

Catalysis of Benzene Deuterium Exchange, and Related Reactions over NiX and NiY

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Benzene deuterium exchange, and hydrogen deuterium equilibration were studied over a range of catalysts prepared by nickel ion exchange with samples of X, Y and intermediate composition, faujasite type zeolites. Experiments were also carried out on the water poisoning of both reactions. The results obtained were almost independent of the silicon to aluminum atom ratio in the zeolites. A mechanism which involves the heterolytic splitting of deuterium or hydrogen is proposed to explain both reactions. The active sites are thought to be associated with nickel ions located on the exterior faces of the crystallites.

INTRODUCTION

The catalysis of the exchange reaction between deuterium and benzene by molecular sieve X containing some nickel ions, has been reported to show some unexpected features (1). For example, the activity of the catalysts increased very rapidly with nickel content, until a critical ion exchange level was reached, after which further addition of nickel had little effect. Traces of water added to the outgassed catalyst had a strong poisoning effect, even though varying the water content by the same amount, by changing the outgassing conditions, hardly altered the rate of reaction at all.

The nickel content required to produce maximum catalyst activity was very low. This, and the water poisoning result, made it clear that the observations could not be explained purely from a knowledge of the crystal structure, because all regular features of the crystal geometry would be repeated too often by the crystal symmetry. It was therefore proposed that the active catalytic sites were associated with nickel ions situated in places where there was an unusually high local concentration of aluminum in the zeolite framework. As aluminum atoms do not generally bond so

as to share an oxygen atom in an aluminosilicate structure (Lowenstein's rule), the number of active sites should be small, though it might be expected to depend strongly on the aluminum to silicon atom ratio in the solid.

To investigate the matter further, we have studied the exchange reaction between benzene and deuterium, and the equilibration of hydrogen and deuterium over catalysts prepared from three different zeolite samples, and the effect of water on both reactions.

METHODS

The apparatus and techniques used were very similar to those of Pope and Kemball (1). This section will therefore be mainly confined to points of difference.

Materials

Benzene was May and Baker "Proanalysis" grade. Hexadeuterobenzene was Koch Light (puriss). Both were dried over sodium, and shown to be pure by mass spectrometry. Deuterium was Matheson Gas Co. C P grade. Hydrogen (99.7% purity) and argon (>99.99% purity) were supplied by N.Z.I.G. Ltd.

The liquids were degassed by freezing,

pumping, melting cycles before use. Deuterium and hydrogen were passed through a trap containing activated molecular sieve 13X pellets at 77 K, before diffusion through a palladium alloy thimble. Argon was led through a trap cooled at 77 K before use.

Binder free sodium X, supplied by BDH. Ltd., with a silicon to aluminum ratio of 1.23 ± 0.04 , and binder free sodium Y, supplied by the Linde Co., with a silicon to aluminum ratio of 2.51 ± 0.06 were used to prepare most of the catalysts. A few experiments were performed with a zeolite sample synthesized in this laboratory (2), which had a silicon to aluminum ratio of 1.78 ± 0.06 . All samples were chemically analyzed, and gave X-ray diffraction patterns corresponding to a single phase. Argon adsorption capacities per unit cell of the sodium forms of the zeolites at 77 K were the same within an experimental error of $\pm 1\%$. Optical microscopy showed all samples to consist of roughly spherical particles which appeared to be mostly 1–4 μm diameter.

Ion exchange, storage, and weighing procedures were all essentially the same as those of Pope and Kemball (1). In this paper we will call, for example, a X zeolite sample in which 20.2% of the exchangeable sodium ions have been replaced by nickel, NiX-20.2.

Experimental Procedure

The mass of hydrated catalyst used was always about 0.1 g. New samples were outgassed at room temperature for 1 hr, before switching on a furnace surrounding the reaction vessel. The temperature reached 420 K in about 1 hr, and the maximum outgassing temperature of 590 K after about 2.5 hr. This temperature was maintained with pumping, for 12–14 hr to complete the pretreatment.

Outgassing a used catalyst before a second, or subsequent run was carried out either overnight at 590 K, or for 1 hr at

the reaction temperature. Both procedures completely restored the adsorption capacity of the catalyst for benzene. Occasionally, after outgassing for 1 hr at a low reaction temperature a small trace of deuterated benzene ($< 1\%$) remaining from the previous experiment was detected. This appeared to have no effect on the results obtained.

A standard benzene dose of 8×10^{18} molecules (about 0.30 molecules/supercage) was used in benzene adsorption experiments. In the benzene hexadeuterobenzene exchange experiment this was an equimolar mixture of the two components. In benzene deuterium exchange reactions 8×10^{19} molecules of deuterium were used, and in hydrogen deuterium equilibration, the standard mixture consisted of 8×10^{18} molecules of benzene, and 4×10^{19} molecules each of hydrogen and deuterium.

The other details of the procedure have been described before (1).

RESULTS

Outgassing

When this work was begun, the initial outgassing was carried out more cautiously than described above (3). This was to avoid the possibility of structural collapse of the zeolite. However, reproducibility of benzene deuterium exchange rates was found to be poor. Table 1 illustrates this.

TABLE 1
COMPARISON OF THE RESULTS AFTER THE TWO
OUTGASSING METHODS^a

Sample	Rate constant for benzene deuterium exchange under standard conditions ($\text{sec}^{-1} \text{g}^{-1}$)	
	Gentle outgassing	Usual method
NiX-2.0	0.32 ± 0.14 (6)	0.36 ± 0.05 (8)
NiX-41.9	3.1 ± 2.2 (5)	4.2 ± 0.9 (7)

^a The errors are standard deviations, obtained from the number of experiments in parentheses.

The "gentle" outgassing method was therefore abandoned, and not used again in this work.

Differences in reproducibility were apparently not linked with different values for the average rate constant. Argon adsorption measurements produced no evidence of structural collapse in any sample before or after catalytic use, with either outgassing procedure. We know no explanation of this set of results.

Benzene Adsorption

Benzene adsorption under reaction conditions was measured on NaX and NiX-20.2 as previously described (1). Adsorption was rapid and reversible. The results were consistent with the heat of adsorption of benzene on both samples being equal at 84 ± 5 kJ mol⁻¹, and constant over the range of surface concentrations studied (0.30–0.05 molecules/supercage). Ion exchange replacement of sodium by nickel decreased the amount of adsorption at a given temperature and pressure, as was reported before (1).

When the poisoning effect of water added to the outgassed zeolite was studied, it was found that the water treated zeolite adsorbed less benzene. The effect was small at 440 K, when nearly all the benzene was adsorbed, but became appreciable at higher temperature. At 505 K, NiX-0.78 adsorbed about 0.08 molecules of benzene/supercage less, when treated with 0.10 water molecules/supercage. It appeared that at suitably high temperatures, and low water doses, 1 water molecule displaced 1 benzene molecule.

Benzene Deuterium Exchange

The exchange was usually studied at 440–480 K, except when low catalyst activity made higher temperatures necessary. The initial run with a new sample of catalyst was often rather slower (typically 20%) than subsequent runs carried out on the same sample under similar conditions.

No further effect was noticed, irrespective of which method of outgassing between experiments was used. All results quoted hereafter ignore initial runs.

The mean number of deuterium atoms entering each reacting benzene molecule in the initial stages of reaction was 1.1–1.5, the higher values generally being associated with faster exchange rates. No cyclohexane formation occurred. Activity of a catalyst as a function of pattern with both X and Y zeolites (Fig. 1). Six data points for the zeolite of intermediate silicon to aluminum ratio, synthesized in this laboratory (2), are also shown. The results of this, and previous work, are summarized in Table 2.

The apparent activation energy of the benzene deuterium exchange reaction decreased with increasing temperature. However, this was almost certainly due to the decreasing amount of benzene adsorbed. The results of applying a correction calculated from the measured benzene sorption, and the assumption that the reaction was

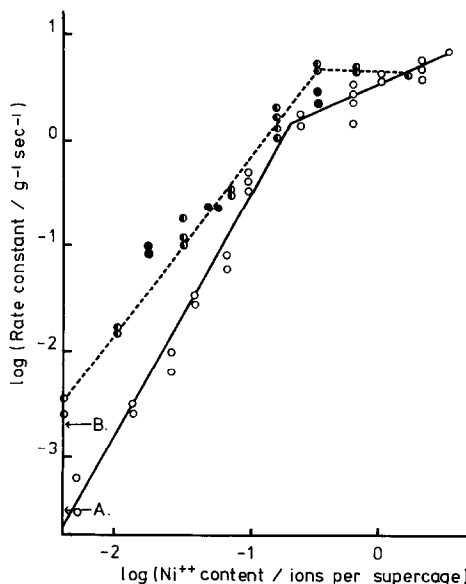


FIG. 1. Benzene deuterium exchange at 453 K. (○) NiX; (●) NiY; (●) Lab synthesis; (A) activity of NaX; (B) activity of NaY.

TABLE 2
SUMMARY OF CATALYST ACTIVITY AS A FUNCTION OF NICKEL CONTENT^a

Zeolite	Si/Al ratio	Slope ^b		Break (Ni ²⁺ /supercage) ^b
		Steep	Shallow	
Linde X	1.26	2.4 ± 0.2	0.5 ± 0.2	0.17 ± 0.06
Linde Y	2.51	1.7 ± 0.1	0.0 ± 0.1	0.3 ± 0.1
Lab. preparation	1.86	1.2 ± 0.2	—	—
Linde X ^c	1.26	3.3 ± 0.3	-0.5 ± 0.3	0.14 ± 0.05
Linde X	1.26	2.3 ± 0.2	0.6 ± 0.2	0.10 ± 0.03
Linde Y	2.51	1.5 ± 0.2	—	—

^a The first four rows are for benzene deuterium exchange, and the last two for hydrogen deuterium equilibration.

^b These descriptions relate to Figs. 1 and 3.

^c Results from Ref. (1).

first order with respect to adsorbed benzene (1), are shown in Table 3.

It can be seen that the corrected results for X and Y zeolites do not differ significantly, and that water poisoning had no effect on the corrected activation energies. There was no trend with nickel content. The apparent activation energies obtained with NaX (65 ± 10 kJ mol⁻¹) and NaY (55 ± 10 kJ mol⁻¹) at about 570 K are also similar to the corrected values in Table 3, when allowance is made for the heat of adsorption of benzene.

The order of the reaction with respect to deuterium in the gas phase was found by varying the deuterium pressure between 0.4 and 7.4 kN m⁻², in the presence of a standard benzene dose. (Most experiments

were performed at a deuterium pressure of about 2.2 kN m⁻².) NiX-20.2 at 444 K gave an order of 0.45 ± 0.09, and NiX-0.79, 0.44 ± 0.08 at 518 K.

The effect of adding water to the outgassed zeolites is shown in Fig. 2. The usual technique was to add the required water dose to the zeolite at the reaction temperature, 10 min before the benzene deuterium mixture. Modifying the procedure by adding the water 1 hr before the reaction mixture, or by adding water at room temperature, and then bringing the catalyst to the reaction temperature, did not alter the results obtained. The poisoning effect depended only on the total amount of water added, and not on whether it was added as a single dose, or

TABLE 3
ACTIVATION ENERGIES FOR BENZENE DEUTERIUM EXCHANGE (kJ mol⁻¹)^a

	Linde X		Linde Y		Lab synthesized	
	U	P	U	P	U	P
Uncorrected for desorption	96 ± 13 (13)	81 ± 14 (5)	89 ± 31 (8)	83 ± 18 (5)	115 ± 8 (3)	93 ± 26 (3)
Corrected	114 ± 10 (13)	116 ± 8 (5)	124 ± 4 (8)	116 ± 9 (5)	134 ± 2 (3)	130 ± 4 (3)

^a U = unpoisoned; P = poisoned, with various amounts of water. The errors quoted are standard deviations, obtained from the number of determinations written in parentheses.

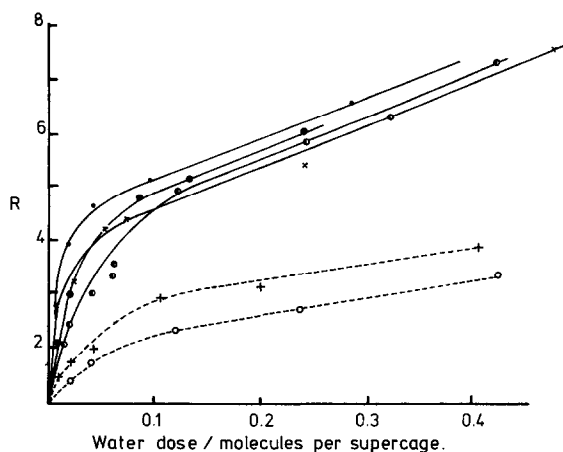


FIG. 2. The effect of added water on benzene deuterium exchange. R is the ratio of the rate constants over unpoisoned and poisoned catalysts. (●) NiX-0.79 at 505 K; (◐) NiX-1.98 at 464 K; (×) NiX-12.5 at 465 K; (◑) NiX-41.9 at 443 K; (○) NiY-0.98 at 485 K; (+) NiY-4.95 at 445 K.

as the cumulative dose obtained after several experiments, separated by brief outgassing periods.

Benzene Hexadeuterobenzene Exchange

This reaction was only studied over NiX-12.5. No reaction was observed below 543 K, at which temperature the rate of exchange of the heavy benzene was $0.24\% \text{ sec}^{-1} \text{ g}^{-1}$. The rate of light benzene exchange was much smaller. At 568 K, heavy benzene exchanged at a rate of $0.39\% \text{ sec}^{-1} \text{ g}^{-1}$, and light benzene at $0.06\% \text{ sec}^{-1} \text{ g}^{-1}$. These different rates suggested that hydrogen originally held by the zeolite was exchanging with the benzene. Analysis of the reaction mixture as a function of time at 568 K indicated that about 1.4×10^{19} zeolite hydrogen atoms were involved.

The product distribution closely followed the sum of two binomial distributions throughout the exchange, showing that the deuterium and hydrogen atoms in the benzenes were exchanging one at a time. The apparent activation energy for the exchange of deuterium atoms in hexadeuterobenzene was about 50 kJ mol^{-1} .

Hydrogen Deuterium Equilibration

Equilibration was usually studied at 400–420 K. The reaction was carried out in the presence of benzene, to make the results directly comparable with those from the exchange reaction. Test experiments carried out in the absence of benzene showed that its presence did not affect the rate of equilibration significantly. The first run on a fresh sample of catalyst took place at a lower rate (by a factor of about 2) than the second and subsequent runs, which were reproducible when they were separated by outgassing periods at the reaction temperature. Outgassing overnight at 590 K resulted in a low activity for the next run, and then the same pattern of behavior as before could be repeated by outgassing at reaction temperature between further experiments. The results reported in this paper ignore the slow, first, runs.

The rate of equilibration depended on nickel content in a similar way to that found for benzene deuterium exchange. (Fig. 3 and Table 2). The rate of equilibration over NaX was negligible at 568 K.

The apparent activation energy was

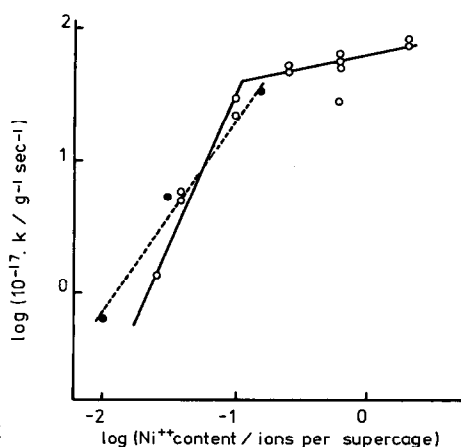


FIG. 3. Rate constant k for hydrogen deuterium equilibration at 405 K. (○) NiX; (●) NiY.

$26 \pm 5 \text{ kJ mol}^{-1}$, and did not depend on nickel content, or on whether X or Y zeolites were used. The order of the reaction was 1.0 within experimental error, with respect to the total pressure ($\text{H}_2 + \text{D}_2$) for the three catalysts studied (NiX-0.79, NiX-1.98, NiX-12.5).

The equilibration reaction was poisoned by water addition, but the effect was not nearly as great as with benzene deuterium exchange. The results are shown in Fig. 4.

DISCUSSION

The results in Table 3 show that the variation of the amount of benzene sorbed

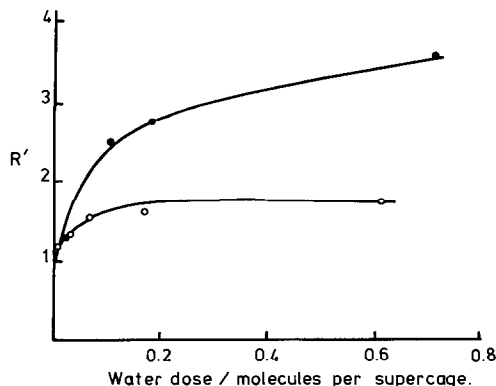


FIG. 4. The effect of added water on hydrogen deuterium equilibration. R' is the ratio of the rate constants over unpoisoned and poisoned catalysts. (○) NiX, 0.79 at 443 K; (●) NiX, 12.5 at 400 K.

with temperature can account for all the differences in apparent activation energy in the benzene deuterium exchange reaction. The catalytically active sites must therefore all be rather similar, whether they occur on X or Y zeolites, whatever the nickel content, and whether the catalyst is poisoned with water or not. It must also be true either that benzene was only adsorbed on these sites, or that it has nearly the same heat of adsorption on the catalytic sites, and any other adsorption site used. The fact that the amount of adsorption decreases with increasing ion exchange, whereas the activity increases, at least initially, must mean that the second alternative is correct, because the exchange is first order with respect to adsorbed benzene (I). This conclusion is supported by observation that the "break" in Fig. 1 occurs when the total number of nickel ions present in NiX is less than the number of benzene molecules adsorbed, at the lower reaction temperatures. (Steric considerations make it seem most unlikely that two benzene molecules could be adsorbed near a single nickel ion.) The small amount of water needed to poison the reaction almost completely (Fig. 2) is also consistent with the idea that only some of the benzene is adsorbed at catalytic sites.

The great similarity between Figs. 1 and 3, suggests very strongly that the two reaction mechanisms are linked. The order of the equilibration reaction with respect to the gaseous species is consistent with a process which involves the cleavage of hydrogen or deuterium molecules at an active site, followed by a recombination of two moieties which do not necessarily arise from the same initial molecule. If one of these species may exchange with a benzene molecule in an activated process, the order of the benzene deuterium exchange with respect to deuterium, the higher activation energy of this reaction, and the stepwise nature of the exchange process can be understood. This is explained fur-

ther after the proposed reaction equations are presented.

Activation of deuterium as the key step in the exchange is supported by the fact that benzene hexadeuterobenzene exchange does not occur until a much higher temperature, and the observations that benzene adsorption is easily reversible, not activated, and involves a heat of adsorption characteristic of physical rather than chemical adsorption.

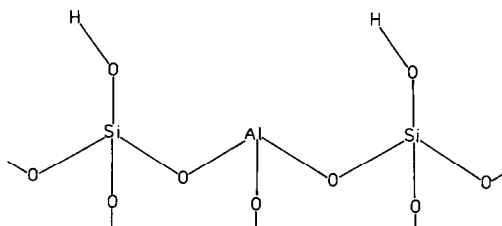
It was surprising to find that the aluminum to silicon ratio in the zeolite framework influenced the results so little, in view of the importance which is usually attached to the electrostatic fields near zeolite cations (4), and the way in which these fields are thought to depend on framework composition (5). We believe, however, that our results may be understood if the catalytic sites are located on the exterior surface of the zeolite crystallites.

Details of faujasite type structures are very clearly discussed by Smith (6). Cleavage of these crystals can only be readily envisaged as the breaking of hexagonal prism units which join the sodalite cages (7). A silicon atom at such a crystal face presumably retains its coordination number of four, and an octet of electrons by being coordinated to three structural oxygen atoms and one hydroxyl group. Aluminum will probably be coordinated to three structural oxygens, leaving a fourth coordination position vacant to accept an adsorbed molecule. Relatively mild outgassing may then remove the adsorbed species, and produce the local arrangement shown in the scheme below. This is similar to that believed to be formed in the bulk

zeolite, in the much higher temperature dehydroxylation of decationated zeolites (7). The crystal face will thus provide a new type of cation site, in which the cation is placed with respect to structural oxygens in much the same way as a cation at site II would be, but which also allows strong interaction with hydroxyl groups associated with any silicon atoms in its vicinity. Usually, there should be three such hydroxyls at each site in an X zeolite, and four in a Y zeolite.

When nickel is ion exchanged into the sodium forms of X or Y zeolites, the high hydration energy of nickel ions should ensure that sites offering at least some water coordination are used preferentially. If water is removed by outgassing, ion migration should occur. Site I would be expected to be preferred when sufficient water has been removed, and this has been demonstrated to be the case in Y zeolites (8). When conditions are not severe enough to dehydroxylate the zeolite, similar arguments would suggest that the crystal face site will be preferred over site I. We think that this is the case under our outgassing conditions. Unfortunately, X-ray results cannot arbitrate here.

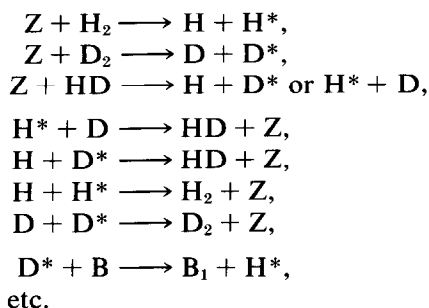
The relative number of crystal face sites will depend on the crystallite size, and can be computed in a way suggested by Uytterhoeven *et al.* (7). If the breaks in our Figs. 1 and 3 also measure the number of such sites, an average crystallite size of about 40 nm is indicated. This is consistent with the broadening of the X-ray diffraction lines observed with our samples, though the result is subject to a rather large uncertainty. It is interesting to note that in our benzene hexadeuterobenzene experiment, the number of hydrogen atoms from the zeolite which equilibrated with the benzene was about three times the number of nickel ions in the structure at the break in Figs. 1 and 3. This correlates well with the number of terminal SiOH groups expected in an X zeolite.



A three-dimensional model of the proposed site shows that a single benzene molecule, or a single water molecule, could be adsorbed over the nickel ion. The profound water poisoning effect on the exchange reaction, and the decreased benzene adsorption observed on a water treated catalyst can then be explained by the much stronger adsorption of water.

Hydrogen deuterium equilibration is postulated to take place via a heterolytic splitting of these molecules at a three coordinated aluminum atom. The process is formally similar to that suggested by Burwell (9) for equilibration catalysed by chromia. The negatively charged part associates with the aluminum, and the proton or deuterium with a neighboring SiOH or lattice oxygen. If the latter position is used equilibration must also involve exchange between the "deuteron" and the "hydrogen" on the neighboring SiOH or the mobility of these species. Examination of a model shows that there should be little steric interaction between a hydrogen or deuterium molecule in the process of being activated, and a benzene or water molecule adsorbed above a cation at the catalytic site. Accordingly, equilibration should not be strongly poisoned by either of these species. Furthermore, the difference between the site for "hydrogen" activation in X and Y zeolites should be rather slight as the nearest neighbor atoms are the same in each case.

A reaction mechanism to account for both the exchange and equilibration reactions can be written formally as



Here Z represents a catalytic site for the activation of "hydrogen." The heterolytic fission of a molecule such as H_2 results in two adsorbed species represented as H and H^* . B is benzene, and B_1 C_6H_5D which are adsorbed at catalytic sites. The adsorption-desorption equilibria of hydrogen and benzene are assumed to be taking place, but are omitted from the kinetic scheme for the sake of clarity.

If the "protonated" SiOH or structural oxygen is the species involved in benzene exchange, this would allow the light-benzene/heavy-benzene exchange reaction to be linked with the high temperature proton mobility observed in some X and Y zeolites (10).

The proposed mechanism does not make it clear why the slope of the curves in Figs. 1 and 3 is so steep below the break. If nickel ions in our outgassed samples fill the crystal face cation sites before any others are used at all, the predicted slopes are 1.5 in Fig. 1 and 1.0 in Fig. 3. These slopes arise as follows. Hydrogen or deuterium molecules adsorbed at the catalytic sites are presumably weakly held, so that the adsorption should be described by Henry's law. Thus, for example

$$[D_2]_{\text{ads}} = k[Ni^{2+}]_{\text{sp}} p_{D_2}.$$

Square brackets denote concentrations. The number of catalytic sites, is, according to our model, equal to the number of nickel ions at special sites, which are written with the subscript sp.

If the adsorbed deuterium molecules are in equilibrium with the adsorbed, dissociated species, then

$$[D][D^*] = K[D_2]_{\text{ads}} = kK[Ni^{2+}]_{\text{sp}} p_{D_2}.$$

K is the equilibrium constant. D and D^* are formed in equal numbers by the dissociation, so that

$$[D] = [D^*] = (kK[Ni^{2+}]_{\text{sp}} p_{D_2})^{1/2}.$$

If the rate of hydrogen deuterium equilibration is controlled by the rate of the sur-

face reaction, then

rate of equilibration

$$\begin{aligned} &= k_2([\text{D}][\text{H}^*] + [\text{D}^*][\text{H}]) \\ &= 2k_2kK[\text{Ni}^{2+}]_{\text{sp}}p_{\text{D}_2}^{1/2}p_{\text{H}_2}^{1/2}. \end{aligned}$$

k_2 is the reaction rate constant.

The rate of benzene deuterium exchange is slow compared with the rate of equilibration, so that this reaction will not affect the concentration of D^* very much. The number of benzene molecules adsorbed at catalytic sites is directly proportional to $[\text{Ni}^{2+}]_{\text{sp}}$, so that

$$\begin{aligned} [\text{B}]_{\text{ads}} &= k'[\text{Ni}^{2+}]_{\text{sp}}, \\ \text{rate of exchange} &= k_3[\text{D}^*][\text{B}]_{\text{ads}} \\ &= k_3k'(kK)^{1/2}[\text{Ni}^{2+}]_{\text{sp}}^{3/2}p_{\text{D}_2}^{1/2}. \end{aligned}$$

k_3 is the rate constant for the exchange reaction.

We have already explained why we do not think that the last equation is quite correct. Our arguments require that only a fraction of the adsorbed benzene molecules should be located at catalytic sites, and that this fraction should increase as the nickel content increases, until all the special cation sites are occupied by nickel ions. This should increase the steep slope in Fig. 1 appreciably.

It is also worth noting that if the nickel ions are not all accommodated initially in

the crystal face sites, this can also affect the slopes a great deal. As few ions are involved, only a very small number of particularly favored ion exchange sites in the bulk of the crystal would be required to explain the experimental results.

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