Hydrogen isotope exchange on Pd/NaY and Pd/HY zeolites

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Mass spectrometry and FTIR were employed to monitor the isotopic exchange of various types of zeolite protons with D_2 at 21 °C. Discrete groups of protons are differentiated by their exchange kinetics. Protons in close vicinity to Pd particles are exchanged as rapidly as H atoms, adsorbed on Pd. For more remote protons, the interchange of O-H and O-D groups follows first order kinetics, but the rate constant is lower for protons in sodalite cages than for those in supercages; the rates are higher for Pd/HY than for Pd/NaHY. Proton exchange is virtually absent for samples which were reduced at 500 °C for several hours, suggesting that the location of Pd inside zeolite cages is essential and that hydrogen spillover is irrelevant.

Keywords: Hydrogen isotope exchange; zeolite isotope exchange

1. Introduction

Isotope exchange of D_2 with O-H groups in zeolites and on oxide surfaces has been extensively studied [1–13]. There is a consensus that this exchange is strongly promoted by metals such as Pt and Pd [1,4–13]. Valuable information has been obtained on the locations of protons in zeolites [1–7] and their intrinsic acidity [2–4].

Recent results strongly suggest that zeolite protons can react with Pd particles, forming adducts $[Pd_n–H_z]^{z+}$ [14–17]. The concentration and the positive charge of such adducts increases with the proton concentration in the zeolite. Two protons are formed during the reduction of each Pd^{2+} ion in PdNaY to give Pd/NaHY; in Pd/HY, where the proton concentration is higher, virtually all Pd clusters seem to be present as adducts [16]. XPS data also suggest the presence of adducts with $z > 1$ [17]. It is conceivable that protons in $[Pd_n–H_z]^{z+}$ can exchange rapidly with D_2 via adsorbed D atoms, while exchange of more remote protons in the same zeolite will be slower. The primary objective of the present study is, therefore, to differentiate various types of protons in Pd/NaHY and Pd/HY by their isotope exchange kinetics.

No differentiation of exchange kinetics between protons of different acidity was found by Dmitriev et al. for Pt/NaHY at 100 ° C [4,6]. A lower temperature of 21 ° C is, therefore, used in the present study which monitors the exchange of H^+ by D^+ by mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR). MS data provide information of all H species, including H atoms chemisorbed on or absorbed in Pd, but FTIR permits the distinction of zeolite H^+ or D^+ at different locations and acidities by their respective O-H and O-D bands. Besides Pd/HY and Pd/NaHY, we also studied proton-free Pd/NaY, prepared by neutralization of Pd/NaHY, and physical mixtures of this Pd/NaY with HY.

2. Experimental part

1. SAMPLE PREPARATION

PdNaY (5.3 wt% Pd) and $PdNH_4Y$ (5 wt% Pd), have been prepared by ion exchange and analyzed by atomic absorption. NH_4Y was prepared by repeated exchange of Linde NaY (LZY-52) zeolite with 5wt% NH_4NO_3 solution to yield about 85% exchange of Na^+ with H^+ [18]. Pd was exchanged into the NaY or NH_4Y zeolite from $Pd(NH_3)_4(NO_3)_2$ solution. Proton-free Pd/NaY (Pd/NaY-neutr) was prepared by repeated neutralization of 2.0g of reduced Pd/NaHY with 800ml pH = 10.5 aqueous NaOH solution in N_2 atmosphere. Absence of protons in the neutralized sample was verified by FTIR.

2. METAL DISPERSION BY H-D EXCHANGE

Samples were calcined at 500 ° C in pure O_2 and reduced at 400 ° C in H_2. Then the samples were either cooled in H_2 and evacuated at 21 ° C, or evacuated at 400 ° C to 8×10^{-6} Torr and cooled under vacuum to 21 ° C. In both cases the total number of exchangeable H atoms was measured by MS in an apparatus described previously [19]. The difference in exchangeable hydrogen between the samples evacuated at 400 ° C and 21 ° C gives the number of H atoms adsorbed on Pd. Some samples were cooled in H_2 to −77 ° C and evacuated overnight to 8×10^{-6} Torr in an attempt to detect Pd hydride formation.

3. FTIR STUDY OF H/D EXCHANGE

4-5mg samples (PdNaY, NaY, $PdNH_4Y$ and NH_4Y) were pressed into 8mm diameter wafers. An IR stainless steel cell was used in transmission mode

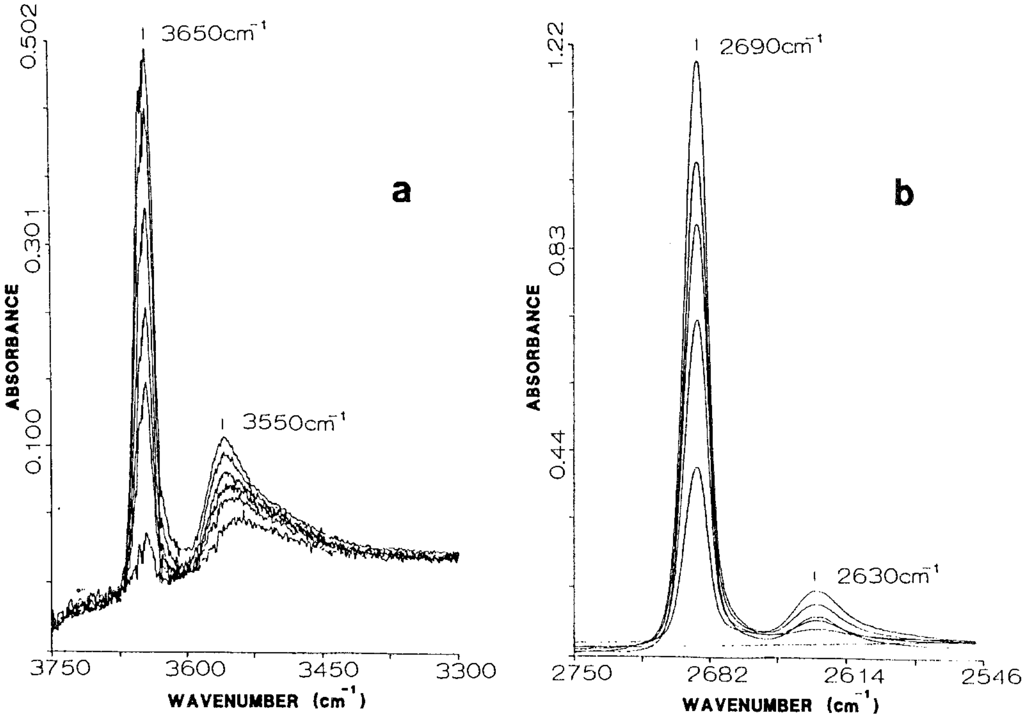

Fig. 1. FTIR spectra of Pd/NaHY, a) O-H bands in decreasing order and b) O-D bands in increasing order, after exposing the sample to D_2 gas for 0, 2, 9, 30, 60 and 240 mins.

measurement. The FTIR spectra were recorded by a Nicolet 60sx single-beam Fourier Transform IR spectrometer (resolution 1 cm^{-1}). Programmed calcination from RT to 500 °C (0.5 °C/min) and holding at 500 °C for 2 hr was followed by purging with He for 20 min at 500 °C. Pd/NaY-neutr and its 1:1 physical mixture with HY were pressed into wafers and loaded into the IR cell. Reduction of all samples was carried out in pure H_2 heating from 21 °C to 400 °C (8 °C/min), followed by purging in a He flow at 400 °C for 20 min. The samples were then exposed to a calibrated volume of D_2 gas at 21 °C. Spectra were taken every 0.5 min for the first 15 min and every 5 min thereafter. The maximal absorbances of the OD bands were used as a measure of the degree of deuteration. The exchange of a physical mixture of Pd/NaY-neutr and HY was also monitored by MS in the batch reactor.

3. Results

1. KINETIC STUDY OF EXCHANGE REACTION

Fig. 1 shows FTIR spectra of hydroxyl groups in PdNaY at various stages of exchange at 21 °C after subtracting the NaY background. FTIR distinguishes two main groups of protons: (a) protons in supercage O-H, absorbing at 3650

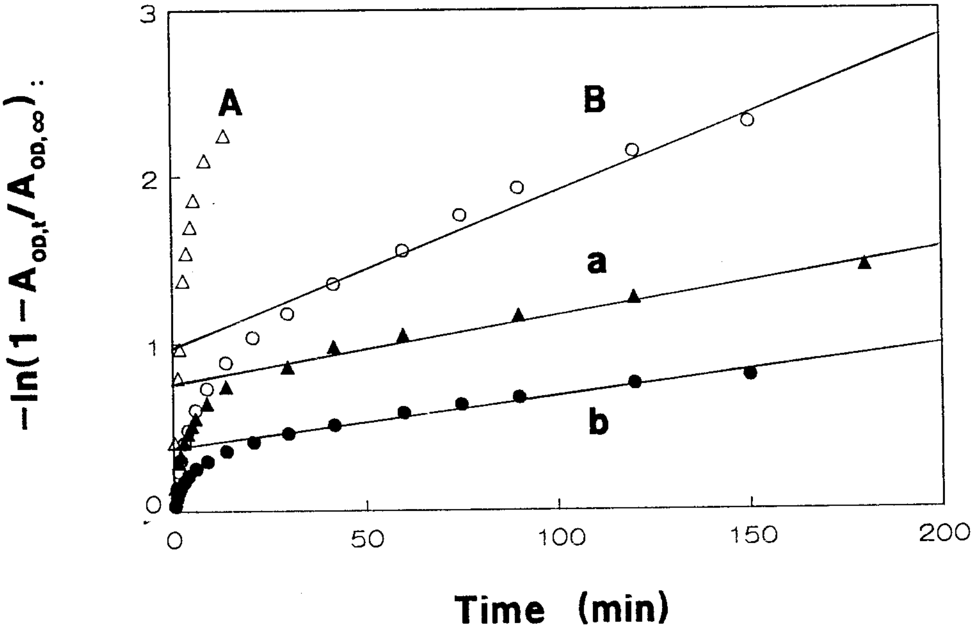

Fig. 2. First order plot of O-H exchange in Pd/HY and Pd/NaY. *For Pd/HY*: A: supercage O-H 3650 cm^{-1}, Δ), a: sodalite cage O-H (3550 cm^{-1}, ▲). *For Pd/NaHY*: B: supercage O-H (3650 cm^{-1}, o), b: sodalite cage O-H (3550 cm^{-1}, ●).

cm^{-1} (or 2690 cm^{-1} for O-D), and (b) protons in sodalite cage O-H groups, absorbing at 3550 cm^{-1} (or 2630 cm^{-1} for O-D). Fig. 1 shows that supercage O-H groups exchange more rapidly with deuterium than the sodalite cages O-H groups. Fig. 2 not only confirms this but also shows that for each group a very rapid initial exchange is followed by a slower exchange, obeying first order kinetics. We attribute the rapid initial exchange of supercage O-H groups in Pd/NaHY to protons which are located in the immediate proximity of Pd particles, whereas first order kinetics is due to interchange of more remote O-H and O-D groups. The calculated exchange rate constants k for the first order regimes as well as the fractions X_{fast} of rapidly exchanged protons, obtained from the intercepts of the first order plots of fig. 2, are compiled in table 1.

MS analysis of the gas phase shows that, in the absence of chemisorbed H on Pd, approximately 30% of the exchangeable H^+ is rapidly exchanged; in the presence of chemisorbed H, the value is about 45%. For Pd/NaHY and Pd/HY, the numbers of fast exchangeable hydrogen species are $H_{fast}/Pd = 0.6 \pm 0.1$ and 1.2 ± 0.2, respectively, per Pd atom in the sample. The latter number thus includes chemisorbed hydrogen and rapidly exchangeable protons. No break is observed in the exchange vs time plots separating H_{ads} from zeolite protons.

Table 1
Rapidly exchanged fraction X_{tast} of OH groups and first order rate constant k of secondary exchange for OH groups in supercages and sodalite cages of Pd/NaHY and Pd/HY at 21° C

Sample	X_{fast}(%) supercages	$k \times 10^5$ (s^{-1}) supercages	X_{fast}(%) sodalite	$k \times 10^5$ (s^{-1}) sodalite
Pd/NaHY	69.9	12.2	32.8	4.5
Pd/HY	> 90	–	52.7	7.0

Pd/HY, Pd/NaHY and a physical mixture of Pd/NaY-neutr & HY (1 : 1) are compared in fig. 3 by plotting the normalized FTIR absorbances, A, of the O-D band, $A_{\text{OD},t}/A_{\text{Od},\infty}$, for supercage O-H groups against time. Whereas the O-H groups in Pd/HY and Pd/NaHY are extensively converted to O-D groups within 20 min at 21° C, the exchange is markedly slower for the physical mixture; only 11% of the exchangeable protons have been exchanged after 3 h. The same result is confirmed by MS.

2. METAL DISPERSION

On the basis of MS results, the total number of exchangeable H species in the solid (H atoms and H^+ ions), N_s, is calculated from the deuterium content in the gas phase, α_g, before and after total exchange, and the number of H + D

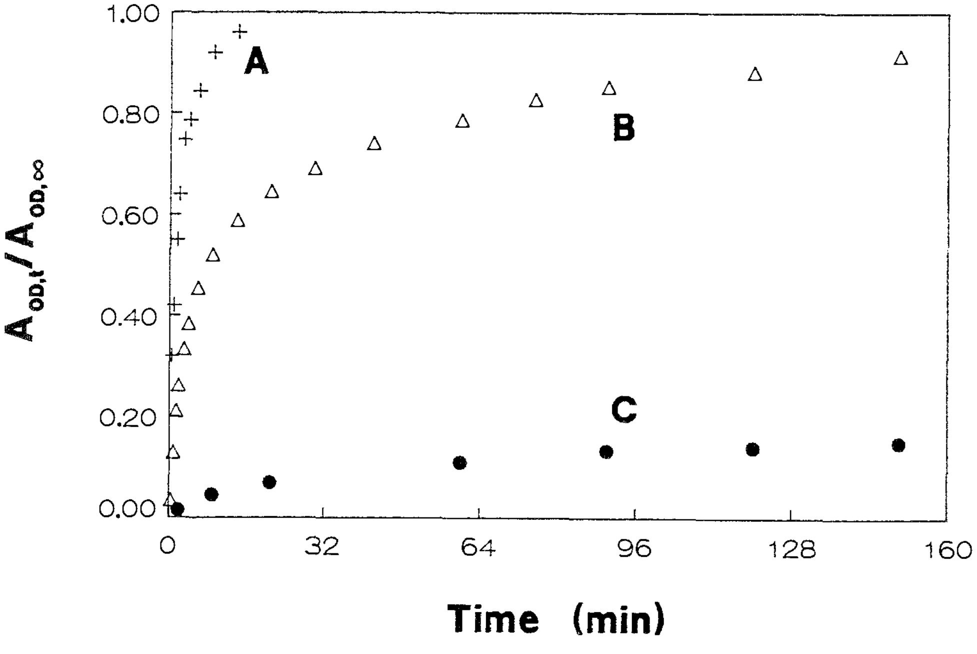

Fig. 3. Exchange rate of supercage O-H groups for: A: Pd/HY(+), B: Pd/NaHY(Δ) and C: a physical mixture of Pd/NaY-neutr and HY (1 : 1) (●).

Table 2
Metal dispersion in Pd/NaHY from different methods

Method	Sample	H/Pd
TPD [25]	2 wt% Pd/NaHY;	0.77
	7 wt% Pd/NaHY	0.74
Isotope [a]	5.3 wt% Pd/NaHY	0.59
exchange	same neutralized	0.47
Volumetric [b]	5.3 wt% Pd/NaHY	0.84
	same neutralized	0.70

[a] Total exchangeable after cooling in H_2 and pumping at 21° C, minus total exchangeable after evacuating at 400 ° C; Final hydrogen pressure before exchange: 8×10^{-6} Torr.

[b] Final hydrogen pressure: 5 Torr.

atoms in the gas, N_g, by assuming that in equilibrium gas and solid will have acquired the same isotopic composition ($\alpha_{g,\infty} = \alpha_{s,\infty}$). It follows from the material balance:

$$N_s = \left[(\alpha_{g,0} - \alpha_{g,\infty})/(\alpha_{g,\infty} - \alpha_{s,0})\right] \times N_g.$$

The number of exchangeable H on Pd/NaHY and Pd/NaY-neutr have been measured for samples that were cooled in H_2 after reduction and for those which were evacuated at 400 ° C before cooling. The differences of these numbers are given in table 2 as H/Pd values and compared with dispersion data obtained by more conventional methods. The results are reproducible within 10%. Note that for isotope exchange the sample was evacuated to 8×10^{-6} Torr before admitting D_2, whereas in the volumetric method the final coverage is in equilibrium with a H_2 pressure of 5 Torr. When considering this, the data obtained by the three methods are in reasonable agreement. The difference between the exchangeable amount of hydrogen after evacuation overnight at −78 ° C or at 21 ° C was found to be negligible, suggesting that Pd hydride is decomposed in both cases.

4. Discussion

The present results show that a regime of first order exchange kinetics is preceded by a very fast exchange reaction. For the sample evacuated at 400 ° C, only zeolite protons are available for exchange, but for the sample evacuated at 21 ° C, chemisorbed H on Pd is also exchangeable. Accordingly, the MS data show different numbers of rapidly exchangeable hydrogen but, remarkably, no break in the kinetic curves separating these subgroups. Chemisorbed H atoms and protons in the immediate vicinity are thus kinetically indistinguishable with this experimental criterion. This leads further credence to our model that some zeolite protons, sharing their cage with a Pd cluster form an adduct of the type $[Pd_n - H_z]^{z+}$. These protons may form hydrogen bridges between Pd cluster and the cage wall: Pd ... H^+ ... O_z. The $[Pd_n - H_z]^{z+}$ adduct model had been proposed previously for the increased activity in catalytic reactions [14,16]. In the adduct, Pd particles exhibit electron-deficient character as detected via ESR [20] and more recently by FTIR, utilizing CO as a probe molecule [15], and by XPS [17].

The present FTIR data show that 69.9% of the total supercages protons in Pd/NaHY are exchangeable at this fast initial rate. Protons in the adduct will be invisible in FTIR. The fast exchange observed by FTIR is attributed to protons in the vicinity of the adduct, possibly with the same zeolite cage. We are speculating that such adducts are able to exchange positions with protons in the vicinity. Further work is required and planned to verify this.

The observation that supercage O-H groups (fig. 2A and 2B) exchange three times faster than sodalite cage O-H groups (fig. 2a and 2b) in Pd/HY and P/NaHY is at variance with results of Dmitriev et al. on Pt/NaHY. However, their data was obtained at a higher temperature, i.e. 100 ° C [6] than that used in the present work. Carter et al. reported different exchange activities of different hydroxyl groups of alumina [10]. We assume that primary exchange occurs between D atoms on Pd and protons in the same supercage. Exchange between a H^+ and a D^+ at opposite sites of the same wall separating a supercage and a sodalite cage might be a mechanism by which the exchanged isotope enters the sodalite cage.

Fig. 3 shows that the exchange rate follows the trend:

Pd/HY > Pd/NaHY > physical mixture Pd/NaY-neutr + HY,

showing the importance of proton concentration in zeolites for the exchange rate. This is in agreement with Baumgartner's statement that on SiO_2, associated O-H groups undergo faster exchange than isolated O-H groups [11–13]. As we had previously found by EXAFS and FTIR, protons can anchor reduced Pd primary particles to the cage walls [21,22], consequently, it is possible that these Pd particles are smaller in proton-rich samples. If so, more Pd particles will be present at the same reduction temperature, i.e. a higher fraction of the supercage will contain a Pd particle in Pd/HY than in Pd/NaHY.

In previous work of Dmitriev et al. [7], rapid exchange was reported for a physical mixture of Pt/NaY and HY. It seems, however, that these Pt/NaY samples were actually Pt/NaHY, as no measures were taken to neutralize the protons formed during reduction of Pt^{2+} ions. The present result in fig. 3 (C) reveals that the exchange is slow in the absence of protons near Pd particles. The reason the exchange rate is not zero is presumably due to the fact that some solid state exchange of H^+ in HY with Na^+ of Pd/NaY-neutr took place [18]. Hydrogen spillover can, therefore, be disregarded for the present exchange data at 21° C.

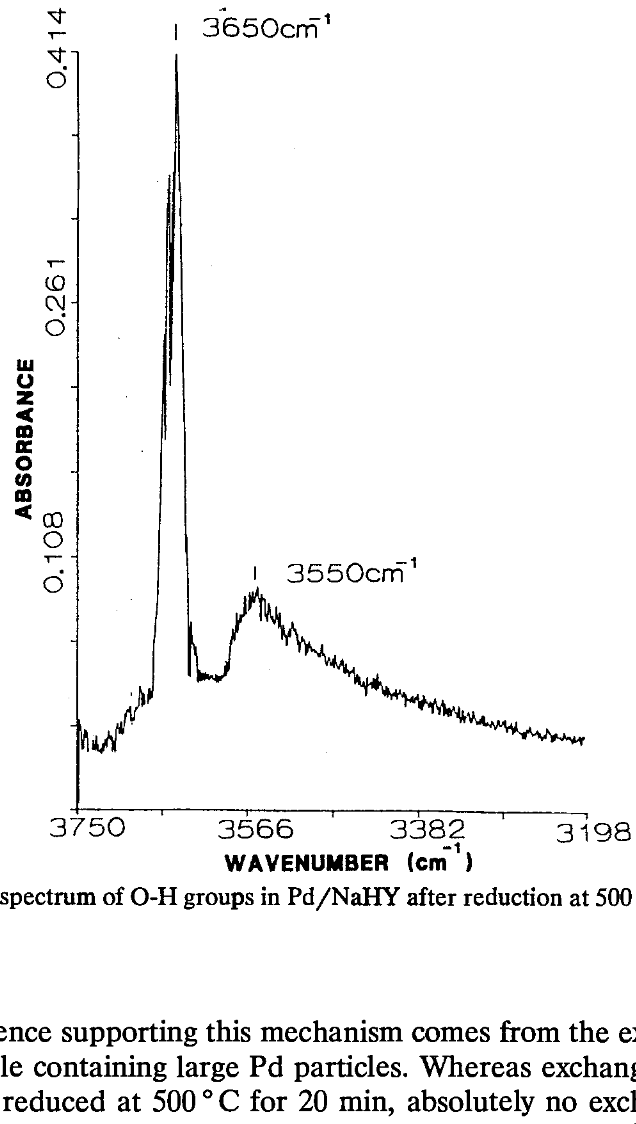

Fig. 4. FTIR spectrum of O-H groups in Pd/NaHY after reduction at 500 ° C for 4 hrs.

Further evidence supporting this mechanism comes from the exchange behavior of the sample containing large Pd particles. Whereas exchange is significant for the sample reduced at 500 ° C for 20 min, absolutely no exchange could be detected for Pd/NaHY after reduction at 500 ° C for 4 hrs (500/4 hr). As dehydroxylation is not significant under these reduction conditions (fig. 4), this result suggests that the fast exchange at room temperature between D atoms adsorbed on Pd particles and zeolite protons requires that the Pd particle is inside a zeolite cage. It is known that after extended reduction large particles are formed at the external surface and in zeolite voids [23]. In a recent paper, Leglise et al. [24] report that the activity of Pd/NaY catalysts for heptane conversion becomes extremely low after prolonged reduction, when large Pd particles are identified. Formation of large metal particles is concomitant with a local destruction of the zeolite framework. Consequently, there will be a negligible concentration of zeolite protons in the vicinity of the Pd particles.

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