JOURNAL OF CATALYSIS 43, 99–110 (1976)

Active Sites in Zeolites

5. Hydrogen–Deuterium Equilibration over Synthetic Faujasites

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Received August 15, 1975

The rate of isotopic exchange between H_2 and D_2 was followed over NaY, NaX, HY, hydrolyzed HY and LaY zeolites with controlled amounts of iron impurities.

Two maxima have been observed in the equilibration rates, one after activation at 520°C, and another at 670°C. At the two maxima, a linear correlation was found between equilibration rates and the iron content of the respective catalysts. The active sites at the first maximum were assumed to be cationic iron, while the activity at the second maximum was ascribed to an iron oxide species. Evaluation of the kinetic parameters showed that the data are consistent with a Bonhoeffer–Farkas mechanism.

INTRODUCTION

Several hypotheses have been advanced as to the nature of the active sites responsible for hydrogen activation in zeolites containing no noble metal atoms.

Turkevich and Ciborowski (*1*) found a near-linear dependence of the H_2–D_2 equilibration activity over NaHY zeolites on the degree of ion exchange and on the extent of dehydration. It was concluded that impurities located near Lewis sites or a combination of Lewis sites in close proximity were responsible for HD formation.

Brown *et al.* (*2, 3*) studied the parahydrogen conversion. They observed a similar behavior of X and A zeolites, containing H^+, Na^+ or Nd^{3+} ions and concluded that the activity is associated with the aluminosilicate framework of the zeolite rather than with the charge balancing cations. In contrast to earlier work (*1*), they observed a promoting effect of hydrogen on the reaction rate. They therefore rejected the impurity hypothesis and invoked activated adsorption to give an active surface hydrogen.

Kemball and McCosh (*4*) observed enhanced activity for H_2–D_2 equilibration over CoX, CaX and MnX zeolites after treatment with hydrogen. The increase in activity was explained in terms of the displacement of water from the cations by chemisorbed hydrogen, but the possibility that a reduction process was involved could not be excluded.

Recently, we found that NaY and HY zeolites showed the same H_2–D_2 equilibration rate and concluded that zeolitic impurities could be the active sites (*5*). Lombardo *et al.* (*6*) found that small amounts of divalent cationic impurities could affect the catalytic activity for *n*-butene isomerization. Imai and Habgood (*7*) reported that transition metal ions present as impurities were responsible for the formation of oxygen radicals.

As to the nature of impurities in zeolites, McNicol and Pott (*8*) detected three

TABLE 1

Anhydrous Unit Cell Composition of the Samples

NaY(1)	$Na_{55}\ (AlO_2)_{55}\ (SiO_2)_{137}$
NaY(2)	$Na_{55}\ (AlO_2)_{55}\ (SiO_2)_{137}$
NaY(4)	$Na_{55}\ (AlO_2)_{55}\ (SiO_2)_{137}$
NaY(3)	$Na_{55}\ (AlO_2)_{55}\ (SiO_2)_{137}$
NaY(s)	$Na_{56}\ (AlO_2)_{56}\ (SiO_2)_{136}$
$NH_4Y(2)$	$(NH_4)_{37.4}\ Na_{17.6}\ (AlO_2)_{55}\ (SiO_2)_{137}$
NaX(2)	$Na_{85}\ (AlO_2)_{85}\ (SiO_2)_{107}$
LaX(2)	$La_{20.0}\ Na_{25.0}\ (AlO_2)_{85}\ (SiO_2)_{107}$
$(Cu)NH_4Y(2)$	$Cu_{0.55}\ (NH_4)_{31.9}\ Na_{17.6}\ (AlO_2)_{85}\ (SiO_2)_{137}$
LaY(2)	$La_{12.9}\ Na_{16.2}\ (AlO_2)_{55}\ (SiO_2)_{137}$

different types of iron in faujasite Y and in mordenite: these were iron in cation positions (Fe_c^{3+}), iron substituting aluminium atoms in the aluminosilicate framework (Fe_s^{3+}) and a paramagnetic iron–oxygen species (Fe_p^{3+}). Derouane *et al.* (*9*). obtained similar conclusions and were even able to estimate the concentration of each of these species.

In this work, the H_2–D_2 equilibration over Y zeolites has been studied at high temperatures (250–400°C). Evidence for the active role of zeolitic impurities, more precisely iron, in this reaction is given. In addition a mechanism for the reaction is presented.

EXPERIMENTAL METHODS

Materials

The notation and anhydrous unit cell composition of the zeolites are shown in Table 1. The parent NaY and NaX zeolites (Lot Nos. 3606–289 and 340080, respectively) were obtained from Linde Co. The Arabic numbers in parentheses refer to different purification procedures applied to the samples: (1) no treatment, the samples are used as received; (2) the samples are exchanged with a 0.1 *N* ultrapure NaCl solution and washed with slightly alkaline bidistilled water until chlorides were no longer detected in the washings; (3) includes treatment (2) followed by successive exchanges with a sodium acetate solution at pH 6.1 followed by washing with distilled water at the same pH; (4) the chemical extraction procedure with dithionite as described by Derouane *et al.* (*9*). The number of successive extractions was three, five and eight for samples (a), (b), and (c), respectively. Sample NaY(2) was used to prepare other samples by ion exchange with NH_4Cl or $La(NO_3)_3$ in solutions of 0.1 total normality as described elsewhere (*10*). Samples derived from NaY(2) are indicated also by the index (2) [$NH_4Y(2)$ and LaY(2)].

Part of sample $NH_4Y(2)$ was treated with a diluted Cu^{2+} solution to give $(Cu)NH_4Y(2)$. Samples $NH_4Y(2)$ heated in shallow bed or under hydrolyzing conditions are denoted as HY and HYh, respectively, followed by the final outgassing temperature (°C). (Cu)HY is a thermally treated $(Cu)NH_4Y(2)$. A NaY sample denoted as NaY(s) was synthesized starting from ultrapure silica and sodium aluminate.

Hydrogen (99.95%) and deuterium (99.50%) obtained from J. T. Baker were passed through a deoxo-unit and a liquid nitrogen trap before use. The salts used for purification or ion exchange were "pro analysis" grade from Merck A. G., unless stated otherwise.

The impurity concentration was determined by neutron activation and is given in Table 2. Iron is the main impurity.

Apparatus

Catalytic reactions were carried out using an all-glass circulating system attached to

TABLE 2

Impurity Content of the Zeolites (ppm)[a]

Impurities	NaY(1)	NaY(2)	NaY(3)	NaY(4c)	NaY(s)	$NH_4Y(2)$	NaX(2)	(Cu)-$NH_4Y(2)$	LaY(2)
Group IA[b]	2.7	2.5	2.4	12.7		2.5	3.2	4.4	2.0
Group IIA[c]	97.0	117.0	13.0	104.0		87.0	14.0	85.0	100.0
Group IIIB[d]	14.8	12.4	7.2	22.6		65.0	2.5	413.0	70.0
Group VIB[e]	5.2	4.9	3.6	6.2		4.3	1.5	5.0	(13.14%)
Group VIII[f]	913.0	841.0	650.0	500.0	24.0	900	1150.0	1202.0	920
Group IB[g]	10.0	—	—	—		—	—	2799.0	
Group IIB[h]	3.7	11.5	12.6	96.0		26.0	5.7	57.0	24.0

[a] Only concentrations higher than the ppm level are reported.
[b] K, Rb, Cs.
[c] Ba, Ca, Mg.
[d] La, Ce.
[e] Cr.
[f] Fe.
[g] Cu, Ag.
[h] Zn, Hg.

a conventional high vacuum system. The circulation system consisted of an all-glass high speed (3–5 liters min^{-1}) pump, a 1000 ml mixing volume which represented 90% of the total volume, and a U-shaped quartz tube reactor which could be maintained at constant temperature within ±1 °C. The mixing bulb was connected to a Balzers quadrupole mass spectrometer through a fine capillary. The dimensions of this capillary were such that a pressure drop of less than 0.1% occurred over the total run.

Procedure

Samples (0.300 g) of the hydrated zeolite were pelletized and crushed. The 40–60 mesh size fraction was placed in the reactor between quartz wool plugs. The standard pretreatment of these samples consisted of evacuation at room temperature down to 10^{-5} Torr followed by a slow heating to the desired temperature. The catalyst was maintained at that temperature for at least 12 hr. Starting from NH_4Y samples, HY zeolites were obtained in this way. To obtain hydrolyzed samples (HYh) the reactor containing the wet NH_4 sample (28% moisture content by weight) under atmospheric pressure, was plunged into a hot oven heated in advance to the desired temperature (between 400 and 750 °C) maintained at that temperature for 12 hr, and finally outgassed at the same temperature for 3 hr.

After the pretreatment the samples were cooled under vacuum to reaction temperature and a gas mixture containing hydrogen and deuterium in a 1:1 volume ratio was admitted to the reaction volume. The equilibration reaction was followed for at least 80 min. Rate constants were determined in the temperature range from 250 to 400 °C at a pressure ranging from 30 to 100 Torr. Standard activity tests were carried out at 400 °C and at a pressure of 40 Torr. It was found that the activity increased during the first hours of contact with hydrogen. After 6 hr at 400 °C in hydrogen, the first order rate constants were reproducible. Therefore a standard treatment of 6 hr in H_2 at 400 °C was applied to all the samples except when stated otherwise.

A mass spectrometer was used to determine the H_2, HD and D_2 concentration. The percentage HD formed was calculated from the mass spectrometric results. Cor-

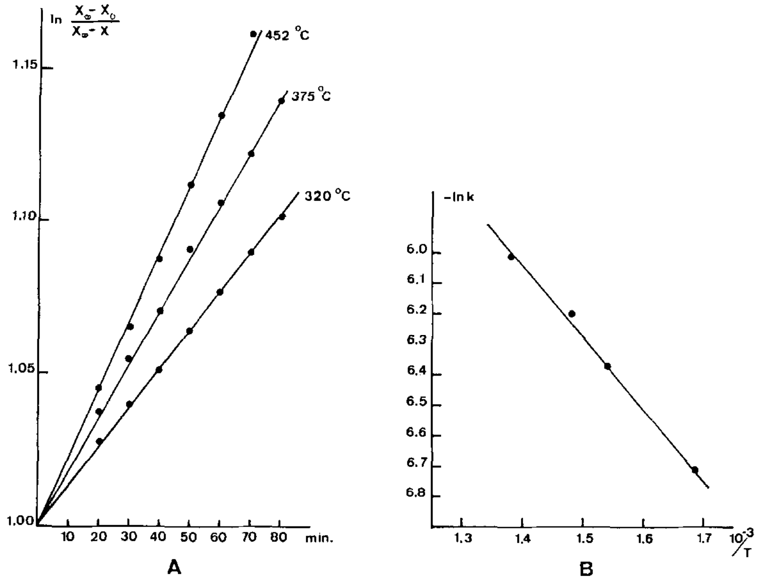


FIG. 1. First order (A) and Arrhenius (B) plot for H_2-D_2 equilibration over catalyst HY-478.

rections for the background spectra were made. Kinetic results were plotted according to a first order rate equation:

$$-\ln(x - x_\infty) = kt - \ln(x_0 - x_\infty), \quad (1)$$

where k ($\min^{-1}$) is the apparent rate constant and x, x_0, x_∞ are the percentage HD at time t, zero and at equilibrium, respectively. The thermodynamic equilibrium composition at the desired reaction temperature was calculated from data given by Urey and Rittenberg (*11*).

Absolute reaction rates R (mole g^{-1} s^{-1}) were calculated as

$$R = \frac{k \cdot n}{W \cdot 60}, \quad (2)$$

n is the number of moles ($H_2 + D_2$) in the reaction volume and W the weight of the catalyst.

Some catalytic runs were interrupted by pumping off the reaction mixture, and a new reaction mixture was introduced. In this way "differential rate constants" valid for 80 min reaction time were calculated to characterize the catalytic activity.

RESULTS

Purification of the Samples

The impurities of the zeolite samples are listed in Table 2. Iron seems to be the main impurity; its content is difficult to reduce by extraction. Sample NaY(s) with a very low iron content was obtained by synthesis starting from ultrapure reagents.

Kinetics

The pressure dependence of the equilibration rate could be described by the equation:

$$R = k_1 P^n. \quad (3)$$

The kinetic order n was obtained from the slope of plots of $\log_{10} R$ versus $\log_{10} P$. In the pressure range between 40 and 80 Torr the order was always close to zero on all the samples and for all the different pretreatments. At lower pressures the rate constant steeply increased. At low pressures (25–15 Torr) the kinetic order was 1. All experiments reported below were zero order with respect to the pressure.

After the standard treatment of 6 hr in hydrogen at 400°C, the hydrogen–deuterium equilibration reaction obeyed first order kinetics with respect to the distance from equilibrium. This was true for all the catalysts in the temperature and pressure range studied. Plots of

$$\ln \{(x_0 - x_\infty)(x_0 - x)^{-1}\}$$

against time at different reaction temperatures are shown in Fig. 1A for a HY-478 catalyst. An Arrhenius plot of the apparent rate constants is shown in Fig. 1B.

Influence of the Pretreatment Temperature

In Fig. 2 absolute reaction rates for the equilibration reaction are plotted against the pretreatment temperature for the NaY(2) and the $NH_4Y(2)$ zeolites. The experimental values of the reaction rates for both samples coincide at the different pretreatment temperatures. The activity path of both catalysts showed two maxima, one after pretreatment around 500°C, another after activation around 670°C. Figure 2 also shows that the activation energy of the reaction increases slightly up to activation temperatures around 570°C. Higher pretreatment temperatures cause a decrease in the activation energy.

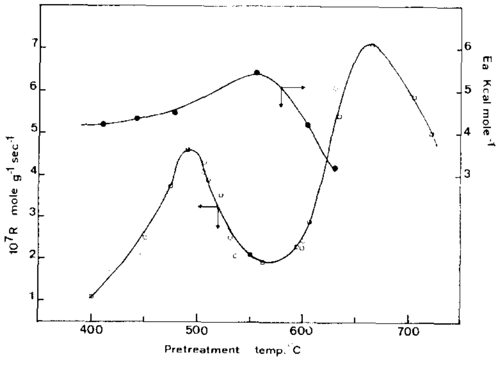


FIG. 2. Influence of pretreatment temperature of zeolites NaY(2) (□) and $NH_4Y(2)$ (○) on the H_2–D_2 equilibration rate constants at $T = 400°C$ and $P = 40$ Torr. of $NH_4Y(2)$. and on the activation energies (●).

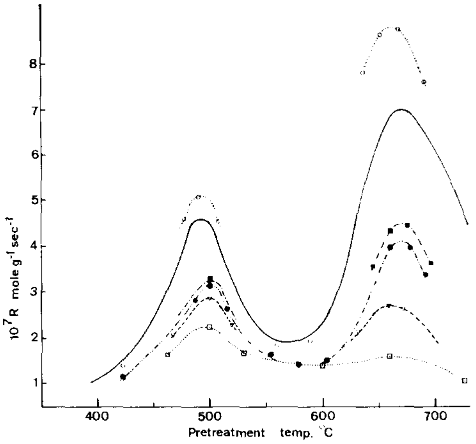


FIG. 3. Influence of the impurity content of Y zeolites on the HD formation at different activation temperatures. NaY(2)$NH_4Y(2)$ (——); $NH_4Y(3)$ (●) (–···); NaY(4a) (■) (–·); NaY(4b) (- - -); NaY(4c) (□) (···); NaY(1) (○).

Influence of the Impurities

In Fig. 3 is illustrated the evolution of the equilibration rate when the impurity content is reduced by extraction. The maxima in the rate of equilibration occurred with all the samples for the same pretreatment temperatures (520 and 670°C). The intensity of these maxima decreased proportionally to the decrease in iron content.

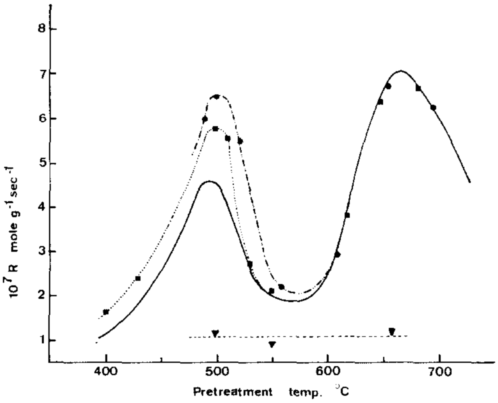


FIG. 4. Influence of the impurity content of Y zeolites on the HD formation at different activation temperatures. NaY(2)$NH_4Y(2)$ (——); LaY (●) (–··); Cu$NH_4Y(2)$ (■) (···); NaY(5) (▼) (– – –).

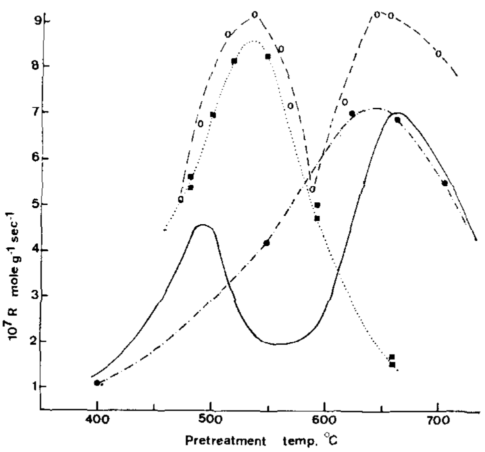


FIG. 5. Influence of the pretreatment of different types of synthetic faujasites on the HD formation at different activation temperatures. NaY(2)NH$_4$Y-(2) ———; NYh (●) (-·); NaX(2) (■) (···) LaNaX(2) (○) (- - -).

According to Derouane *et al.* (*9*) most of the amorphous precipitated iron is removed after three extractions with dithionite. Further extractions result in a decrease of the amount of cationic iron and framework iron. The data in Fig. 3 show that extraction with dithionite provokes a pronounced decrease in the intensity of both maxima. The height of the maximum at 520°C decreased after three extractions, but proportionally more for two additional extractions. Increasing the number of extractions had a smaller effect on the maximum at 520°C. The maximum at 670°C could be further reduced by additional extractions.

In Fig. 4 is shown the effect of introducing Cu^{2+} and La^{3+} ions. The solid line is for NaY(2) and NH$_4$Y(2) already shown in Fig. 2. It is clear that the maximum at 670°C is unchanged but the peak at 520°C increases by introduction of the ions. Unfortunately, together with the Cu^{2+} ions about 300 ppm of additional iron is introduced in the sample. During the exchange with La^{3+} the increase in the iron content is negligible, but La^{3+} may have an effect on the location of Fe cations. The ultrapure synthetic sample [NaY(s)] contained only negligible amounts of impurities. Its activity for H_2–D_2 equilibration was low and independent of the activation temperatures.

Different Types of Zeolites

Pretreatment of NH$_4$(2) in a hydrolyzing atmosphere resulted in a complete suppression of the maximum at 520°C. The second maximum was unaltered but broadened in the direction of lower temperatures (Fig. 5).

A NaX(2) sample had only one pronounced peak in the rate of H_2–D_2 equilibration with a maximum at 530–540°C. Exchange with La into NaX(2) results in the two maxima pattern of the Y samples. The activity of the X samples is always higher than that of the Y samples. Introduction of La ions in the X zeolite results also in an increase of the first maximum.

Activation and Poisoning

The increase in activity upon pretreatment from 400 up to 520°C is probably related to a dehydration effect. Indeed, the equilibration rate constant on NaY(2)-500 decreased again to the level of NaY(2)-400 when small doses of water are readsorbed at 400°C. Similar changes upon addition of water were observed on the other samples. At the second maximum the catalysts were much less sensitive to water poisoning.

Preliminary experiments revealed that for samples pretreated below 500°C, successive reactions with hydrogen produced increasing differential rate constants. Only after 6 hr treatment with hydrogen were reproducible equilibration rates obtained. For samples activated above 600°C this increase of the differential rate constant was not observed. Addition of oxygen at 400°C after a standard pretreatment in hydrogen, restored the initial equilibration activity. Reactivation with H_2 was again possible. These observations are indications of a redox phenomenon.

Poisoning experiments are commonly used to determine the number of active sites. Addition of successive doses of a poisoning agent and extrapolation to zero activity allows the determination of an upper limit of active sites. Acetonitrile was used as a poisoning agent. It was added in small slugs to the samples after the pretreatment and at the reaction temperature of 400°C. The results of the experiments are shown in Fig. 6. Sample HY-510 suffers from a gradual decrease in activity after addition of successive doses of acetonitrile until a constant activity was reached after addition of 3.3×10^{19} molecules g^{-1}. The rate constant at that moment was comparable to the rate constant of a nonpoisoned sample HY-570. The rate constant over zeolite HY-620 decreased by a factor 5.1 upon addition of 5.1×10^{19} molecules of CH_3CN/g of catalyst and reached the level of the blank experiments with the empty reactor loaded with quartz wool. The iron impurity level of this sample is 2×10^{19} ions/g. Thus CH_3CN cannot suppress completely the activity corresponding to the mechanism involved in the 520°C maximum, but deactivates completely the catalysts pretreated at 620°C. It is worth mentioning that acetonitrile cannot enter the sodalite cages. We found that the pulses of acetonitrile that poisoned the equilibration reaction were decomposed on the zeolite. In this case HCN and CH_4 appeared in the reactor. When the H_2–D_2 exchange activity was minimum, acetonitrile upon further addition had no poisoning effect and was no longer decomposed. This indicates that acetonitrile is decomposed on the sites used for the equilibration reaction. Therefore, it is tempting to assign the deactivation to the formation of iron carbide. Although the details of the deactivation mechanism are not known, the *upper limit* of active sites determined in this way can only be correlated with the impurity content of the zeolite.

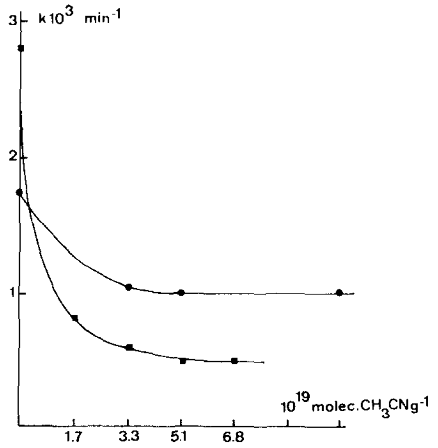


FIG. 6. Poisoning experiments with CH_3CN at 400°C on HY-510 (●) and HY-620 (■).

DISCUSSION

Previous Hypotheses on the Nature of the Active Sites

Turkevich and Ciborowski (*1*) and Minachev *et al.* (*12*) advanced the hypothesis that H_2–D_2 equilibration over zeolites is associated with the presence of Lewis sites. This is contradicted by our observation that NaY and NH_4Y act in an identical way, and is also not consistent with the two-maxima-activity path observed in this work. Several factors may explain the discrepancies. In order to observe the two maxima a large number of observations must be made at increasing temperatures. At the time these works (*1*, *12*) were published, the effect of the hydrolyzing conditions were not known. Therefore we believe that the samples investigated by these authors resemble our HYh samples which show indeed a regular increase in the H_2–D_2 exchange rate up to 620°C.

The hypothesis that impurities may act as active centers was first advanced by Turkevich and Ciborowski (*1*). It was based on the low number of active sites found after "H_2 poisoning." However, this observation is in contradiction with all previous work on A, X, and Y zeolites (*2–4*) which report an increase of the activity upon prolonged contact with

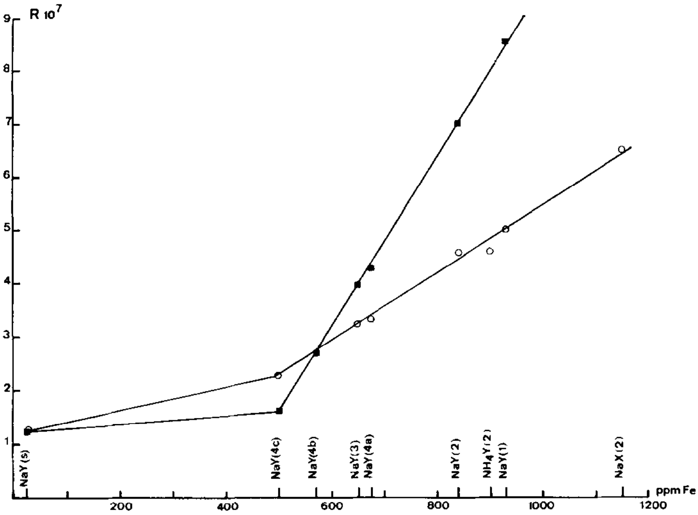


FIG. 7. Influence of the iron impurity concentration on the absolute rate constants for H_2–D_2 equilibration over different zeolites pretreated at 500°C (○) and 660°C (■).

hydrogen. This increase in activity is confirmed in this work.

Brown *et al.* (*3*) rejected the "impurity hypothesis" on the basis of the contradictory effect of activation in hydrogen. Instead they suggested that activated adsorption of hydrogen may occur. However, we believe that their observations can also be explained if changes in the nature of the impurities occur by contact with hydrogen. In fact, their observations on X and A at high reaction temperatures are in agreement with our results in Y zeolites, to which we propose an alternative explanation.

Nature of the Active Sites

The data reported in this work support the hypothesis that the iron present as impurities is responsible for the activation of the hydrogen, an essential step in the equilibration of H_2–D_2 mixtures. The facts supporting this hypothesis can be summarized as follows:

i. similarity of the activity of NH_4Y and NaY samples. This rules out the influence of structural parameters which are properties of the acid zeolites derived from NH_4Y and generally known for acid catalyzed reactions.

ii. Parallelism between the decrease in activity and the decrease in the iron content realized by several chemical extraction techniques. This parallelism is illustrated in Fig. 7 where the intensities of the maxima at 520 and 660°C are correlated with the iron content.

iii. Correspondence between the upper limit of active sites derived from the poisoning experiments and the iron content of these catalysts.

The existence of two maxima in the activity depending on the pretreatment temperatures, and the corresponding variation in activation energy suggest that two different mechanisms exist, both related to the iron impurities. It is our belief that the maximum at the lowest temperature corresponds to iron present as exchangeable cations. We ascribe the second maximum after pretreatments at 660°C to an iron oxide phase separate from the zeolite lattice.

The attribution of the maximum at 520°C pretreatment temperatures to cationic iron is supported by the fact that the activity is decreased by all the treatments which decrease the iron content following an ion exchange mechanism, these are treatments 2 and 3 and to some extent 4. The increase of the activity by increasing the activation temperature from 400 to 520°C, and the poisoning effect of water molecules can be understood in terms of availability of cations for the activation of hydrogen. Iron contents lower than 500 ppm have no catalytic effect. It is a generally known fact that polyvalent cations in dehydrated zeolites have tendency to be located in sites I (*16, 17*) and this is also the case for iron (*13–18*). The limit of 500 ppm can thus be explained by assuming that this fraction of the iron is located in unfavorable positions. The increasing effect of reduction by hydrogen during the first 6 hr may also be related to a change in the availability of iron. Reduction of Fe(III) cations in zeolites Y proceeds to the Fe(II) state (*13–15*). It is possible that this decrease in valency has an influence on the location of the cations in unaccessible sites. However, Fe(II) by itself may be more active than Fe(III) in the activation of hydrogen. Finally, the introduction of La^{3+} ions produces a drastic increase in activity which we ascribe to a displacement of the iron from sites I by the excess La^{3+} ions.

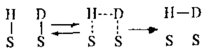
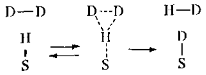
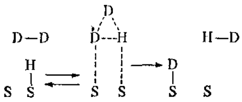
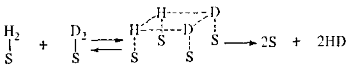
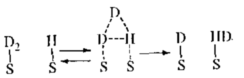
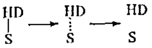
Pretreatments at high temperatures result in the migration of the iron. This was shown by Singer and Stamires (*21*) who demonstrated the appearance of ferromagnetic Fe_3O_4 or of mixed ferrites containing Al upon activation of NH_4Y and NaY zeolites containing trace amounts of ionic iron impurities. McNicol and Pott (*8*) using ESR made a similar observation mainly with trace amounts of iron in lattice positions. They observed a signal indicative of a Fe/Al oxide species with a maximum after activation at 750°C. Meisel *et al.* (*22*) showed the formation of superparamagnetic α-Fe_2O_3 upon thermal activation of Fe(III) exchanged zeolites. All these observations lead us to ascribe the maximum at 660°C to an iron oxide (or mixed oxide) species resulting from a segregation of the iron impurities from the zeolite lattice. Our arguments are the following. The correlation of the intensity of this maximum with the iron content is obvious (Fig. 7). This iron must be present in an unreducible form since it is not influenced by a prolonged treatment with hydrogen. Furthermore, in the sample HYh, which is pretreated in conditions where the migration of the iron must be favored, the low temperature maximum has disappeared, but the high temperature maximum was broadened towards lower activation temperatures. The formation of this oxide phase probably does not discriminate between cationic and lattice iron. Our samples are taken from the same batch as those used by Derouane *et al.* (*9*), in which the content of lattice iron is very low. McNicol and Pott (*8*) have shown that the presence of NH_4^+ ions facilitates the formation of the oxide phase. In our work the presence of NH_4^+ ions has no effect on the position of the second maximum because of the low content of lattice iron. Since the pretreatment procedures result in a thorough dehydration, we must consider that the zeolite lattice is the supplier of the oxygen ions.

The decrease in the H_2–D_2 equilibration rate at temperatures exceeding 650°C must not be related to a destruction of the zeolite lattice. Instead, the decrease of the catalytic activity in conditions where the ferromagnetic signal would persist can be explained by a sintering of the iron oxides. That such a sintering occurs was shown by Meisel *et al.* (*22*).

The data obtained with X samples support these interpretations. The 520°C maximum can be ascribed to cationic iron since the NaX(2) sample fits the relation shown in Fig. 7. The 650°C maximum is not occurring in NaX(2). Since this sample is thermally less stable we assume that lattice destruction prevents migration of iron through a more dense amorphous

TABLE 3

Possible H_2–D_2 Exchange Mechanisms[a]

	Scheme	n in Eq. (3)	Change of k at increasing P
1. Bonhoeffer–Farkas		1 at low coverage 0 at high coverage	Decrease
2. Eley		1.5 at low coverage 0 at high coverage	Increase
3. Rideal		1.5 at low coverage 0.5 at high coverage	Decrease
4. Schwab–Killmann		2 at low coverage 0 at high coverage	Decrease
5. Boreskov–Vassilevitch	Surface transport rate controlling 	1.5 at low coverage 0.5 at high coverage	Decrease
	Desorption of sites of low adsorption energy is rate controlling 	0 at high coverage	Decrease

[a] S = site on catalyst.

matrix. Singer and Stamires (*21*) reported also that the ferromagnetic material is not formed in X zeolites. Introduction of lanthanum stabilizes the X zeolite and the second maximum is then appearing as in the Y samples.

Mechanism of the Equilibration

Several authors (*24*, *25*) have shown that for the exchange of isotopes between the gas phase and a solid catalyst three possible reaction pathways can be distinguished kinetically.

$$\left.\begin{array}{l} D_2(g) + H(s) \rightleftarrows HD(g) + D(s) \\ HD(g) + H(s) \rightleftarrows H_2(g) + D(s) \end{array}\right\} (R')$$

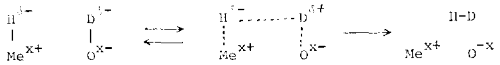
$$\left.\begin{array}{l} D_2(g) + 2H(s) \rightleftarrows H_2(g) + 2D(s) \\ HD(g) + 2H(s) \rightleftarrows H_2(g) + D(s) \\ \qquad\qquad + H(s) \\ HD(g) + 2D(s) \rightleftarrows D_2(g) + D(s) \\ \qquad\qquad + H(s) \end{array}\right\} (R'')$$

$$D_2(g) + H_2(g) \rightleftarrows 2HD(g) \qquad (R)$$

g and s refer to the gaseous and solid state, respectively. Per reactive collision with the catalyst the isotope molecule exchanges either one (R′) or two (R″) of its atoms. The exchange could also take place in the gas phase without detectable participation of the catalyst isotopic atoms (R). The relative contribution of these three mechanisms can be derived from the change in composition of an equilibrium mixture $H_2 : D_2 : HD$ with time. If $\psi = (HD)^2 \cdot (H_2)^{-1} \cdot (D_2)^{-1}$, it can be shown that $d\psi/dt = 0$ if only R and R′ reactions operate. Over a freshly pretreated sample at different pretreatment temperatures no variation in composition of this equilibrium mixture with the time was found. This is a reliable experimental criterion to eliminate the occurrence of the R″ reaction. Consequently, only the Bonhoeffer–Farkas, the Eley and the Rideal mechanisms, in which the hydrogen (deuterium) is dissociatively adsorbed (Table 3) can be considered to occur on the zeolite.

Recently, Richard *et al.* (*26*) investigated the relationship between the experimental first-order rate constant and the pressure of the reaction mixture for different hydrogen–deuterium equilibration mechanisms. In this work, the equilibration reaction was first order at low and zero order at high pressures. Furthermore, the rate constant (*k*) decreases at increasing pressures. Table 3 shows that only the Bonhoeffer–Farkas mechanism accounts for all these observations. This mechanism has also been suggested by Brown *et al.* (*2, 3*) for the H_2–D_2 equilibration and the parahydrogen conversion on A- and X-type zeolites. The results of Brown *et al.* (*2, 3*) are obtained in a pressure region at low fractional coverage of the active sites, while our work was done in a higher pressure region at nearly complete coverage of the active sites. The Bonhoeffer–Farkas mechanism involves (Table 3) a rapid and dissociative adsorption. The rate limiting step is a slow and associative desorption.

These arguments are only valid if gas phase exchange (R mechanism) occurs at a negligible rate. At the reaction temperatures used in this study (200–400°C), it is known that the rate of exchange in the gas phase (R) can be neglected (*11*). In previous work (*27*) the rate of D incorporation in the zeolites was measured at the solid phase. It turns out that both the D_2–OH exchange (heterophase) and the H_2–D_2 exchange show identical kinetic parameters (absolute rate constants and activation energies). This supports the conclusion that no R mechanism is involved in the H_2–D_2 equilibration reaction. Moreover, from the identical numerical values of rate constants and activation energy a common slow step for both reactions may be proposed. Kemball and McCosh (*4*) on CoX zeolites observed identical kinetic parameters for the H_2–D_2 equilibration and the D_2–H_2O exchange. In view of these considerations, the H_2–D_2 equilibration over zeolites activated to the first maximum may be visualized as follows:



In the Y zeolites used in this work Me^{x+} represents cationic iron and O^{x-} a lattice oxygen. Although the reaction is highly endothermic, we prefer to consider the heterolytic dissociation of hydrogen. Indeed, the large fields in the zeolite and the strong interaction of the products with cations and lattice oxygen atoms might favor heterolytic dissociation (*4*).

After high temperature activation it seems that the zeolite behaves more as an inert support for iron oxide species. Therefore, it seems not so straightforward that H_2 molecules undergo a heterolytic dissociation. However, it is not possible to test this hypothesis since after these severe treatments the catalyst hydrogen is strongly reduced and it becomes practically impossible to compare rate constants of H_2–D_2 and OH–D_2 exchange.

ACKNOWLEDGMENTS

We are grateful to Professor Hoste and Dr. C. Dewispelaere (University of Ghent) for the neutron activation analyses. One of us (P.A.J.) has a research position as "Aangesteld Navorser" at the N.F.W.O. (Belgium). C.F.H. had a grant from I.W.O.N.L. (Belgium). Support from the Belgian Government (Diensten van het Wetenschapsbeleid) is gratefully acknowledged.

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