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Reactions of *p*-Xylene with Deuterium on Supported Platinum Catalysts

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The exchange of the hydrogen atoms in *p*-xylene with deuterium and the deuteration of *p*-xylene were used as test reactions to examine the role which supports play in determining the catalytic properties of platinum on various substances. After allowing for differences in the dispersion of platinum by expressing rates in terms of the platinum available to chemisorb hydrogen, there was a remarkable similarity between the results obtained for catalysts on the same support but from different sources. The rates of the reactions at 100°C followed the order: exchange of ring atoms $\geq$ exchange of the methyl hydrogen atoms $>$ deuteration, but the relative rates varied as the support was changed from γ alumina to α alumina or to silica. In discussing the effect of the supports on the activity of the metal, attention is directed to a possible role of strongly held water on the supports.

INTRODUCTION

The role which supports play in determining the over-all activity of supported metal catalysts has been the subject of several recent investigations. Although it has been stated (*1*) that supports do not seem to interact with noble metal catalysts, there is growing evidence to indicate a contrary view. A change of the support from silica to alumina has been shown to cause differences in the infrared spectrum of carbon monoxide on platinum (*2*) and in the activation energy for the hydrogenolysis of ethane (*3*). Hirota and Ueda (*4*) found that the exchange of both ring and methyl hydrogen atoms occurred when *p*-xylene and heavy water reacted over nickel on alumina (prepared by two methods) but that only the methyl hydrogen atoms were replaced when the support was kieselguhr or silica. Platinum on α alumina or silica was found by Shephard and Rooney (*5*) to be much less active than platinum on γ alumina in catalyzing reactions of C_9 alkyl aromatics. McHenry *et al.* (*6*) have suggested that the active component for dehydrocyclization in the Pt/Al_2O_3 system is a platinum-alumina complex which is soluble in aqueous hydrofluoric acid and Johnson and Keith (*7*) have linked this complex to the oxidized state which leads to high dispersion of platinum on reduction.

We believed that the reactions between an alkyl aromatic molecule and deuterium would be particularly valuable for testing the catalytic behavior of platinum on a number of supports. The choice of *p*-xylene as the reactant permits three reactions to be followed simultaneously: (1) exchange of the six identical hydrogen atoms in the methyl groups, (2) exchange of the four identical hydrogen atoms on the ring, and (3) deuteration to form 1,4-dimethylcyclohexane. All these reactions have been shown (*8*) to take place at comparable rates on evaporated platinum films at 0°C. Since any differences observed in the catalytic activity with various supports might be a consequence of different degrees of dispersion of the platinum as well as of the interaction of the support with the metal, we planned to characterize our catalysts by measuring the platinum surface available for reaction by

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the hydrogen/deuterium exchange technique used by Hall and Lutinski (*9*). Measurements of this kind enabled us to compare the activity of different catalysts by expressing rates in terms of the weight of platinum which was available for the chemisorption of hydrogen, thus correcting for differences in platinum dispersion on the various supports.

EXPERIMENTAL

The reactions were carried out in a static system consisting of an all-glass reaction vessel (187 ml) which was separated from the nearest stopcock of a conventional vacuum apparatus by a gold foil trap. The reaction vessel was also connected by means of a glass capillary leak to a Metropolitan-Vickers MS2 mass spectrometer which enabled continuous analyses of the reaction mixture to be made during the course of runs. In all other respects, the apparatus was essentially similar to one described previously (*10*).

Deuterium, prepared by electrolysis of 99.95% heavy water, was purified by diffusion through palladium and *p*-xylene (99.6%), obtained from Imperial Chemical Industries, Ltd., was dried with activated molecular sieves (Linde 5A), outgassed, and distilled under vacuum. The catalysts obtained from Imperial Chemical Industries, Ltd. (ICI) and Johnson, Matthey & Co., Ltd. (JM) were in the form of irregular 20–40 B.S.S. mesh particles; those from Universal-Matthey Products Ltd. (UMP) were uniform spheroids about 1 mm in diameter and were related to the duofunctional catalysts described by Haensel and Bloch (*11*).

All catalysts were pretreated in much the same way. Samples placed in the reaction vessel were evacuated while the temperature was raised slowly to 350°C (430°C for the UMP catalysts) and outgassed overnight to less than 10^{-5} mm pressure. After cooling to room temperature, about 25 mm of deuterium was admitted and the temperature raised to 340°C (400°C for the UMP catalysts) for 30 min and then evacuated for 5 min; a further 15 mm of deuterium was added and the samples were then cooled to reaction temperature and evacuated for 10 min before admission of the reaction mixture.

A measure of the fraction of the total platinum on each catalyst available for reaction was determined by using a simplified version of the hydrogen/deuterium exchange technique described by Hall and Lutinski (*9*). A 1.0 g sample was outgassed overnight at 400°C, cooled to room temperature, and contacted with 25 mm deuterium. The temperature was raised rapidly to 400°C, which caused the hydroxyl hydrogen atoms on the support to equilibrate with the gasecus deuterium. Analysis of the mixture by the mass spectrometer enabled the total hydrogen on the support to be estimated and the mixture was then evacuated and 10 mm of deuterium added before cooling the sample to 0°C. Repeated exchange with fresh samples of deuterium at 0°C completely covered the exposed platinum with chemisorbed deuterium atoms and the sample was cooled to −195°C, evacuated for 10 min, and exposed to 2 mm of hydrogen. Raising the temperature to 0°C allowed the deuterium on the platinum to equilibrate with the gaseous hydrogen and analysis of the gas phase gave the amount of platinum available for chemisorption. The hydrogen atoms on the supports did not begin to exchange until the temperature had been raised to at least 80°C and so there were no complications from this source in the determination of the platinum areas.

The standard reaction mixture consisted of 1.52 mm of *p*-xylene and a 23:1 ratio of deuterium:*p*-xylene. The mass spectrometric analyses were carried out with an ionizing beam of 16-V electrons and the methods used to determine the exchanged *p*-xylenes and 1,4-dimethylcyclohexanes have been described (*8*). The relative sensitivity of the mass spectrometer for xylene:dimethylcyclohexane was found by calibration to be 3.55:1.

RESULTS

The Catalysts

The catalysts used are listed in Table 1 together with details of the surface areas given by the suppliers and the results of the hydrogen/deuterium exchange investigations of the catalyst surfaces. The symbol A is used for platinum supported on γ alumina which in the cases of A4 and A5 had been activated by a fluorine treatment and in the cases of A6 and A7 by a chlorine treatment. The symbols B and C are used for platinum supported on α alumina and silica, respectively. The column headed "Fraction Pt available" represents the fraction of the total platinum on the catalyst which is present as surface atoms on the assumption that each such atom can chemisorb a deuterium atom (*12*) under conditions used in the exchange experiments. The results so obtained may not have great significance as absolute values but they are valid as a comparison of the series of catalysts. The final column gives the total hydrogen on the supports exchangeable with deuterium at or below 400°C.

Evaluation of the Reaction Results

The methods of determining the rates of exchange of the two kinds of hydrogen atoms in p-xylene have been described in detail by Crawford and Kemball (*13*) but the equations used will be summarized briefly. The course of an exchange reaction of any molecule in which all the hydrogen atoms are equally easily exchanged is given (*14*) by the equation

$$-\log_{10}(\phi_\infty - \phi) = k_\phi t/2.303\phi_\infty - \log_{10}\phi_\infty \tag{1}$$

where k_ϕ is the initial rate of entry of deuterium atoms into 100 molecules of reactant in unit time, ϕ is defined as

$$\phi = \sum_i i d_i \tag{2}$$

d_i, representing the percentage of the isotopic species containing i deuterium atoms present at times t, and ϕ_∞ is the equilibrium value of ϕ.

When there are two groups of hydrogen atoms (A and B) exchanging at different rates, a plot according to Eq. (1) will not be linear but the initial and final sections will approach asymptotically to straight lines having different slopes. The value of k_ϕ determined from the gradient of the first section is the sum of the initial rates of exchange of the two groups of hydrogen atoms, i.e.

$$k_\phi = k_A + k_B \tag{3}$$

The final section of the plot may be represented by the equation

$$-\log_{10}(\phi_\infty - \phi) = k_B t/2.303\phi_{B\infty} - \log_{10}\phi_{B\infty} \tag{4}$$

which describes the course of the exchange of the slower group of hydrogen atoms (B) on the assumption that the group A hydro-

TABLE 1
DATA ON THE SUPPORTED PLATINUM CATALYSTS

Number	% Pt	Support	Supplier	Surface area (m^2/g)	Fraction Pt available	OH on support (ml H_2/g)
A1	0.5	γ-Al_2O_3	ICI	—	0.28	7.7
A2	0.1	γ-Al_2O_3	ICI	—	0.37	—
A3	0.2	γ-Al_2O_3	JM	17	1.01	—
A4	0.375	γ-Al_2O_3,F	UMP	180	1.1	9.6
A5	0.75	γ-Al_2O_3,F	UMP	180	0.93	10.9
A6	0.375	γ-Al_2O_3,Cl	UMP	180	0.83	10.2
A7	0.75	γ-Al_2O_3,Cl	UMP	180	0.94	8.3
B1	0.5	α-Al_2O_3[a]	ICI	25	0.18	0.8
B2	0.5	α-Al_2O_3[b]	ICI	6	0.08	0.3
C1	0.9	SiO_2	ICI	—	0.43	12.0
C2	0.2	SiO_2	JM	83	0.33	12.1

[a] Fired at 1000°C.

[b] Fired at 1200°C.

gen atoms have attained an equilibrium isotopic content of deuterium. The gradient of the final section of the plot gives the value of k_B and the intercept at $t = 0$ is used to determine $k_{B\infty}$ and hence the number of hydrogen atoms in each group (n_A and n_B) from the relations

$$\phi_\infty = \phi_{A\infty} + \phi_{B\infty}, \quad \text{and} \quad \phi_{A\infty}/\phi_{B\infty} = n_A/n_B \qquad (5)$$

Two experiments are used to illustrate the application of Eq. (1) and Eq. (4). Figure 1 shows the distribution of the isotopic p-xylenes formed during the exchange over

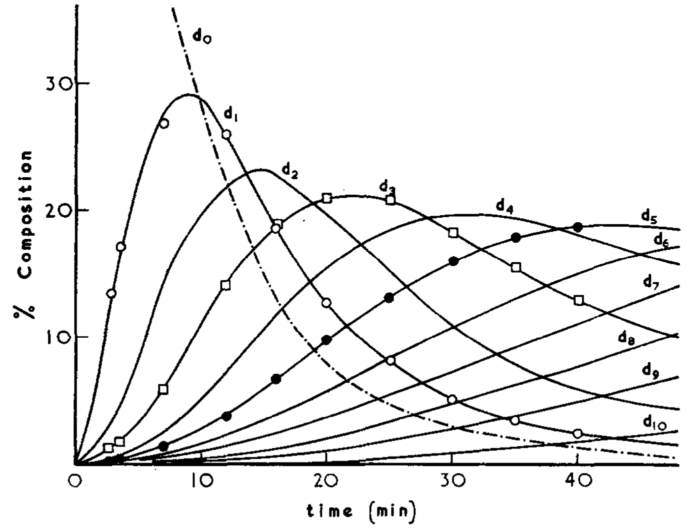

FIG. 1. Distribution of isotopic p-xylenes formed during exchange with deuterium on Catalyst A2 at 100°C. Experimental points are given for three isotopic species to indicate the accuracy of the results.

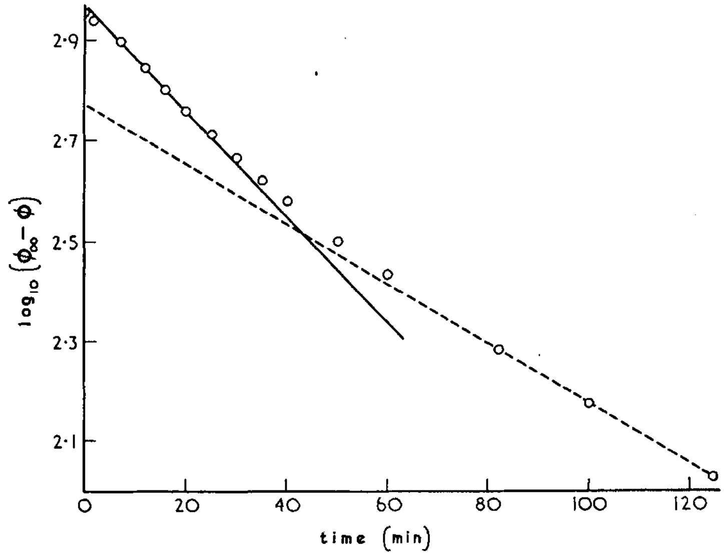

FIG. 2. The plot according to Eq. (1) and Eq. (4) for the results in Fig. 1.

Catalyst A2 at 100°C; there is a fairly regular build-up of the amounts of the various species with increasing deuterium content and, as shown in Fig. 2, there is not a substantial difference between the slopes of the initial and final sections of the plot according to Eq. (1). On the other hand, there is a definite break in pattern of isotopic species after the formation of the d_4 compound during reaction over Catalyst B2 at 95°C (Fig. 3) and a correspondingly greater change of slope in the plot according to Eq. (1) (Fig. 4). Both these experiments indicate that the hydrogen atoms on the ring of the p-xylene molecule were exchanged more rapidly than the hydrogen atoms on the

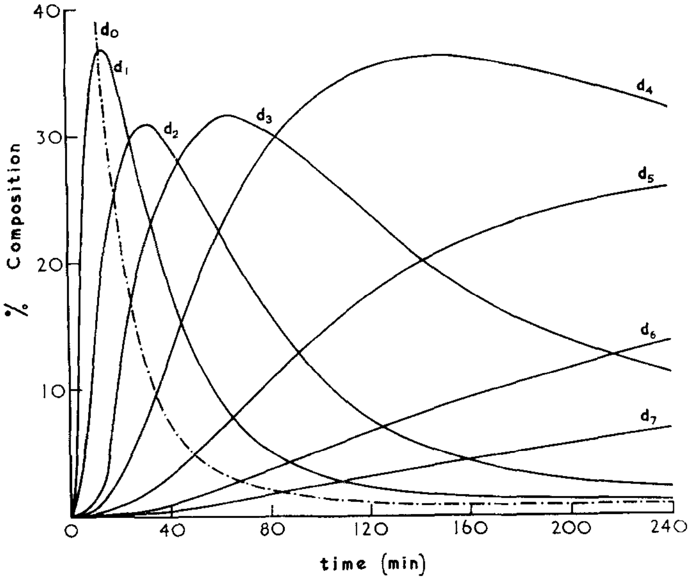

FIG. 3. Distribution of isotopic p-xylenes formed during exchange with deuterium on Catalyst B2 at 95°C.

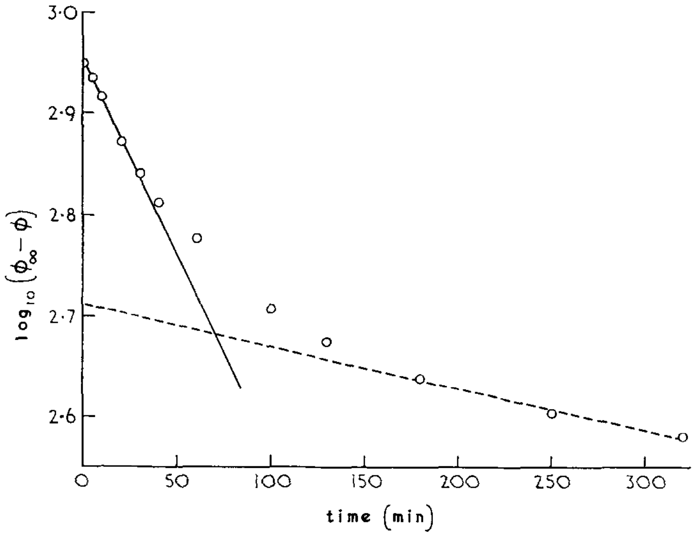

FIG. 4. The plot according to Eq. (1) and Eq. (4) for the results in Fig. 3.

methyl groups and this was also observed with all the other supported catalysts whenever there was a noticeable difference in the rate of exchange in the two groups of hydrogen atoms. In general, the values of $\log_{10} \phi_{B\infty}$ determined from the intercepts of the lines drawn through the latter points ranged from 2.72 to 2.77. Thus, the values of $\phi_{B\infty}$ lay between 525 and 589 in reasonable agreement with the expected value of 534 derived from the assumption that there were six hydrogen atoms in group B and the substitution of the experimental $\phi_\infty = 890$ in Eq. (5).

The initial rate of disappearance of the light p-xylene in per cent per unit time k_0 was obtained by the equation

$$-\log_{10} d_0 = k_0 t/230.3 - \log_{10} 100 \quad (6)$$

and the mean number of hydrogen atoms replaced initially in each molecule undergoing exchange was given by the ratio

$$M = k_\phi / k_0 \quad (7)$$

Results on the Supported Catalysts

Physical adsorption of p-xylene on the high surface area supports required the use of small amounts of catalyst (100 mg or less) and relatively high temperatures (80°C or greater). If all the p-xylene present in the reaction vessel had been physically adsorbed in a monolayer, it would have covered some 3.7 m² (assuming that one molecule occupies 50Å²) and in several cases the surface area of the catalyst sample actually exceeded this value. We were not able to increase the pressure of p-xylene and so minimize complications from the physical adsorption because condensation would have occurred in the sections of the apparatus at room temperature such as the gold trap. The mass spectrometric peak heights were quite sensitive to temperature fluctuations in cases where adsorption was extensive and it was essential to maintain temperatures to well within ±0.5°C (usually by means of a water bath) in order to obtain reliable results. In most cases, the rates of reaction were too rapid for detailed study at temperatures above 100°C and so we could not examine the majority of the catalysts over a sufficient range of temperature in order to obtain activation energies for the various reactions.

The principal results with the various catalysts are set out in Table 2. The ratio k_A/k_B refers to the rate of exchange of the ring hydrogen atoms relative to those in the methyl groups determined by use of Eq. (1) and Eq. (4) and the symbol (1) means that both groups exchanged at the same rate, i.e. a linear plot was found according to Eq. (1). The ratio of exchange/deuteration was determined from the total percentage of dimethylcyclohexanes present at the point

TABLE 2
RESULTS OF REACTIONS AT 100°C

Catalyst	Sample weight (mg)	k_ϕ (D atoms/100 molecules, min)	k_A/k_B[a]	M (k_ϕ/k_0)	Exchange/Deuteration (k_0/k_D)	Normalized rates at 100°C for 1.0 mg of available Pt	
						k'_ϕ	k'_0
A1[b]	100	46	2.5	2.3	7	516	224
A2	100	21	1.9	1.5	41	568	378
A3	100	105	(1)	2.0	11	520	248
A4	20	82	(1)	3.1	16	1000	320
A5	8.0	76	(1)	4.3	18	1360	314
A6	11.7	58	(1)	3.2	28	1600	494
A7	9.8	85	(1)	4.4	15	1240	280
B1[c]	100	14	8.0	1.1	1700	190	174
B2[c]	100	8	19.0	1.1	1000	235	213
C1	100	20	4.1	1.5	320	89	47
C2	100	6	7.4	1.9	10	52	35

[a] (1) means that there was no detectable difference between k_A and k_B.
[b] Reaction temperature 87°C.
[c] Reaction temperature 95°C.

when 20% of the p-xylene had undergone exchange. The units for k_D were %/min and, in cases where the rate of deuteration was appreciable, it was observed that the reaction was zero order with respect to xylene and the rate of formation of the total dimethylcyclohexanes remained constant with time. The last two columns of Table 2 give the two initial rates of the exchange process, k_ϕ and k_0, corrected to the values, k'_ϕ and k'_0, which would have been expected for catalysts containing 1.0 mg of platinum available for chemisorption on the basis of the data in Table 1. When the experiments were carried out at temperatures below 100°C use was made of the activation energies determined for platinum films (*8*) in order to estimate rates at 100°C. This procedure was justifiable because the maximum temperature difference from 100°C was only 13°C, so that any differences between the activation energies over the supported catalysts and films would not have introduced substantial errors in the normalized rates.

Approximate activation energies for the over-all exchange process k_ϕ were found from experiments at 80°C in addition to those reported in Table 2 for Catalysts A4 and A6; the values were 9.8 and 8.2 kcal/mole, respectively, and they correspond fairly closely to those observed for ring hydrogen exchange (8.6) and methyl hydrogen exchange (10.4) for films by Harper and Kemball (*8*).

The distributions of the isotopic p-xylenes formed at an early stage in the reaction over some of the catalysts are given in Table 3; some of these results were obtained from experiments at 80°C because the rates were too rapid at 100°C to enable the pattern of products to be estimated sufficiently early in the reaction. The results with Catalysts A5 and A6 are not quoted since they were almost the same as those found with A4 and A7; likewise, C2 gave almost the same pattern as C1. One result is included in Table 3 for exchange on a single spheroid of A4 crushed to powder before use. The rate of exchange measured by k_0 was much the same as found for an uncrushed spheroid, 1.5%/min as opposed to 1.7%/min, but the value of M was lower with consequent change in the pattern of products.

The isotopic distribution of the 1,4-dimethylcyclohexanes present after 20% of the p-xylene had exchanged is shown in Table 4 for the catalysts which gave rise to appreciable amounts of deuteration. In each case, the average deuterium content of the saturated molecules exceeded 14, which showed that about 8 of the 10 atoms in the p-xylene had been exchanged during the deuteration. The ratio of the *cis*:*trans* isomers of the dimethylcyclohexanes was determined in the products formed over Catalysts A3 and C2 and found to be about 3:2 in both cases; the equilibrium ratio at 100°C is about 1:6.

Control experiments were carried out with a number of the supports in order to check that the activity was negligible compared with the catalysts containing platinum. The exchange activities of 100 mg of the α alumina used in the preparation of B1 and of the silica samples used for C1 and C2 were very small ($k_\phi < 0.5$%/min) at 250°C. Rather larger activity was found for the

TABLE 3

Typical Distributions of Isotopic Xylenes after 20% Exchange

Catalyst	Temp. (°C)	Sample weight (mg)	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	M
A1	87	100	9.4	2.5	1.2	1.1	1.0	1.1	1.2	1.2	0.8	0.5	2.3
A2	100	100	14.8	3.0	1.3	0.5	0.3	0.1	—	—	—	—	1.5
A4	80	2.0	7.5	3.3	2.1	1.6	1.5	1.2	1.2	0.9	0.6	0.1	2.9
A4	80	2.3[a]	16.7	2.6	0.4	0.2	0.1	—	—	—	—	—	1.1
A7	80	2.4	7.7	3.2	2.0	1.4	1.2	1.2	1.4	1.2	0.6	0.1	2.4
B1	95	100	16.2	3.0	0.7	0.1	—	—	—	—	—	—	1.1
C1	100	100	13.7	3.5	1.4	0.6	0.3	0.2	0.2	0.1	—	—	1.5

[a] Single spheroid crushed to powder.

TABLE 4

DISTRIBUTIONS OF 1,4-DIMETHYLCYCLOHEXANES AFTER 20% OF THE XYLENE HAD BEEN EXCHANGED AT 100°C

Catalyst	% of Total dimethylcyclohexanes								Mean deuterium content
	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	
A1[a]	—	—	5	10	15	25	30	15	14.1
A3	—	—	3	6	15	18	29	29	14.5
A4	2	2	6	7	11	16	27	29	14.2
A5	1	2	5	8	14	15	26	29	14.3
A6	2	3	4	5	17	21	29	19	14.0
A7	1	2	4	7	15	16	27	28	14.3

[a] Reaction temperature 87°C.

support of A1 and A2 ($k_\phi = 5\%$/min at 200°C) and, in particular, for that of A3 ($k_\phi = 19\%$/min at 150°C). However, the contributions of the activity even of these supports at 100°C would have been negligible compared with that of the platinum samples. No deuteration was observed on any of the supports upon which exchange was found to occur.

DISCUSSION

Comparison of Supported Catalysts and Platinum Films

We shall consider firstly the main differences between the results on the supported platinum catalysts and those obtained on evaporated films (*8*) which are summarized in Table 5. Both types of catalysts exhibit similar rates at 100°C for the exchange of the ring hydrogen atoms in *p*-xylene; the estimated rate in Table 5 is 310%/min for 1 mg of available platinum on films and this is in general accord with the values of k'_0 in Table 2 for the A and B catalysts. We have not given separate values of k'_0 for the two kinds of exchange in Table 2 but the proportion of k'_0 contributed by the exchange of the methyl hydrogen atoms is obviously not greater than one-half, and in most cases considerably less, because of the values of k_A/k_B observed.

TABLE 5

COMPARATIVE DATA FOR REACTIONS ON FILMS[a]

	Rate at 0°C (k_0 or k_D %/min 10 mg)	E (kcal/mole)	Normalized rates at 100°C (%/min mg of available Pt)[b]
Side-chain exchange	2.23	10.4	2400
Ring exchange	0.74	8.6	310
Deuteration	1.77	6.3	250

[a] Reference *8*.

[b] Assuming that a 10-mg film has an area of 400 cm² equivalent to 5×10^{17} surface atoms or 0.16 mg of platinum available for chemisorption.

In contrast, the films are much more active for the exchange of the methyl hydrogen atoms and for deuteration than the supported platinum catalysts. This might mean that the evaporated films possess a higher proportion of the types of sites essential for these reactions or alternatively that the supported catalysts are partially poisoned in some manner. A potential source of poison is the surface water strongly held on the supports and it is worthwhile examining this possibility in some detail. The likely effect of water on the exchange reactions of alkyl aromatics with deuterium may be seen by examining the results obtained when heavy water is used instead of deuterium as the source of the heavy isotope. A comparison of the work of Hirota and Ueda (*4*) and of Garnett and Sollich (*15*) with that of Harper and Kemball (*8*) indicates that the exchange reactions are much slower with heavy water than with deuterium. Furthermore, in the reaction with heavy water, aromatic hydrogen atoms are replaced on platinum as rapidly (*4*) or more rapidly (*15*) than the alkyl hydrogen atoms in contrast to the results with deuterium (*8*). This evidence indicates that the presence of the water interferes with the activity of the sites which are essential for the exchange of the alkyl hydrogen atoms and could, therefore, account for the main difference observed between supported catalysts and platinum films.

It is obvious from the data presented in Table 1 that there is a substantial quantity of hydrogen retained on the supports, presumably as surface hydroxyl groups, and that the outgassing temperatures we used were not sufficient to remove all the adsorbed water from the catalysts. The average concentration of hydrogen on the support of the UMP catalysts (A4 to A7) after outgassing overnight at 430°C was 2.9×10^{14} atoms/cm^2, which is larger than the figure of 1.5×10^{14}/cm^2 reported by Hall and Lutinski (*9*) for the surface hydroxyl groups on platinum supported on fluorinated alumina catalysts and provides further evidence for the incomplete removal of water in the present work. There seems to be no obvious way in which to eliminate possible interference from strongly held water in the study of supported metal catalysts of the type examined in this investigation. The use of sufficiently high outgassing temperatures to remove all the adsorbed water would inevitably lead to sintering and other undesirable changes in the nature of the catalysts.

There are two main limitations on the possibility of deriving fundamental conclusions from our investigations. Firstly, much too little information is available about the exact nature of the supported catalysts and the way in which the metal atoms or crystallites are held on the support. Secondly, there is the problem of possible interference by adsorbed water (or indeed other substances) with the metal sites responsible for activity. Our results do indicate some striking differences between platinum catalysts on different supports and so provide evidence of an interaction between the support and the metal, but we cannot be sure whether such interaction is a consequence of geometrical considerations and some sort of bonding between the support and the metal or whether the apparent interaction may be attributed to the proximity of strongly held water on the support which affects the activity of the metal to varying extents depending on the nature of the support. Despite these limitations, we believe that the examination of the differences between the behavior of a series of catalysts for a group of related and comparatively simple reactions of p-xylene and deuterium is a worthwhile contribution to the understanding of the general properties of the catalysts. Even if adsorbed water is partially responsible for some of the effects we note, we may expect the same effects to be important in the use of the catalysts for many other types of reactions too.

Comparison of the Different Supported Catalysts

Platinum on γ alumina. The data in Tables 2, 3, and 4 show that there is a remarkable similarity between the results on all the catalysts supported on γ alumina despite the fact that they were obtained from three different sources. With only minor variations, all show the following characteristics:

(a) similar activity for exchange at 100°C with values of k'_0 (Table 2) lying between 200 and 400;

(b) approximately the same activity for the exchange of both groups of hydrogen atoms; the largest value of k_A/k_B is only 2.5 (Table 2);

(c) much the same extent of multiple exchange with values of M of about 3 and similar patterns of products (Table 3);

(d) comparable values for k_0/k_D of about 20 ± 10 (Table 2) for the ratio between exchange/deuteration at 100°C;

(e) extensive and similar degrees of exchange *during* the deuteration reaction as shown by the patterns of isotopic dimethylcyclohexanes (Table 4).

In regard to (a), it seems likely that our method of comparing activities in terms of the amount of platinum available for the chemisorption of hydrogen or deuterium is a useful criterion which could be more widely applied in the comparison of supported metal catalysts. It is possible that there may be some contribution to the apparent values of

M, the extent of the multiple exchange, by consecutive reactions resulting from diffusional control inside the porous supports. The role of diffusion has been demonstrated (*16, 17*) in the reaction of molecules like dicyclopropylmethane on catalysts similar to some used in the present work. The reduction of the value of M from 2.9 to 1.1 at 80°C on crushing a spheroid of Catalyst A4 is possibly a further indication of the effect of diffusion in the case of the uncrushed material, but the results might also be attributed to some poisoning of the sites responsible for the multiple exchange process caused by the crushing. There are no striking differences between the catalysts prepared on the treated (F or Cl) aluminas and the untreated γ aluminas, although the former tend to show slightly greater values of M with the consequence that the values of k'_ϕ are about twice as large as those for the other series A catalysts in Table 2. Again, within the range studied, the percentage of the metal on the support does not appear to be an important factor in determining the catalytic properties.

Platinum on α alumina. Although the total exchange activity of the two platinum catalysts supported on α alumina was almost as great as those supported on γ alumina, as shown by the values of k'_0 in Table 2, there were a number of differences in the other characteristics. The ratios of k_A/k_B were high and those of k_0/k_D exceptionally high. The extent of multiple exchange was lower (M in Table 2 and the distribution in Table 3) but this may be partly accounted for by the lower surface areas of the series B catalysts with a consequential decrease in any complications due to diffusional control. In relation to the extremely low activities of these catalysts for the deuteration of p-xylene, it is perhaps worth noting that even on the series A catalysts, activity for this reaction was easily poisoned. When consecutive experiments were carried out on the same catalyst sample after outgassing between runs overnight at 350°C, exchange activity decreased by a factor of about 2 but hydrogenation activity virtually disappeared.

Platinum on silica. The principal difference between the series C catalysts and those in the A and B series, was the lower activity for exchange at 100°C (k'_0 in Table 2). This might result from the relatively high concentrations of surface hydroxyl groups ($7.8 \times 10^{14}/\mathrm{cm}^2$ in the case of C2) and in this connection Hall *et al.* (*18*) have shown that water is less easily removed from silica than from alumina. The ratios of k_A/k_B, the values of M, and the nature of the product distribution (Table 3) were intermediate between the corresponding quantities for the series A and series B catalysts. No valid comment can be made upon the ratios of k_0/k_D because there was a marked divergence between catalysts C1 and C2.

Possible influence of acidity of the supports. Some of the effects which we have observed may be connected with differences in the acidity of the various supports. Homogeneous acid-type catalysts are active for the exchange of ring atoms in the aromatic molecules by a carbonium ion mechanism but have little effect on the side group hydrogen atoms (*19*). Most supports have at least some acidity, as shown by their ability to chemisorb ammonia (*20*), the aluminas possessing greater acidity than silica gel. We can exclude a direct catalysis of the exchange of the ring hydrogen atoms by the supports on the basis of our control experiments and also because we found that a temperature of over 200°C was required to give a reaction between p-xylene and deuterium on an acidic silica-alumina catalyst. However, there remains a possibility that the acidities of the supports which are also affected by water (*21*) may work in conjunction with the platinum to modify the catalytic properties of the metal.

Comparisons with other work. Bond (*22*) examined the reactions of ethylene and deuterium on a series of supported platinum catalysts. The rates of the principal reaction, the formation of deuteroethanes, were similar in all cases but there was some variation in the pattern of products on the different catalysts. Two subsidiary reactions, the exchange of olefin with deuterium and the exchange of deuterium with hydrogen atoms originally present in the olefin, were also affected by the nature of the catalyst but both these reactions were substantially slower than the rate of formation of ethane. It is obvious that our results with an aromatic molecule as reactant are substantially different from those obtained by Bond for an unsaturated aliphatic molecule. We find marked variations in the rate of deuteration with different supported platinum catalysts and this suggests that the hydrogenation or deuteration of aromatic molecules is much more dependent on the nature of the catalyst than the hydrogenation of aliphatic olefins and therefore more suitable as a test reaction for the study of supported catalysts. Furthermore, the exchange of the aromatic molecule occurs more readily than deuteration on all the supported platinum catalysts in contrast to the results obtained by Bond for ethylene.

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