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H/D Exchange of Cyclopentane on Pt/Mordenites: Probing for Monoatomic Pt Sites

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H/D exchange of cyclopentane on Pt/Mordenite catalysts has been studied. With 0.5% Pt/HMor reduced at or below 200°C, an isotope distribution pattern characteristic of prevailing stepwise exchange (i.e., one atom exchanged per residence of an adsorbed molecule) is observed. It is attributed to monoatomic Pt_1 sites for which Pt atoms in side-pockets of the main channels are likely candidates. In contrast, Pd_4 clusters in NaY display prevailing multiple exchange with the characteristic *double-U-shaped* distribution pattern that is also observed on other supported and unsupported Pt and Pd catalysts. Physisorbed cyclopentane plugs the narrow one-dimensional pores; molecules inside these pores become largely isolated from the gas phase, though *single-file* diffusion permits some leakage. Molecules which have been trapped inside the channels for some time are found in isotopic equilibrium with the zeolite protons. © 1993 Academic Press, Inc.

I. INTRODUCTION

The unique cage and channel structure of zeolites enables these materials to support very small and fairly uniform metal clusters. The genesis, size, and location of such particles and their transformation to carbonyl and other ligated clusters has been studied extensively in recent years by a variety of methods (*1–8*). An important feature distinguishing zeolites from amorphous supports for metals is the formation of isolated Pt atoms, e.g., in sodalite cages of zeolite Y. They were first detected by the unique propensity of Pt atoms to be oxidized by zeolite protons to Pt^{2+} ions + H_2 under conditions where such reaction would be thermodynamically impossible for multiatomic Pt particles (*9*). The formation of H_2 at 500°C was detected by gas analysis, the concomitant consumption of protons by FTIR. While being an object of academic curiosity, isolated Pt atoms in sodalite cages are of little importance to catalysis because of their inaccessibility to potential reactants. We therefore were excited when H_2 release at 500°C was observed also with highly dispersed Pt in mordenite, as this observation suggests that isolated Pt atoms might also be formed in that zeolite, where their most probable location would be in the side-pockets of the main channels (*10*). This opened the perspective that Pt/Mor might be a catalyst with Pt_1 sites accessible to reacting molecules. In this paper an isolated Pt atom (symbol: Pt_1) is meant to have no chemical bonds with other metal atoms. It will, however, be anchored to the zeolite wall, probably via a proton or several protons (*3*, *6*, *7*, *11*). Preliminary data lend some support to the existence of Pt_1 in side pockets of mordenite channels: methylcyclopentane, which is known to be oriented in narrow zeolite channels with its long axis parallel to the pore and therefore preferentially hydrogenolyzed to 3-methylpentane when bumping with its flat bottom end onto a Pt particle (*12–14*), was found to be attacked at its flanks by finely dispersed Pt in mordenite; ring opening thus results in the preferential formation of 2-methylpentane (*10*).

In the present research a different strat-

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egy has been tried to detect a catalytic action specific for isolated Pt atoms in mordenites. It makes use of the isotope exchange of H atoms in a hydrocarbon molecule against D atoms. An abundance of data shows that for the H/D exchange of paraffins or cycloparaffins with D_2 over transition metal catalysts two basic types of exchange can be discerned: *stepwise* exchange and *multiple* exchange. In stepwise exchange one H atom is exchanged during a chemisorptive interaction of the hydrocarbon molecule with the catalyst; in multiple exchange two or more H atoms are exchanged against D atoms during one residence at the catalyst surface (*15–17*). The preferred route for multiple exchange includes a reversible stepping over of a mono-adsorbed molecule to an α,β-diadsorbed complex, with two vicinal C atoms forming chemical bonds with surface atoms (*18–20*). Neopentane, which does not possess any H atoms attached to vicinal C atoms, gives stepwise exchange only, but with cyclic molecules, such as cyclopentane or cyclohexane, multiple exchange prevails. Burwell and Schrage concluded that the diadsorbed complex has the eclipsed configuration of the molecule attached to the surface (*21*, *22*). Observations on bimetal catalysts suggest that the rate-limiting step of stepwise exchange requires only one transition metal atom (*23*). A tentative hypothesis for the present research can be formulated, in its most simple form, as follows:

(1) Multiple exchange requires an ensemble of several contiguous metal atoms;

(2) Stepwise exchange *might* be catalyzed by Pt_1 atoms.

On the basis of this hypothesis it was decided to use cyclopentane as probe molecule, because H/D exchange with cyclopentane has been extensively studied over a variety of transition metals; multiple exchange has always been found to prevail (*15–17*, *21*, *22*, *24*). Exchange due to repeated changeover between mono-adsorbed and eclipsed α,β-diadsorbed complexes can replace all five H atoms at one side of the C_5-ring during one residence of the molecule on the metal surface. This process is followed either by desorption of $C_5H_5D_5$ or by "flipover" of the adsorbed molecule so that the H atoms at the other side of the C_5 ring can also be exchanged. When total exchange is limited by kinetics, i.e., far from equilibrium, a distribution pattern results with maxima at d_1, d_5, and d_{10}, which has been called the *double-U-shaped* pattern. In this terminology d_i indicates the relative concentration of cyclo-$C_5H_{10-i}D_i$. This distribution has been observed for transition metals on amorphous supports and in zeolite Y (*25*, *26*) and for metal films. The present research tries to find, whether mordenite that supposedly contains Pt largely in the form of isolated atoms differs from other Pt catalysts in displaying a stepwise exchange pattern with cyclopentane in the kinetic regime. Experimentally, prevailing stepwise exchange characterized by a smooth decrease from d_1, following a binomial distribution, is easily distinguished from both the familiar multiple exchange distribution of cyclopentane with the characteristic double-U shaped pattern and the equilibrium distribution which is, again, given by a binomial distribution, but centering around a D/H ratio equal to that of the hydrogen fraction.

One important complication must be mentioned now. Mordenite is a cageless zeolite with narrow, one-dimensional channels; under the conditions of the exchange experiments used in this work, these channels will be largely filled with physisorbed cyclopentane. As cyclopentane molecules with a diameter of 5.8 Å (*27*) are unable to pass each other in the one-dimensional channel with a free diameter of 6.7 × 7.0 Å (*28*), molecular transport in mordenite is completely different from ordinary diffusion. Kärger *et al.* compare this *single-file diffusion* to the movement of beads on a string (*29*). A cyclopentane molecule inside such a pore will be virtually unable to escape to the gas phase as the path to the channel orifice is blocked by numerous physisorbed molecules. For this reason measurements of cyclopentane adsorption have been included in the present work. The extent of isotope exchange of molecules *inside* the pores has been determined in separate experiments where the physisorbate was desorbed and analyzed via a mass spectrometer.

For the H/D exchange of molecules inside such pores it is important to visualize how D atoms travel to this region. Once Pt particles at the external surface or near pore orifices are covered with adsorbed D atoms, secondary exchange with zeolite protons starts, as was shown by FTIR measurements following the decrease in OH and the increase in OD band intensities (*30*). After some time (depending on the temperature, the density of Pt particles and the concentration of zeolite protons), the isotopic composition of zeolite protons and adsorbed hydrogen atoms on all Pt particles will be virtually in isotopic equilibrium with gaseous H_2, D_2 and HD, irrespective of pore plugging of zeolite channels by physisorbed hydrocarbon molecules. We therefore also included experiments in which cyclopentane in the absence of gaseous D_2 is contacted with a Pt/Mor catalyst that had previously been equilibrated with gaseous D_2. Some H/D exchange experiments with neopentane have also been included for comparison.

II. EXPERIMENTAL

Ammonium mordenite (NH_4Mor LZ-M-8, UOP) was washed with 0.1 *M* NH_4NO_3 solution. A dilute solution of $Pt(NH_3)_4^{2+}$ ions was added dropwise to a slurry of this zeolite. The exchange samples were stirred for 24 h and filtered, and the zeolites were then washed with water and dried at room temperature. The calculated Pt contents are 0.1, 0.5, and 2.0 wt%, respectively.

Catalysts were calcined at 500°C in O_2 flow (200 cm^3/min/g) at a heating rate of 0.5°C/min and held at 500°C for 2 h before purged with Ar at 500°C for 20 min. Reduction was conducted in flowing H_2 by heating from room temperature to the desired reduction temperature at a heating rate of 8°C/min and held at that temperature for 30 min. They were subsequently purged with Ar for 20 min and evacuated to a residual pressure of $<10^{-4}$ Torr before cooling to the isotopic exchange temperature. These zeolite catalysts will be referred to as Pt/HMor/T_R, where T_R is the reduction temperature. A 0.7-wt% Pt/Al_2O_3 and a 5.0-wt% Pd/NaY catalyst were also used for the exchange studies, and their preparations are detailed elsewhere (*3, 31*).

Exchange measurements were performed in a recirculation flow system as described previously (*32*). The isotope exchange was monitored by a mass spectrometer (Dycor M100) with a variable leak valve from the reaction system. All exchange reactions were carried out with a deuterium to hydrocarbon ratio of 25, a total pressure of 52 Torr, and temperature of 100°C, unless stated otherwise. The initial product distribution (at less than 10% conversion) was calculated according to the method of van Broekhoven and Ponec (*33*). The initial rate of the disappearance of undeuterated cyclopentane, $[-d(d_0)/dt]$, was corrected for physisorption of cyclopentane and calculated by standard means (*15*). The d_i fraction is defined as the ratio of the deutero-cyclopentane molecules with *i* D atoms to the total number of all cyclopentane molecules. The analysis of neopentane in the mass spectrometer was complicated by the extremely low concentration of the parent ions; therefore analysis of the $C_4(H,D)_9^+$ ions was used which are formed by loss of a methyl group and an electron from the parent molecule.

III. RESULTS

Pt/HMor vs Pt/Al_2O_3

No H/D exchange of cyclopentane at 100°C was observed with blank HMor or Al_2O_3 even after extensive time. On a 0.5% Pt/HMor/500 sample exchange occurs readily at 100°C; the product distribution at three conversion levels is shown in Fig. 1. The initial product shows extensive multiple

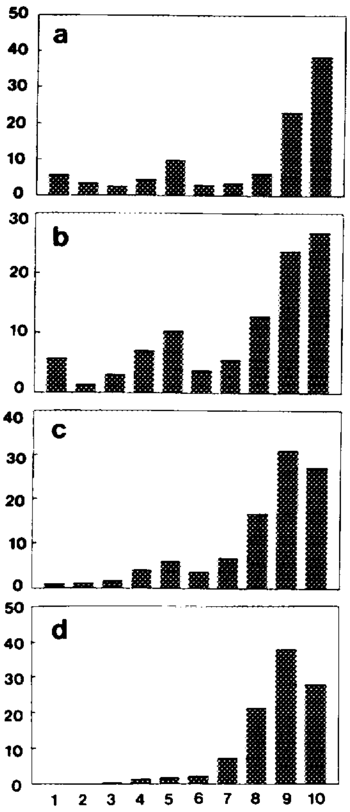

FIG. 1. (a) Initial product distribution and product distributions at a conversion of (b) 40%, (c) 60%, and (d) 90% of cyclopentane/D_2 exchange at 100°C on 0.5 wt% Pt/HMor/500.

exchange with d_{10} as the predominant product. A local maximum at d_5 is also observed. As the conversion increases, the exchange product shifts to higher D content, mainly d_8, d_9, and d_{10}. At 80% conversion, the product shows an apparent equilibrium distribution pattern with a maximum at d_9. None of the usual features typical for H/D exchange of cyclopentane in the kinetic regime, viz., maxima at d_5 and d_{10}, are observed at this stage.

A Pt/Al_2O_3 sample with a dispersion of 67% was used as a reference. Figure 2 shows the product distributions. The initial distribution (Fig. 2a) displays the familiar double-U-shaped pattern with maxima at d_1, d_5, and d_{10}. For this catalyst, unlike Pt/HMor/500, the double-U-shaped pattern is retained while conversion increases. A much higher d_5 fraction was observed, which indicates preferential exchange at one side of the cyclopentane ring.

Variation of Metal Loading

H/D exchange of cyclopentane on Pt/HMor/500 samples with loadings of 0.1%, 0.5%, and 2% Pt was compared; initial product distributions are shown in Fig. 3. For 0.1% Pt/HMor/500, the initial product shows maxima at d_5 and d_{10} which are symptomatic for H/D exchange of cyclopentane in the kinetic regime. With increased Pt loading, the d_1–d_5 fraction decreases drasti-

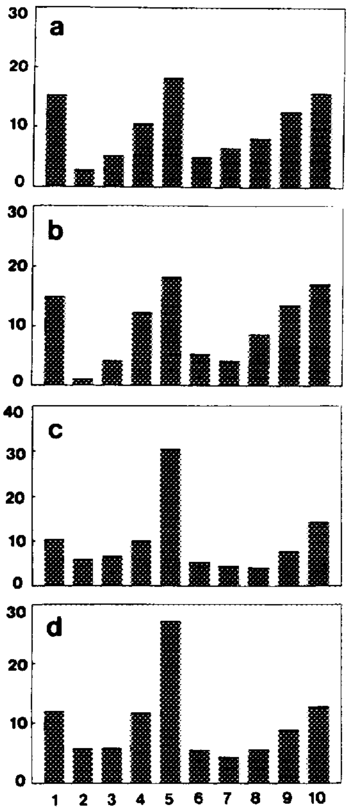

FIG. 2. (a) Initial product distribution and product distributions at a conversion of (b) 40%, (c) 60%, and (d) 80% of cyclopentane/D_2 exchange at 100°C on 0.7 wt% Pt/Al_2O_3 with Pt dispersion of 67%.

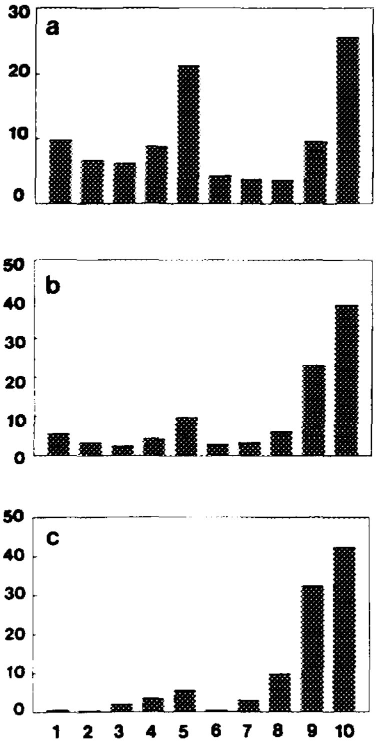

FIG. 3. Initial product distributions on cyclopentane/D_2 exchange at 100°C on (a) 0.1 wt%, (b) 0.5 wt%, and (c) 2.0 wt% of Pt/HMor/500.

cally; at the same time the d_8–d_{10} fraction increases.

Variation of the Reduction Temperature

Figure 4 shows the initial product distributions over 0.5% Pt/HMor that was reduced at different temperatures, T_R. It is known that metal dispersion is lower at higher T_R. In the T_R range between 200 and 500°C, the d_1 fraction was found to increase significantly with decreasing T_R, while the d_5 fraction decreases. Although the d_1–d_5 fractions are relatively small in comparison with the d_6 to d_{10} fractions both for Pt/HMor/500 and Pt/HMor/350, the double-U-shaped pattern is still visible in the initial distributions. However, for Pt/HMor/200, a very different pattern is observed, only d_1 and d_{10} maxima appear, but no d_5 maximum. This distribution pattern could be interpreted as a superposition of two populations: one representing equilibrium with high D content and one showing stepwise exchange in the kinetic regime.

H/D exchange between cyclopentane and deuterated Pt/DMor/200, that had been reduced with D_2 at 200°C, was carried out in the absence of D_2. The product distributions are shown in Fig. 5. The initial product (Fig. 5a) shows a maximum at d_7. As the exchange proceeds, the maximum shifts to lower D contents and finally d_1 becomes the highest peak. All distributions in this figure have the appearance of an equilibrium pattern, but the average D content of the cyclopentane decreases as the zeolite gets exhausted of D and more cyclopentane enters the reaction. We have compared the initial product distribution with the calculated binomial distribution for a D/(H + D) = 0.71; the result is shown in Fig. 6.

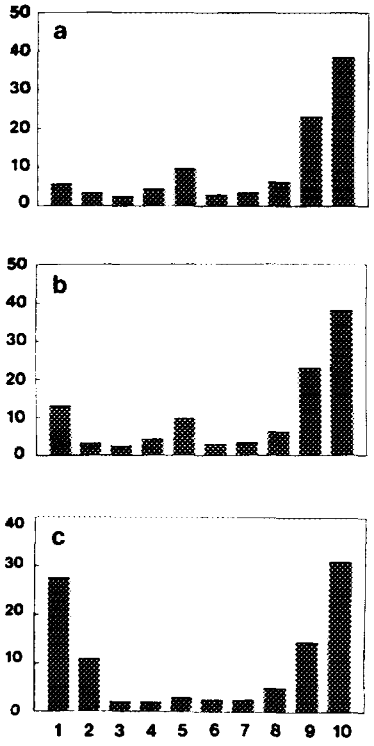

FIG. 4. Initial product distributions of cyclopentane/D_2 exchange at 100°C on 0.5 wt% of (a) Pt/HMor/500, (b) Pt/HMor/350, and (c) Pt/HMor/200.

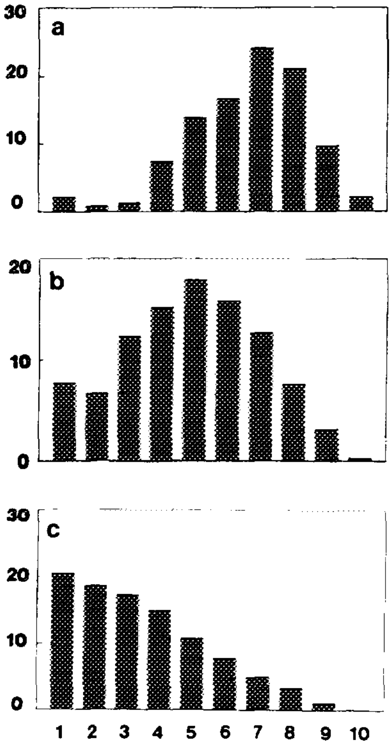

FIG. 5. H/D exchange at 100°C of cyclopentane with deutero-Mordenite (0.5 wt% Pt/HMor/200 prereduced by deuterium at 200°C). Product Distributions at a conversion of (a) 1%, (b) 5%, and (c) 10%.

Physical Adsorption of Cyclopentane

Sorption of cyclopentane by a calcined H-mordenite was determined at 100°C and the same cyclopentane pressure as used under exchange conditions. Sorption was monitored by mass spectrometry; the amount of sorbed cyclopentane was calculated from the intensity change of the cyclopentane peak. At 100°C, 1.6 cyclopentane molecules are found to be sorbed per unit cell. Upon assuming that the average pore length in each mordenite crystallite is in the order of 1 μm (*28*), it follows that about 1100 molecules of cyclopentane are sorbed in each one-dimensional pore, or one molecule per 9 Å of pore length.

Desorption of Exchange Products

The exchange products trapped in the zeolite channels after very brief exposure to D_2 were analyzed after desorption. For this purpose an exchange reaction was carried out at room temperature with either Pt/HMor/500 or Pt/HMor/200; exchange was terminated within 30 s by evacuating the system to less than 1 Torr. The temperature was then raised to 100°C to desorb the exchange products from the zeolite pores. For Pt/HMor/200 the product distribution (Fig. 7a) shows only one maximum for d_1, the concentration d_i falls off with higher values of i, as expected for stepwise exchange. There is no indication of maxima for d_5 or d_{10}. In contrast, the Pt/HMor/500 catalyst produces, again, the familiar double-U-shaped distribution (Fig. 7b), indicating an important effect of metal particle size on product distribution. In addition, a maximum at d_8 is visible in the desorption product, indicating rollover of the 1,2-diadsorbed $C_5H_5D_3$ intermediate to the other side of the cyclopentane ring (*34*).

For the study of catalysts reduced at 100°C, it suffices to use unreduced samples which will be reduced by the reaction mixture of cyclopentane + D_2. Some Pt^0 is also formed during calcination at 510°C in *auto-reduction* of Pt^{2+} ions by their NH_3 ligands. The results of testing such catalysts is shown in Fig. 8a. Again a steep decrease in product abundance from d_1, indicative of stepwise exchange, is observed, though a slight increase in the higher d_i fractions is

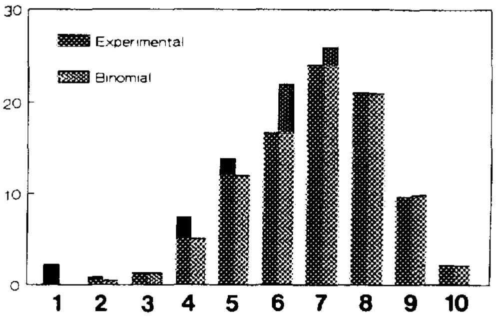

FIG. 6. Comparison of production distribution of Fig. 5a with calculated binomial distribution. Binomial distribution calculated on the basis that the average number of deuterium in cyclopentane is 7.1.

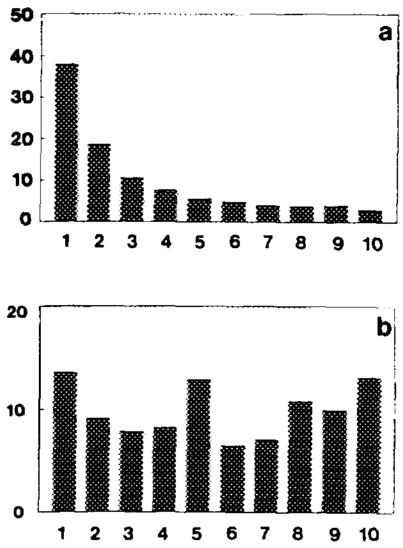

FIG. 7. Product distributions from desorption of exchange products on 0.5 wt% of (a) Pt/HMor/200 and (b) Pt/HMor/500. Cyclopentane/D_2 exchanges were carried out at room temperature for 30 s and terminated by evacuating the system, and the exchange products are quickly desorbed at 100°C for analysis.

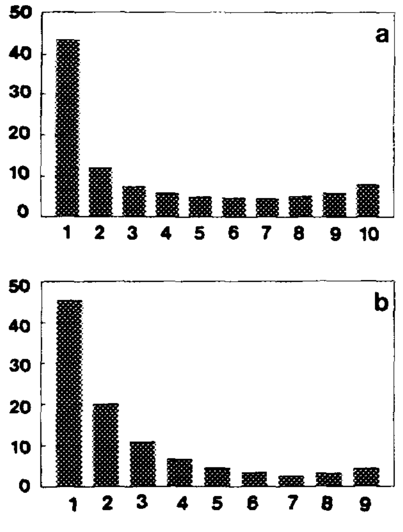

FIG. 8. Initial product distributions of (a) cyclopentane/D_2 and (b) neopentane/D_2 exchange at 100°C on 0.5 wt% Pt/HMor after calcination. The analysis of products from neopentane/D_2 exchange was made in terms of the $C_4X_9^+$ ions, where X represents *H* or *D*.

also noticed. For comparison the H/D exchange has also been studied with neopentane under identical conditions, the result is shown in Fig. 8b. The similarity in the initial product distributions of cyclopentane and neopentane indicates that with this catalyst the same stepwise exchange mechanism is valid for both molecules.

Comparison with Pd/NaY

In Fig. 9 the distribution pattern is shown of exchange with 5% Pd/NaY at 100°C. This catalyst has been analyzed by EXAFS, it is assumed to contain tetrahedra of Pd (*3*). The distribution of the exchanged molecules shows the familiar double-U-shaped pattern which is typical for a significant contribution of multiple exchange with flipover.

Comparison of Initial Rates

The initial rates of disappearance of d_0 are listed in Table 1 for various catalysts. A distinct trend is the decrease of the rate with decreasing reduction temperature of the Pt/HMor samples. The drop in rate from Pt/HMor/200 to the Pt/HMor sample that was only calcined and reduced by the reaction mixture fits in this pattern.

IV. DISCUSSION

Single-File Diffusion Effects

Since blank HMor does not show any H/D exchange ability under the reaction condition, we conclude that all exchange

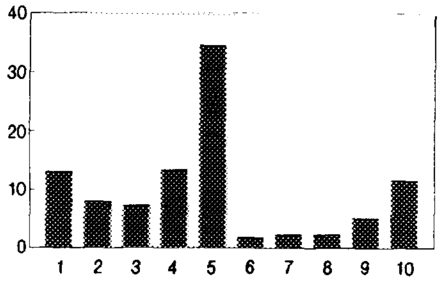

FIG. 9. Initial product distribution of cyclopentane/D_2 exchange at 100°C on 5.0 wt% Pd/NaY. Preparation of this catalyst is described in Ref. (*3*).

TABLE 1

Initial Rate of Disappearance of Undeuterated Cyclopentane (d_0)

Samples	Rate (%/min-15 mg)
Pt/HMor/500	39.0
Pt/HMor/350	27.1
Pt/HMor/200	24.2
Pt/HMor (calcined)[a]	11.9
Pt/Al_2O_3[b]	30.8

[a] Sample is reduced under reaction condition (D_2 at 100°C).

[b] Reduced at 500°C with a dispersion of 67%.

reactions take place on the Pt metal sites. The initial product distribution of Pt/Al_2O_3 shows the familiar double-U-shaped pattern with comparable fractions of d_1, d_5, and d_{10}. This is evidence for the simultaneous operation of stepwise exchange, via a monoadsorbed intermediate, and multiple exchange, via interconversion between monoadsorbed and α,β-diadsorbed intermediates. Most patterns obtained with Pt/HMor deviate from this scheme; one cause of deviation is plugging of pores with physisorbed molecules and the concomitant difficulty of reaction products to leave the catalyst via *single-file diffusion*. Our adsorption data show that under steady state condition during the exchange experiments, each channel of 1000 nm carries roughly 1100 cyclopentane molecules. When such molecules ultimately emerge in the gas phase they have reacted many times, the product distribution of this fraction is, therefore, not kinetically controlled but represents isotopic equilibrium. This is evident from the high concentration of d_9 in Fig. 1, even at short reaction times, and the increasing trend towards the typical equilibrium pattern at extended conversion. A significant contribution of a highly exchanged "isotopic equilibrium" mixture is visible for the 2%, the 0.5%, and the 0.1% Pt/HMor catalysts. Two reaction paths lead to high D content of the trapped molecules: (1) D_2 and HD are so small that they will be able to diffuse through channels largely filled with cyclopentane, and (2) the isotopic equilibration of hydrogen adsorbed on Pt particles via exchange with zeolite protons (deuterons) is not impeded by physisorbed hydrocarbons.

The conclusion that molecules trapped in the channels of mordenite swiftly reach isotopic equilibrium at 100°C is confirmed by two sets of independent data. First, exchange of cyclopentane with D atoms in Pt/DMor in the absence of gaseous D_2 gives an equilibrium distribution even at short contact times (see Fig. 5). This is confirmed by the agreement of the *observed* pattern with the *calculated* distribution for binomial equilibrium in Fig. 6. It is also relevant that the average D content of the hydrocarbon *decreases* with reaction time, as the zeolite exchanges its D^+ ions against H^+ ions, while more fresh cyclopentane interacts with it.

The second proof is the isotope analysis of the desorption product after only 30-s reaction time, shown in Fig. 7. Clearly, the D content of this product is much higher than that found for other runs after 10 min. While normal runs mainly reflect catalysis at channel orifices, this run shows that in the interior of the channels a much higher degree of exchange is achieved, although distribution is still far from equilibrium.

In spite of the superposition of kinetically limited distributions with populations that are essentially at equilibrium, an interesting effect of metal loading is noticed. In Fig. 3, the d_1–d_5 fraction for the 0.1% sample is comparable to the d_6–d_{10} fraction. For the 2% sample, the d_6–d_{10} fraction is much higher than the d_1–d_5 fraction. The d_{10}/d_5 ratio generally gives an indication for the ease of flipover of the cyclopentane ring on metal sites. For the three samples, the d_{10}/d_5 ratios are 1.2, 4.0, and 8.4 for 0.1%, 0.5%, and 2% samples, respectively. This suggests that with increasing metal load, the fraction of those molecules increase which have reacted many times with a catalytic site. A long residence time of some molecules in a channel between two Pt particles, but a finite chance of leaking from this pore to the gas phase, would be a physical model for this situation.

Effect of Reduction Temperature

Although the initial rates of disappearance of d_0 listed in Table 1 show a trend, in that lower rates are observed for samples reduced at lower temperature, it is not possible to derive turnover frequencies from these data, as diffusion effects are crucial. It is noteworthy, however, that pore plugging by larger Pt particles, that are possibly produced at higher reduction temperature, is apparently not dominant; rates seem to be higher when particles are larger.

Of relevance is, however, the effect of the reduction temperature on the product distribution pattern. The lack of a d_5 maximum and the absence of the double-U-shaped pattern for samples reduced at or below 200°C is in sharp contrast to the evidence on all other supported (*34–36*), and unsupported (*37, 38*) metal catalysts reported in the literature and in this lab. It appears that Pt/HMor of low metal load and when reduced at low temperature is unique among Pt catalysts in that stepwise exchange apparently prevails for H/D exchange of cyclopentane. This is valid also for molecules inside the pores, as is evident from Fig. 7. The catalyst which was reduced at 500°C displays the double-U-shaped pattern, but the sample reduced at 200°C shows a smooth monotonically decreasing distribution curve. A TPR study of this sample shows that the reduction is completed at this temperature. Thus this unusual distribution is not due to some dilution of the metallic sites by Pt^{n+} ions. As pattern recognition plays a large role in this discussion, it is of interest to compare the pattern for H/D exchange of cyclopentane and neopentane in Fig. 8. Neopentane is conventionally considered as the stepwise exchanging molecule *par excellence* (*39, 40*). Indeed the catalyst that was reduced only by the reaction mixture at 100°C reveals very similar patterns for neopentane and cyclopentane. In contrast, H/D exchange of cyclopentane on a calcined Pt/Al_2O_3 sample that was reduced in the same manner still shows the familiar double-U-shaped pattern.

The totality of these data shows that the very small Pt particles which are formed by reduction at low temperature in mordenite direct the H/D exchange of cyclopentane towards a stepwise mechanism, in contrast to all other Pt catalysts with larger Pt particles where the multiple mechanism prevails in the kinetic regime. As independent evidence suggests that isolated Pt atoms are formed in the side pockets of the mordenite channels (*10*), the question arises, whether these isolated Pt atoms are responsible for the unusual exchange mechanism reported in this paper. The data shown, only suggest that *very small* Pt particles are the sites responsible for this extraordinary behavior, but these particles could still consist of several atoms.

The comparison of the low-load, low-T_R Pt/HMor with better characterized Pd/NaY samples gives, however, some credence to the idea that in the former samples Pt_1 sites prevail. For the Pd/NaY sample used in this comparison, EXAFS analysis showed that the Pd atoms have a heavy element coordination number of 2.4 (*3*). This suggests that the Pd clusters in that zeolite consist predominantly of Pd_4 tetrahedra or even smaller particles. It is therefore of interest that this catalyst, when probed with the D/H exchange of cyclopentane gives, again, the familiar double-U-shaped distribution pattern. This indicates that the Pt centers in Pt/HMor responsible for the stepwise exchange are significantly smaller than Pd_4 tetrahedra.

Catalysis on a single atom site can occur via interconversion of various ligands of one metal atom. This type of mechanism is not unusual in homogeneous catalysis and has been extensively discussed (*41*). For heterogeneous catalysts Rooney *et al.* have proposed, on the grounds of analogy with homogeneously catalyzed processes, that catalysis by a single atoms is quite a reasonable prospect (*42*). Activation of hydrogen occurs readily on a variety of mononuclear transition metal complexes, such as $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ (*43*). The discovery of hydrogen complexes of transition metals and their ability to undergo facile exchange with D_2 to give HD (*44, 45*) also sheds some light on the activation of hydrogen. The activation of alkane has been demonstrated by Shilov *et al.*, who reported the ability of $PtCl_4^{2-}$ to catalyze H/D exchange between CH_3COOD and various alkanes (*46, 47*). The fact that these coordination complexes activate hydrogen and alkanes indicates that appropriately structured monoatomic sites are able to catalyze these reactions. Siegel *et al.* have proposed a stepwise exchange mechanism for H/D exchange of CH_4 on a single metal site, assuming replacement of only one hydrogen atom by one deuterium atom per sojourn at the site (*41*). A similar mechanism could also be applied to H/D exchange of cyclopentane on Pt_1 sites. Indeed, present concepts on metathesis, hydroformylation, and Ziegler–Natta catalysis explicitly use the concept that ligands at the same metal ion interact with each other. For supported metals, however, results obtained with alloys and data on structure sensitivity prove the importance of large ensembles for many important processes; others appear to use only one metal atom in the rate limiting step, which may, however, be preceded or followed by fast steps on multiatomic ensembles. The suggestion that some reactions can indeed be entirely catalyzed by an isolated atom may help to further narrow the gap between homogeneous and heterogeneous catalysis.

V. CONCLUSIONS

Isotopic distribution obtained from exchange reaction of cyclopentane with deuterium on Pt/HMor samples have provided detailed information on the catalyst surface. The fraction of the monodeutero species increases significantly when the reduction temperature is lowered. This is attributed to the increase in the numbers of the extremely small Pt particles, possibly monoatomic Pt sites. These isolated Pt atoms probably in the side-pockets of the mordenite main channels, are responsible for the stepwise exchange process which produces monodeutero cyclopentane as the sole primary product. The characteristic double-U-shaped product distribution is still typical for particles, such as Pd_4 tetrahedra. H/D exchange of cyclopentane is a useful diagnostic tool for the identification of isolated Pt sites.

Single-file diffusion in one-dimensional channels which are too narrow for cyclopentane molecules to pass each other efficiently isolates molecules in the interior of the zeolite from the gas phase. The isolated molecules reach isotopic equilibrium with zeolite protons and adsorbed hydrogen as a consequence of their long residence inside a pore.

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