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Mechanism of Hydrogen Spillover and Its Role in Deuterium Exchange on PtY Zeolite

R. V. DMITRIEV,* K. -H. STEINBERG,† A. N. DETJUK,* F. HOFMANN,‡ H. BREMER,‡
AND KH. M. MINACHEV*

* *N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, USSR;*
† *Sektion Chemie, Karl-Marx-Universität Leipzig, German Demoncratic Republic, and* ‡ *Sektion Chemie, TH "Carl Schorlemmer" Leuna-Merseburg, German Democratic Republic*

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The exchange of the surface hydroxyl groups of HNaY zeolite with D_2 takes place in the presence of platinum much faster than in the absence of platinum. To cause this effect it is sufficient to arrange the platinum at a distance of a few millimeters from the HNaY zeolite. The transport of the activated deuterium to the OH groups of the HNaY zeolite, i.e., its spillover, does not occur through the gas phase but on the surface of whatever solid is situated between the platinum and the HNaY zeolite. The transport of the activated deuterium takes place on oxide materials at the same rate, independent of their chemical nature, but it occurs only very slowly on the surface of stainless steel. It is proposed that the mechanism of spillover probably involves the participation of lattice oxygen of the solid surface.

INTRODUCTION

Hydrogen activated on metals such as Pt, Pd, and Ni is able to induce surprising reactions on solids situated in the vicinity. For example, it is able to reduce transition metal oxides at low temperature (*1*–*3*), to impart hydrogenation properties to oxides such as alumina (*4*), and to accelerate efficiently the isotopic exchange of surface hydroxyls at relatively large distances (*5*, *14*).

This effect, described in the literature as hydrogen "spillover", is based on the transport of activated hydrogen (or deuterium) over relatively large distances. Relatively little is known about the nature of the activated H_2 (D_2) and its mechanism of transport and what little is known is somewhat contradictory. Levy and Boudart (*6*) attribute the spillover to the migration of protons or proton-adsorbate complexes. Keren and Soffer (*7*) propose a transport as electron–proton pairs based on the observed electronic or ionic surface conductivity. Contrary to this, Fleisch and Abermann (*8*) as well as Vannice and Neikam (*9*) suggest a diffusion of hydrogen atoms.

In a previous study (*5*) of the exchange kinetics of D_2 with surface hydroxyls of ion-exchanged Y zeolite using a greaseless high-vacuum circulation apparatus with mass spectrometric analysis of the gas phase (*10*), we found that the presence of Pt alone suffices to increase the exchange rate by a few orders of magnitude. On a 0.75 HNaY zeolite the deuteration of the surface hydroxyls occurs above 523 K and reaches equilibrium within a few hours (*11*), but in the case of a mechanical mixture of a 0.5% Pt/NaY zeolite and the 0.75 HNaY zeolite this happens already at room temperature (*5*). The surface hydroxyls of the 0.75 HNaY zeolite are deuterated at nearly the same rate even if the 0.5% Pt/NaY zeolite is placed at a distance of 3 to 10 mm. These experimental results mean that the deuterium activated on Pt can migrate over large

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distances and give rise to reactions, as other authors have also observed for hydrogen in other systems (*4*, *6*). For the transport of the activated hydrogen (deuterium) over distances of the order of millimeters, either diffusion in the gas phase or transport on the surface of any solids present (wall of the reactor, support) must be taken into consideration.

We attempted to answer this question by two means. First, we measured the deuteration kinetics of the surface hydroxyls by mass spectrometric analysis of the gas phase using a constant distance between the 0.75 HNaY zeolite and the 0.5% Pt/NaY zeolite along the reactor wall but a different geometric distance through the gas phase. Second, we investigated the deuteration kinetics of the surface hydroxyls by ir spectroscopy with variation of the nature of the material connecting the 0.75 HNaY zeolite and the 0.5% Pt/NaY zeolite.

EXPERIMENTAL

Catalysts

The 0.75 HNaY zeolite (A) was prepared by NH_4^+ exchange of a NaY zeolite (SiO_2/Al_2O_3 = 4.4) and thermal treatment under shallow bed conditions. The 0.5% Pt/NaY zeolite (B) was produced from the same NaY zeolite by ion exchange with $[Pt(NH_3)_4]Cl_2$ solution followed by thermal decomposition and reduction.

Reactants

Electrolytically produced D_2 greater than 96% pure was used in the mass spectrometric measurements and D_2 greater than 99.5% pure was used in the ir experiments. H_2 and D_2 used for pretreatments were purified by thermodiffusion through a Pd capillary. For the experiments on the transport mechanism we used as the connecting support 1 × 20 × 10-mm tablets pressed from powders of ZnO p.a. (about 0.5 m^2/g, no OH groups after evacuation at 723 K), Fe_2O_3 p.a. (0.5 m^2/g, no OH groups), Aerosil (220 m^2/g, 1 mmol OH/g) or zeolite (A), or a plate of stainless steel.

Method Adopted for Checking Possible Diffusion of the Activated Deuterium through the Gas Phase

The equipment for the mass spectrometric investigation of the deuteration kinetics was described earlier (*5*, *10*). The use of four static circulation setups which were periodically connected to the mass spectrometer made possible four measurements at the same time. A good reproducibility was obtained by using greaseless metal high-vacuum valves. Figure 1 shows a scheme of the sample arrangement in the reactor which made it possible, by using special quartz holders made of thin rods ("needles"), to arrange tablets of the two zeolites parallel to each other at different distances (2–8 mm) without any change in the length of the quartz rods (about 60 mm) holding the two zeolites. We used rectangular tablets of zeolites A and B (about 1 g) with a size of 4 × 8 × 35 mm and placed them at distances of 2, 4, 6, and 8 mm. After pretreatment, the deuteration kinetics of the hydroxide groups on the HNaY zeolite were investigated at 2.6 kPa D_2 and 293 to 573 K. The pretreatment was the following:

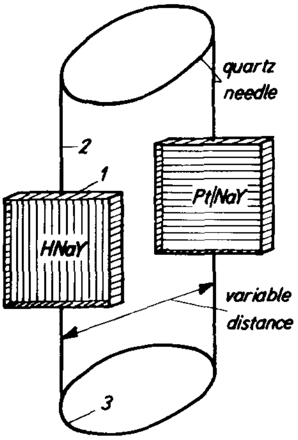

FIG. 1. Holder made from quartz glass for testing the transfer of activated deuterium through the gas phase. 1, Cage for tablets of 4 × 8 × 35-mm size; 2, quartz glass rods (needles), length 30 mm, diameter 1 mm; 3, adjusting rings of quartz glass for variation of the tablet separation distance from 2 to 8 mm.

1. Evacuation at 10^{-2} Pa during heating at 10 K/min up to 773 K with intermediate stops for 20 min at 383, 523, and 673 K.
2. Treatment with 101 kPa O_2 at 773 K for 1 hr with intermediate evacuation repeated three times.
3. Evacuation at 10^{-2} Pa and 773 K for 30 min.
4. Reduction with 13.3 kPa H_2 at 773 K for 1 hr with intermediate evacuation repeated three times.
5. Cooling in H_2 to 298 K and evacuation at 10^{-3} Pa for 1 hr.

Method Adopted for Testing Participation of Surface Diffusion in Spillover

These investigations were carried out by the arrangement of the zeolites within the ir cell outlined in Fig. 2. We investigated the D_2 exchange kinetics using a vertically placed thin disk (12 mg/cm^2) of a mechanical mixture of 20 mg zeolite A and 20 mg zeolite B, or a thin disk (9 mg/cm^2) of 30 mg zeolite A, placed at a distance of 5 mm from a cube of 50 mg zeolite B on different, horizontally placed supports (tablets of ZnO, Fe_2O_3, SiO_2, zeolite A, and a plate of stainless steel).

Before the deuterium exchange the samples were in all cases pretreated *in situ* according to the procedure already described but at a maximum temperature of only 723 K. The spectra were registered simultaneously by a UR 20 spectrometer (VEB Carl Zeiss, Jena) in the region of the OD and OH stretching vibration after different times of D_2 treatment. The pressure of D_2 was always 2.6 kPa. The exchange was carried out at 298 and 373 K.

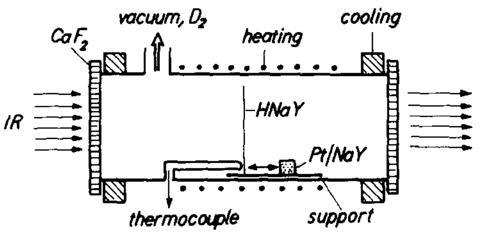

FIG. 2. Sample arrangement in the ir cell.

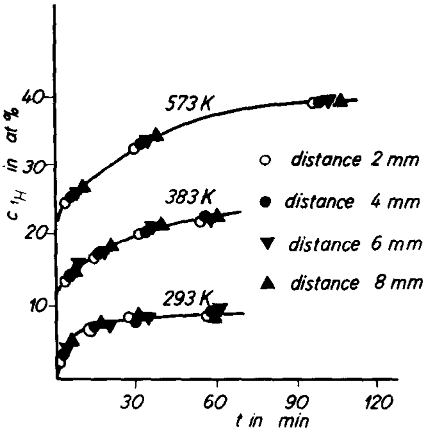

FIG. 3. ^{1}H increase in the gas phase at 2-, 4-, 6-, and 8-mm distances of both zeolites at various temperatures.

RESULTS AND DISCUSSION

Figure 3 presents the results of the mass spectrometric determination of the deuteration kinetics on the HNaY zeolite for the case of the arrangement (Fig. 1) of the Pt/NaY zeolite at a distance of 2 to 8 mm but with both zeolites held at a constant distance over the surface of the quartz holders. The figure shows that the geometrical distance between both zeolites does not influence the exchange kinetics. This means that the deuterium activated on Pt does not diffuse through the gas phase but must be able to migrate over a distance of about 60 mm on the quartz holder surface to the zeolite A.

To evaluate the results it is necessary to recall that zeolite A contains 2.5 mmol OH groups per gram but zeolite B only 0.25 mmol/g (*12*). This means that the deuteration of the OH groups of the HNaY zeolite is what is actually measured.

A possible diffusion of Pt to zeolite A can also be eliminated because the rate of deuteration of the HNaY zeolite is independent of the existence of a mechanical contact between both zeolites during the pretreatment (*12*).

If the transport of the activated deuterium takes place on the surface of the solid existing between the two zeolites, the rate of transport should depend on the nature of this solid. For this reason we varied the material of the support in the ir cell outlined in Fig. 2. We chose insulator oxides rich in surface and hydroxyl groups, semiconducting oxides of different conductivity type and poor in surface and hydroxyl groups, as well as stainless steel. The results are shown in Fig. 4. The quotient of the extinction of the most intensive OD band and the corresponding OH band is plotted against the time of exchange. One can see that the isotopic equilibrium is already reached in the case of the mechanical mixture of both zeolites at 298 K after about 2 h. In the case of the arrangement of zeolite B at a distance of 5 mm from zeolite A the deuteration rate of the OH groups on the HNaY zeolite is the same for all oxide supports, independent of whether the support is an insulator oxide, a semiconducting oxide, or a material rich or poor in surface hydroxyl groups. If the support is stainless steel, the deuteration of the OH groups on the HNaY zeolite takes place much more slowly.

From these results we can conclude that the surface diffusion of the activated deuterium must involve the participation of surface groups only existing on oxides but not on the metal surface. These surface groups cannot be hydroxyl groups, because the various materials differ strongly in their concentration of OH groups and yet the transport of the activated deuterium takes place with the same rate. In our opinion the transport of the activated deuterium, i.e., its spillover, occurs with the participation of the lattice oxygen of the surface. The surface diffusion of the activated deuterium must be a very fast reaction and take place on only a small part of the surface-oxide oxygen, because the specific surfaces of the oxide material used differed strongly but nevertheless the same exchange rates were observed.

A definite statement on the nature of the migrating particles is impossible at this time. Contrary to the opinion of Boudart and co-workers (3, 6), they are likely to be noncharged particles, because otherwise in our experiments a significant dependence of the diffusion rate on the nature of the support material should have been observed.

On the surface of HNaY zeolites different types of OH groups exist which significantly differ from each other as regards their concentration and surface chemical properties (13). The most important types of OH groups absorb in the ir spectrum at 3650 and 3550 cm^{-1} (OD region: 2690 and 2630 cm^{-1}). Moreover, they

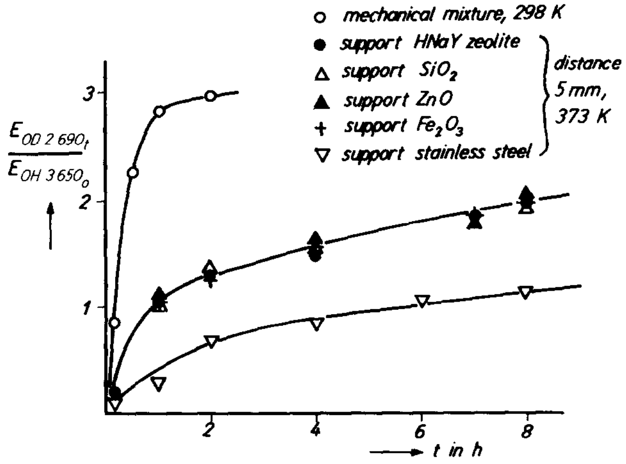

FIG. 4. Relative extinction of the 2690-cm^{-1} OD band as a function of the time of exchange and the material of the support.

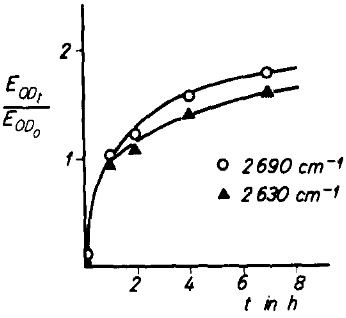

FIG. 5. Relative extinction of the 2690- and 2630-cm^{-1} OD band as a function of the time of exchange at 373 K and 13.3 kPa D_2. Distance between the Pt/NaY zeolite and the HNaY zeolite, 5 mm.

differ in their acidity. Despite the different acidity the deuteration of both OH groups occurs with the same rate in the presence of Pt in the vicinity as is shown in Fig. 5. Here the relative extinction of the OD groups is plotted against the time of exchange. Figure 5 shows that the deuteration rates of both types of OH groups are almost the same.

This result permits an important statement on the mechanism of the heteromolecular isotopic exchange of OH groups on solids, namely, that in the absence of metals able to activate hydrogen (deuterium) the ease of dissociation of the proton (i.e., the acidity) plays an important role in the rate-limiting step (*11*). But in the presence of metals with hydrogenation properties another rate-limiting step exists. This is the size of the spillover, which means that the transfer of the activated hydrogen (deuterium) is rate limiting.

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