd}(^3\eta\text{-}\mathrm{C_3H_5})_2]$, and acetonitrile for $[\mathrm{Pd(CH_3CN)_2Cl_2}]$. The NaY zeolite was heated in flowing argon from 25 to 400°C over 2 h, in order to remove physisorbed water, and impregnated with the exact volume of solution which fills the pores completely. The solvent was then removed in vacuo (10^{-3} mbar) by gently heating to 50–60°C.

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[1] Present address: AKZO Chemicals, Inc., 1 Livingstone Avenue, Dobbs Ferry, NY 10522.

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For chemical vapor deposition (CVD), both NaY and NaHY zeolites were first placed over a quartz frit in a U-tube reactor, and heated in flowing argon from 25 to 400°C over 2 h. After cooling to room temperature, a weighed amount of $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$ was placed at the bottom of the U-tube under argon. Sublimation was carried out overnight in flowing argon (10 ml/min) at 25°C (11).

The kinetics of thermal decomposition to metal, of the absorbed organometallic precursor, was studied by temperature-programmed reductive decomposition (TPRD). The supported material was heated in a H_2(5%)/He flow from ambient temperature to 500°C at 3°C/min. Decomposition products were then detected downstream by on-line quadrupole mass spectrometry. Further details have been reported elsewhere (12).

The two catalysts prepared by CVD will be indicated by "Pd/NaY" and "Pd/NaHY." A non-acidic Pd/NaY catalyst was prepared by ion-exchange of a dilute solution of $[Pd(NH_3)_4](NO_3)_2$, and following calcination, reduction, and neutralization of acid sites, as already reported (8). This catalyst will be indicated by "neutr.-Pd/NaY(IE)."

Conversion of Methylcyclopentane

The methylcyclopentane (MCP) reaction was carried out at 300°C and atmospheric pressure in a continuous-flow, glass microreactor using a H_2/MCP ratio of 20 : 1. On-line analysis of reactants and products was made by a Carlo Erba Instruments 5160 gas chromatograph equipped with a 50-m, 0.2-mm PONA capillary column and flame ionization detector.

After the catalytic reaction, the used catalysts were analyzed for their carbon content by temperature-programmed oxidation (TPO). The samples were heated from room temperature to 500°C at 3°C/min in an O_2(2%)/He flow. The CO_2 formed by combustion of the carbonaceous deposits was monitored as a function of the increasing temperature by quadrupole mass spectroscopy and gas chromatography, as reported elsewhere (13, 14).

EXAFS Sample Preparation

EXAFS spectroscopy was applied to evaluate the Pd particle sizes prepared by the vapor phase absorption of $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$ in zeolite NaY after different pretreatments. A dehydrated NaY sample which absorbed the Pd precursor in an Ar stream at room temperature for 12 h is denoted by Pd/NaY-1. A sample further reduced in H_2 at a rate of 3°C/min to 300°C is denoted by Pd/NaY-2. Pd/NaY-3 is a sample after similar pretreatments but followed by MCP conversion at 300°C at atmospheric pressure for 3 h. All samples used for EXAFS study were about 400 mg with Pd loading of 2 wt%. The powdered samples after corresponding pretreatments were sealed in glass tubes. The glass tubes were opened in a glove box, and the samples were pelletized and sealed following the procedure reported previously (15).

EXAFS Data Collection

EXAFS data, following the Pd *K*-edge (24350 eV), were collected at an electron energy of 2.5 GeV and beam current of 120–180 mA in beam line X-18B of the National Synchrotron Light Source (NSLS) at Brookhaven. The monochromator (Si-220) was detuned by 30% during data collection. A stainless steel cell was used in transmission measurement at liquid-nitrogen temperature. A detailed description of the cell and sample handling can be found elsewhere (15).

EXAFS data were analyzed with the University of Washington software package. The *R* window used for inverse Fourier transform is from 2.0 to 3.0. A 0.025-mm Pd foil were used as reference structure for EXAFS analysis of the Pd particle size. The coordination number (CN) of Pd in reference foil is taken as 12, and the nearest Pd–Pd bond distance (*R*) in the foil is assigned to 2.75 Å.

RESULTS

Choice of the Organometallic Precursor

Most of the organopalladium complexes having the correct size and geometry to enter and diffuse throughout zeolite channels are soluble in organic solvents; they were introduced into the zeolite support by incipient wetness impregnation. $[Pd(^3\eta\text{-}C_3H_5)_2]$ as the pentane solution was initially chosen for impregnating the NaY zeolite. Unfortunately, zeolite cavities are completely filled with this non-polar solvent, preventing the organometallic precursor from entering and diffusing inside the zeolite structure. In addition, the complex started to decompose already during the removal of the solvent *in vacuo*. A gray-black material was left after impregnation; it was inhomogeneously spread throughout the sample.

A different strategy was then developed in the case of the $[PdCl_2(CH_3CN)_2]$ complex, using the acetonitrile ligand as the impregnation solvent. This polar solvent should help to drive the precursor molecules into the cages, without inducing their decomposition upon solvent removal. As expected, a very homogeneous yellowish powder was obtained after incipient wetness impregnation. The kinetics of ligand removal in flowing hydrogen to form entrapped metal particles was investigated by TPRD. CH_3CN was evolved from the catalyst in two steps, a narrow peak at 80°C and a second, broad one centered at 300°C (Fig. 1a). Pure NaY zeolite impregnated with pure acetonitrile gave a TPRD profile with a single evolution peak centered at 300°C (Fig. 1b). The high tem-

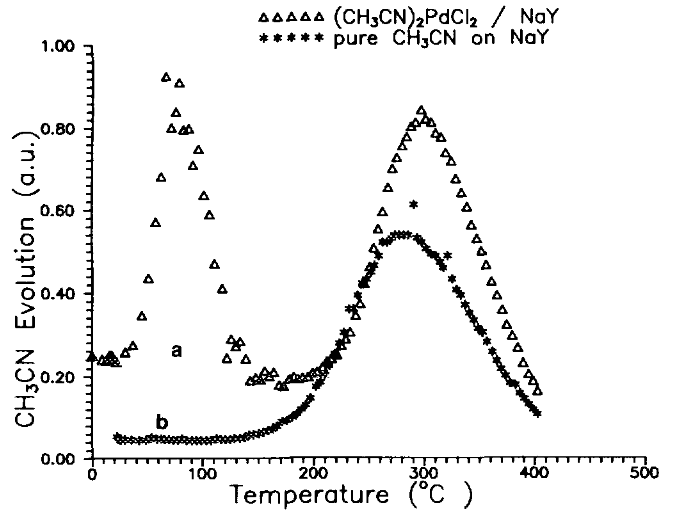

FIG. 1. (a) TPRD profile of CH_3CN evolution (at m/z = 41) in $H_2(5\%)/He$ flow of $[PdCl_2(CH_3CN)_2]$ on NaY; (b) TPRD profile of CH_3CN evolution in $H_2(5\%)/He$ flow of pure CH_3CN adsorbed on NaY.

perature peak in the TPRD profile of $[PdCl_2(CH_3CN)_2]$/NaY is to be ascribed to the acetonitrile solvent clathrated inside cages, whereas the low temperature evolution is due to the decomposition of the palladium complex located on the external zeolite surface. Accordingly, $[PdCl_2(CH_3CN)_2]$ deposited on silica decomposes in TPRD in a single, narrow peak at 90°C (Fig. 2).

Previous work on Re carbonyls (16) indicated that the chemical vapor deposition (CVD) technique is the most effective method for introducing organometallic precursors inside zeolites. After a long search, the $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$ complex was found to meet all the requirements of size, volatility, and thermal stability to be deposited from the vapor phase, at 25°C in Ar flow, inside large-pore NaY zeolite (11). The entrapped $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$ complex is then easily transformed into metallic particles by removal of ligands in hydrogen atmosphere. A TPRD investigation (Fig. 3) shows that propane is evolved in a single and narrow path at 70°C, whereas a broader evolution peak of cyclopentane is observed around 100–120°C.

The effect of intrazeolitic protons on the chemical reactivity of the intrazeolitic Pd precursor has been studied in a model catalyst, by depositing $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$ inside a NaHY zeolite, where Na^+ ions have been partially replaced by protons. The allyl ligand is still removed in TPRD as propane in the same temperature range (around 70°C) as for the non-acidic Pd/NaY sample. On the contrary, the evolution of cyclopentane is significantly less intense, being spread out over a much larger temperature range (compare Figs. 3 and 4).

The sharpness of the evolution profile of cyclopentane can here be assumed as a probe of the presence of intrazeolitic protons, probably favoring cationic polymerization of cyclopentadiene prior to its hydrogenation to cyclopentane.

Catalytic Activity in Methylcyclopentane Reforming

Methylcyclopentane (MCP) reaction at atmospheric pressure was chosen as a model reaction in order to investigate the mono- or bifunctional nature of the active sites in Pd/Y zeolite catalysts. The $[PdCl_2(CH_3CN)_2]$-based catalyst did not show any catalyst activity for this reaction as a result of the presence of large Pd particles on the external surface of zeolite crystal. In contrast, Pd/NaY

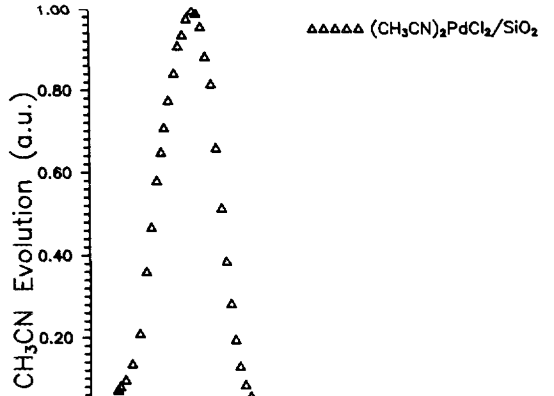

FIG. 2. TPRD profile of CH_3CN evolution (at m/z = 41) in $H_2(5\%)/He$ flow of $[PdCl_2(CH_3CN)_2]/SiO_2$.

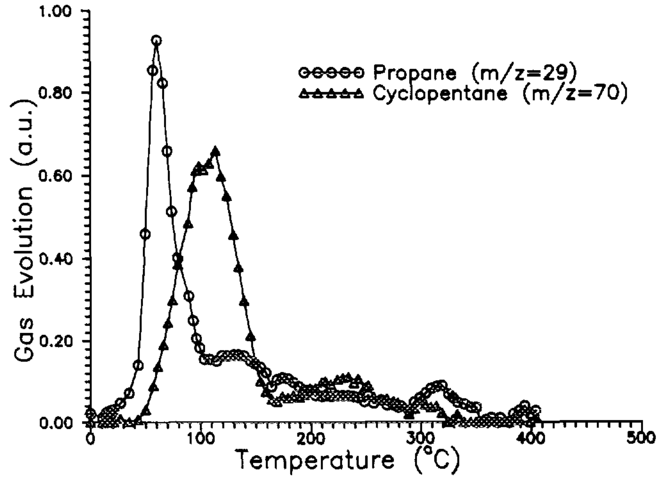

FIG. 3. TPRD profiles in $H_2(5\%)/He$ flow of $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]/NaY$.

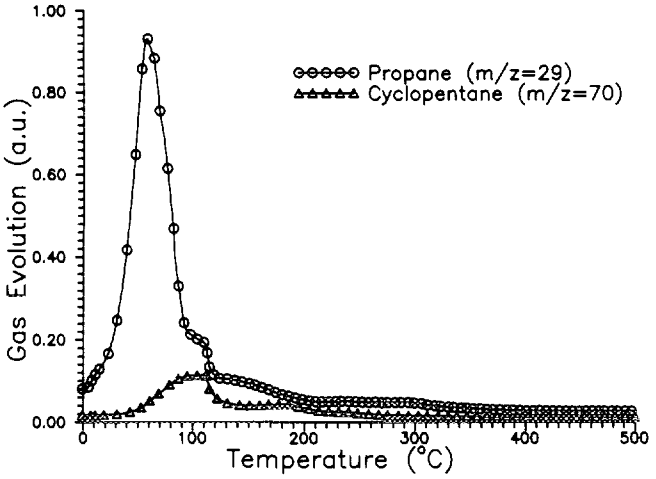

FIG. 4. TPRD profiles in H_2(5%)/He flow of [Pd($^3\eta$-C_3H_5)($^5\eta$-C_5H_5)]/NaHY.

and Pd/NaHY catalysts obtained via the CVD technique are active in MCP conversion, and methylcyclopentane undergoes secondary reactions over the acid sites of NaHY. It is noteworthy that both samples were prepared inside the reaction vessel, by vapor deposition of [Pd($^3\eta$-C_3H_5)($^5\eta$-C_5H_5)] and subsequent decomposition to metal by heating in flowing H_2 at the reaction temperature.

The total conversion of MCP at 300°C and 1 atm is reported as a function of time on stream in Fig. 5. As expected, Pd/NaHY has a higher initial activity than Pd/NaY (13% against 4%), with a faster deactivation rate (17).

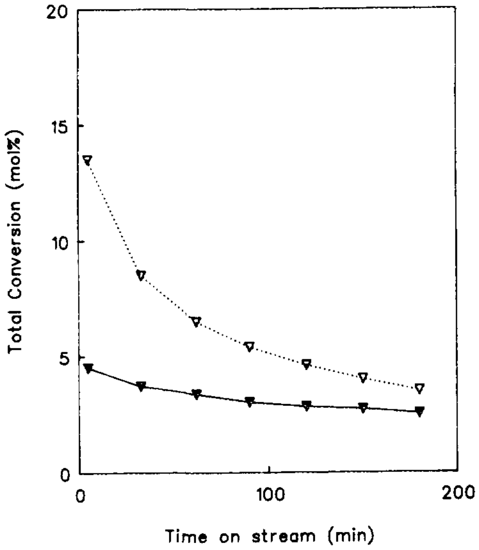

FIG. 5. Deactivation patterns in MCP conversions at 300°C and 1 atm for the Pd/NaY (▼) and Pd/NaHY (▽) catalysts.

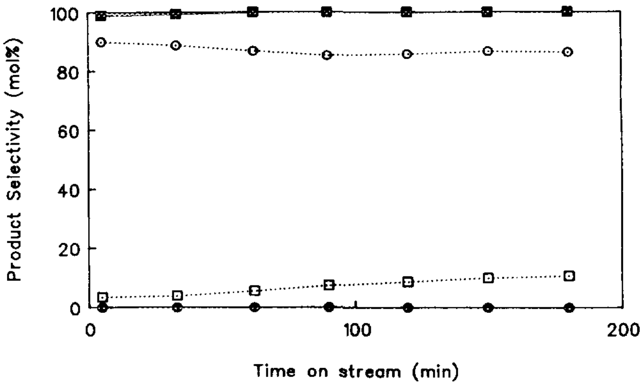

FIG. 6. Selectivity changes in MCP conversion at 300°C and 1 atm for the Pd/NaY (filled symbols) and Pd/NaHY catalysts (open symbols) [RO, ring-opening (squares); RE, ring-enlargement (circles)].

Under the present conditions, MCP is converted to (i) ring-opening (RO) products, *n*-hexane methyl-2-pentane, methyl-3-pentane, and (ii) ring-enlargement (RE) products, cyclohexane and benzene. Cracking (CR), i.e., production of molecules with less than 6 carbon atoms, was found to be negligible. Although conversions are varying with time on steam, ring-opening and ring-enlargement are essentially parallel reactions; secondary interconversions of open-chain paraffins and cyclohexane can be instead disregarded. Therefore, selectivity data will be indicative for the initial selectivity.

Pd/NaY shows a constant 100% selectivity towards ring-opening; with the bifunctional Pd/NaHY catalyst, ring-enlargement is predominant with the ratio between RE and RO depending on time on stream (Fig. 6).

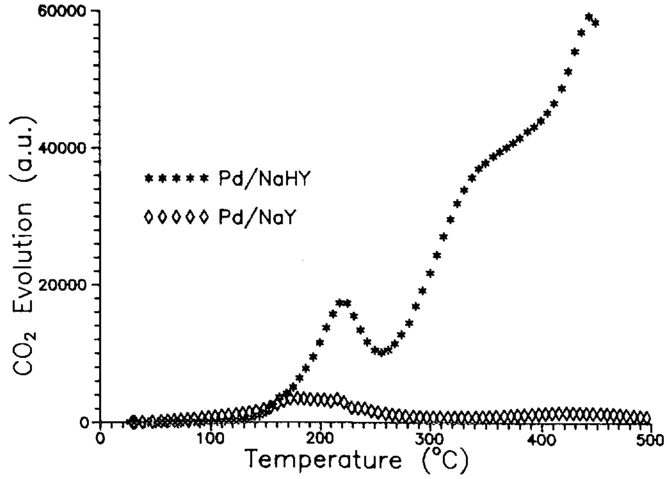

FIG. 7. TPO profiles in O_2(2%)/He flow of spent Pd/NaY and Pd/NaHY catalysts after 2 h catalytic run.

At the end of the catalytic run, a TPO investigation has been carried out on both catalysts in order to characterize coke deposition (13) (Fig. 7). CO_2 evolution is negligible for the monofunctional Pd/NaY sample, indicating the absence of a significant coke deposition during the catalytic run. On the contrary, two peaks at 225 and 450°C are observed in the TPO trace for Pd/NaHY, with an evident shoulder around 360°C. A ratio C/Pd greater than 30 is derived by integration of the CO_2 evolution.

For comparison, a neutralized Pd/NaY catalyst obtained by ion-exchange and subsequent post-neutralization of protonic acidity was tested under the same experimental conditions. With respect to the CVD-based Pd/NaY catalyst, the initial activity was slightly higher (Fig. 8); a faster deactivation in the first 30 min was instead observed. Selectivity for ring-opening was always higher than 96%, with a small residual activity (< 4%) for ring-enlargement. The TPO investigation carried out after the catalytic run was very similar to that of the Pd/NaY sample, and it is not reported here. The absence of a significant coke deposition is thus confirmed also for the neutr-Pd/NaY(IE) sample.

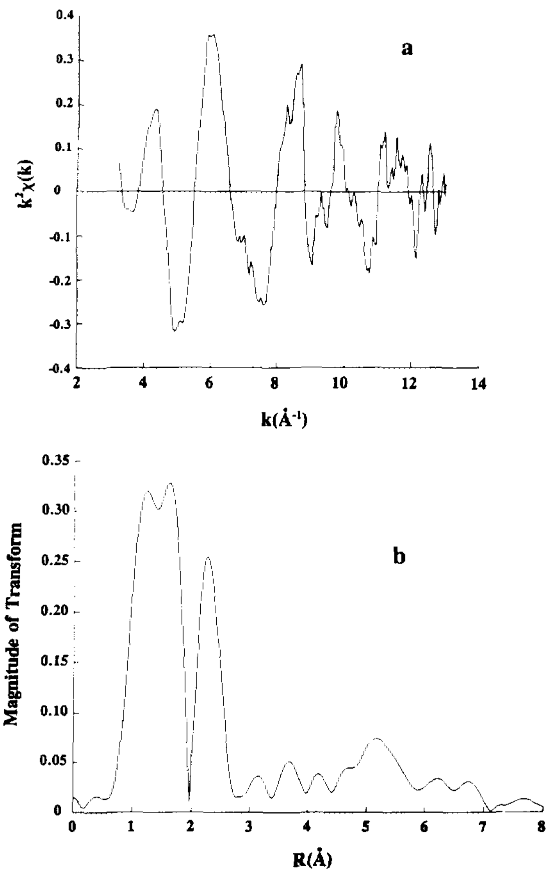

FIG. 9. (a) k^2-weighted EXAFS function and (b) Fourier transform of $k^2 \cdot \chi(k)$ for the Pd/NaY-1 sample.

The EXAFS $k^2 \cdot \chi(k)$ function of Pd/NaY-1 is shown in Fig. 9a, and the corresponding Fourier transform is shown in Fig. 9b. The three major peaks in Fig. 9b are at 1.24, 1.62, and 2.27 Å (phase shift uncorrected), respectively. As the nearest Pd–Pd bond distance in the Pd foil is 2.51 Å (phase shift uncorrected), the peak at 2.27 Å is unlikely to be due to Pd–Pd bonds. One possible origin is the interaction of Na^+ ions with Pd in the complex. Because of the complexity of the carbon coordination and the lack of proper reference structures, a fit to this spectrum was not attempted. This spectrum is, instead, used as a visual reference for those obtained on samples after reduction and after MCP conversion. Figure 10a shows the EXAFS $k^2 \cdot \chi(k)$ function of Pd/NaY-2, the reduced sample. The corresponding Fourier transform is displayed in Fig. 10b. The coordination shell of carbon seen in Fig. 9 disappeared from Fig. 10. Only one major peak is observed in the Fourier transform. Curve fitting on the inverse Fourier transform of this first Pd–Pd shell with Pd foil reference gives $R_{Pd-Pd} = 2.72$ Å, $CN_{Pd-Pd} = 6.1$, and $\Delta\sigma = 0.0026$ Å with a χ^2 of 9.6×10^{-3}.

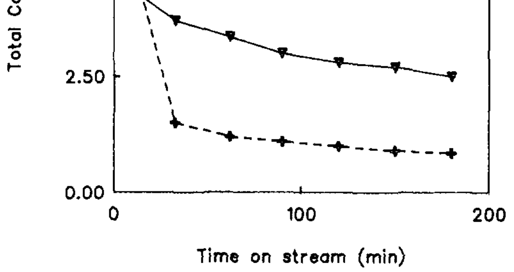

FIG. 8. Deactivation patterns in MCP conversions at 300°C and 1 atm for the Pd/NaY (▼) and neutr-Pd/NaY(IE) (+) catalysts.

Figure 11 shows the EXAFS $k^2 \cdot \chi(k)$ function (a) and corresponding Fourier transform (b) of Pd/NaY-3, a catalyst after time on stream in MCP conversion for 3 h. The growth of Pd particle size is qualitatively evidenced by the increase of the amplitude of the EXAFS function and the intensity of the Fourier transform with respect to those of Pd/NaY-2. Curve fitting of the first Pd–Pd shell gives $R_{Pd-Pd} = 2.73$ Å, $CN_{Pd-Pd} = 7.39$, and $\Delta\sigma = 0.0022$ Å with a χ^2 of 9.6×10^{-3}.

DISCUSSION

The utilization of neutral organopalladium complexes as precursors of nonacidic palladium particles inside Y zeolite is very demanding. The conventional incipient wetness technique is generally inadequate for selectively depositing the organometallic molecule inside the zeolite support, as already suggested by a previous work on PtRe carbonyls (18). Cavities and cages are immediately filled with the organic solvents, both apolar or polar, used for impregnation, preventing the precursor molecules from entering and diffusing inside the zeolite. In addition, some decomposition of the precursor is often experienced upon thermal removal of the solvent. This drawback cannot be completely overcome even by using a ligand as the impregnation solvent. As is demonstrated with the $[Pd(CH_3CN)_2Cl_2]$ complex, the CH_3CN solvent tends to stabilize the precursor against decomposition, but it leaves the complex on the external surface of the zeolite crystals. Consequently, NaY zeolite behaves exactly like an amorphous silica surface.

The volatile $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$ precursor was introduced via the vapor phase inside Y-zeolite cavities using CVD. In the absence of intrazeolitic protons, a simple mechanism of reductive elimination of ligands is then expected to take place in hydrogen atmosphere, transforming the organopalladium species into metal particles without any formation of protons:

$$[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]/NaY + H_2 \rightarrow 1/n\ Pd^0_n/NaY + C_3H_6 + C_5H_6.$$

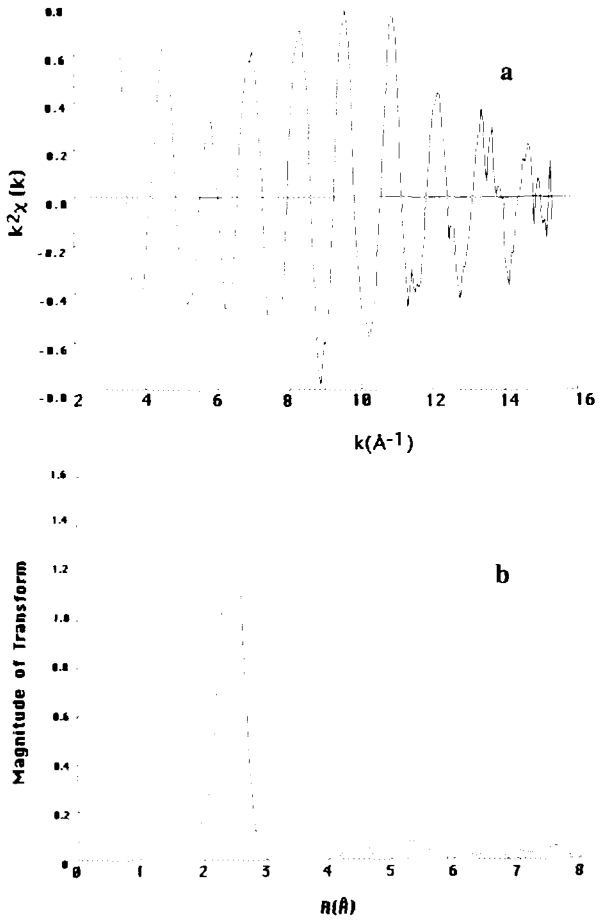

FIG. 10. (a) k^2-weighted EXAFS function and (b) Fourier transform of $k^2 \cdot \chi(k)$ for the Pd/NaY-2 sample.

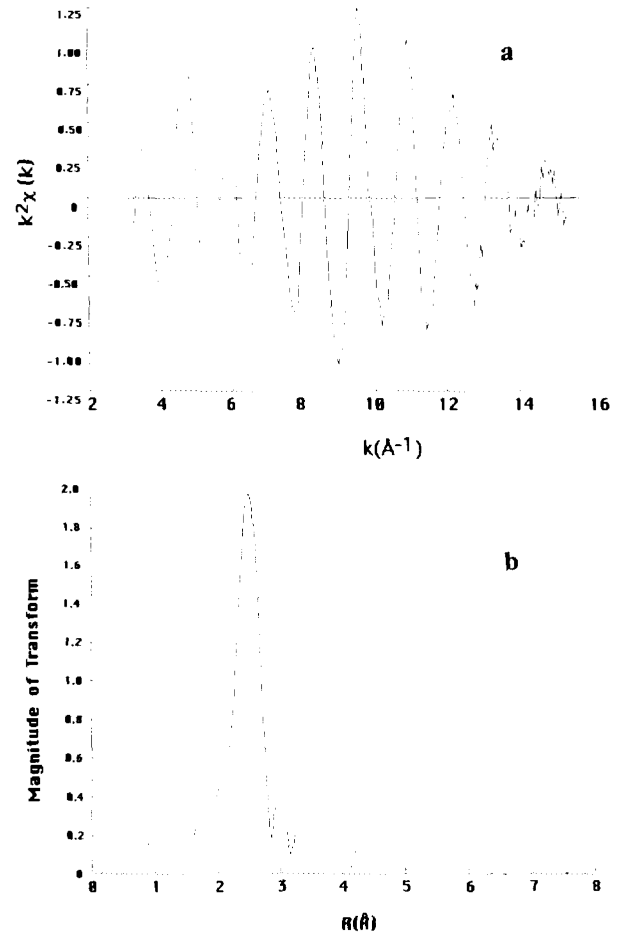

FIG. 11. (a) k^2-weighted EXAFS function and (b) Fourier transform of $k^2 \cdot \chi(k)$ for the Pd/NaY-3 sample.

However, the two unsaturated hydrocarbons, propene and cyclopentadiene, which should originate from the proposed intrazeolite reaction, are not significantly evolved under TPRD conditions (Fig. 3). Evolution of propane and cyclopentane is observed instead, as the result of the high hydrogenation activity of the Pd clusters formed in the decomposition reaction. This reactivity is highly beneficial for ensuring a "clean" decomposition to metal of the organometallic precursor, preventing any coke formation via metal-catalyzed Diels–Alder dimerization or polymerization reactions of adsorbed cyclopentadiene.

The catalytic results in MCP conversion support the hypothesis of total absence of protons. The Pd/NaY catalyst is 100% selective for the ring-opening reaction of MCP, in agreement with Gault's conclusions that this reaction is the sole one catalyzed by the metal function (19). Accordingly, a neutralized Pd/NaY(IE) shows initial activity and selectivity that are very similar to the Pd/NaY(CVD) system. There is a very low RE activity, probably caused by some residual acidity left after neutralization. However, the two non-acidic catalysts show different deactivation profiles with time on stream. It is noteworthy that the fast deactivation at the beginning of the catalytic run is also observed for Pd/NaY samples where protonic acidity was removed by reaction with NaN_3 (17). This behavior is thus a characteristic of neutralized Pd/NaY prepared by ion-exchange. This difference is likely to be interpreted on the basis of a different behavior of the entrapped metal particles upon starting the catalytic run. The possibility of coke deposition as the major cause of deactivation is rejected on the basis of the TPO. In an ion-exchanged sample, small Pd clusters are formed upon reduction because protons act as chemical anchors for the growing particles (20). The neutralization process removes such anchors, but particle growth is likely to be insignificant at low temperature. However, during actual catalysis at elevated temperatures, sintering of these "free" Pd clusters will be appreciable.

A different growth pattern is expected for the CVD-based catalyst. During removal of the ligands from the entrapped organopalladium precursor naked Pd atoms will be formed. These are extremely mobile and large Pd particles, filling zeolite supercages, will be formed before the catalytic run. Accordingly, the initial catalytic activity will be lower than that of the neutr-Pd/NaY(IE) catalyst, but these cage-filling particles grow only slightly during the catalytic run. As confirmed by the EXAFS data, the initial mean coordination number of 6.09 with a Pd–Pd distance of 2.72 Å only increases to 7.39 after 3 h under catalytic conditions. By comparison with previously reported data on ion-exchanged Pd/NaY catalysts, we conclude that the Pd/NaY catalysts prepared by CVD preparation method are more stable.

A further advantage of CVD-based catalysts is that the H^+/Pd ratio can be varied widely, by simply introducing the desired amount of acidity in the starting zeolite before the CVD process. The added acidity also has a profound effect on the decomposition chemistry of the entrapped organopalladium precursor, by completely modifying the evolution profile of cyclopentane in the TPRD of $[Pd(^3\eta\text{-}C_3H_5)(^5\eta\text{-}C_5H_5)]$/NaHY. The interaction of protons with metal centers is likely to take place upon removal of the allyl ligand, by forming a pseudo-hydride $[H\text{-}Pd(CP)]^+$ adduct. In fact, the evolution of propane is not affected by the presence or absence of protons, as experimentally observed. The cyclopentadienyl ligand would also interact even more strongly with an "electron-deficient" Pd center, making its removal more difficult than in the non-acidic Pd/NaY catalyst. An intimate contract between the palladium particles and the protonic sites is thus obtained as the consequence of this proton-mediated reactivity. The high activity and RE selectivity in MCP conversion, as well as the high-temperature CO_2 peaks in the TPO profile indicate the true bifunctional character of such Pd/NaHY catalyst (17).

CONCLUSIONS

The main drawback of the ion-exchange technique, viz., the creation of protonic sites upon H_2 reduction, can be virtually eliminated by the use of suitable neutral organopalladium complexes as metal precursors, deposited via the vapor phase into zeolite cages. These catalysts compare well with other non-acidic Pd catalysts; in particular, a lower deactivation rate under catalytic condition is observed.

When a bifunctional material is needed, protons can be introduced in the zeolite prior to the CVD process. In addition, the H^+/Pd ratio can be freely varied as desired.

A second major advantage of the CVD technique is that the preparation and the activation of the catalyst can be directly carried out inside the reaction vessel. The metallic phase is, in fact, simply obtained by heating the entrapped precursor in a stream of flowing hydrogen. This process does not critically depend upon the experimental conditions, but rather is governed by the reactivity of the ligands. All the conventional drying, calcination, and reduction procedures, which traditionally affect the final properties of the catalyst, can therefore be avoided.

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