Differences in the Catalytic Activity of Nickel, Platinum and Palladium as Observed in the Isotopic Exchange Reaction of Paraxylene with Deuterium Oxide

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In our former reports on the isotopic exchange reaction of paraxylene with deuterium oxide, it was established that nickel powder exchanges the hydrogen of the methyl groups of paraxylene at 55~100°C with a much higher velocity than it does the hydrogen attached to the benzene ring[1], while platinum black can exchange both hydrogens under similar experimental conditions, as was reported preliminarily[2]. These results are interesting, because such a reaction would serve as an example wherein the difference in catalytic nature between nickel and platinum is shown definitely. Therefore, research has been extended to other metals and to nickel supported on several oxide carriers, using the NMR method for the analysis of products in addition to the infrared and mass-spectrometric methods hitherto adopted. The aims of the present paper are to confirm the above-mentioned difference in the catalytic activity of platinum and nickel and and further to investigate that of the palladium catalyst and the effects of carriers on the activity.

Experimental

Materials.—Deuterium oxide obtained from the Norsk Hydro Co. (99.7% D_2O) was used without any further purification.

Paraxylene (technical grade) was shaken with mercury to make it free from sulfur compounds and was separated from *o*- and *m*-xylene by recrystallization which was repeated five times. The paraxylene thus purified was dried over metallic sodium and distilled into a store vessel.

Raney nickel was developed from Ni-Al alloy consisting of 50% nickel by the method of W-2.

Ni-kieselguhr catalyst, K. S. Y.-6-FC, which had been prepared by the Nikko Co. (Tokyo) was used without any further treatment.

Nickel-alumina and nickel-silica were prepared by decomposing nickel formate supported on alumina and on silica at 270°C, according to the method already reported[1]. The preparation of the nickel-formate-alumina was as follows: 80% formic acid was added to a nickel carbonate solution in which alumina was suspended. In order to complete the

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[1] K. Hirota, K. Kuwata and T. Ueda, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **81**, 362 (1960); K. Hirota, H. Kusumoto and T. Ueda, This Bulletin, **33**, 423 (1960); H. Kusumoto, J. Itoh, K. Hirota and T. Ueda, *J. Phys. Soc. Japan*, **15**, 728 (1960).

[2] K. Hirota and T. Ueda, Abstr. of the 7th Symposium on IR and Raman Spectroscopy (Japan), 60 (1960); K. Hirota, T. Ueda, K. Kuwata and M. Hatada, *Catalyst* (*Tokyo*), **2**, 181 (1960).

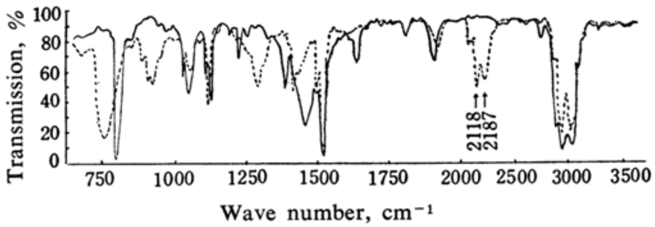

Fig. 1. IR spectra for the liquid samples.
—— Normal *p*-xylene, ---- Partially deuterated *p*-xylene on Raney Ni catalyst (No. 1) (NaCl prism)

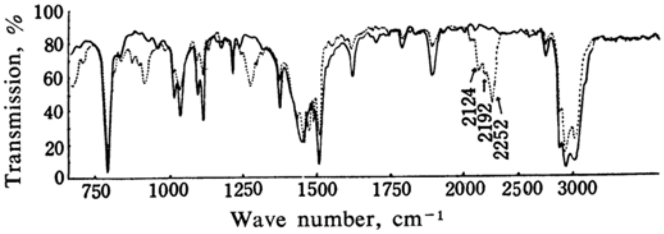

Fig. 2. IR spectra for the liquid samples.
—— Normal *p*-xylene, ---- Partially deuterated *p*-xylene on Pt catalyst (No. 11) (NaCl prism)

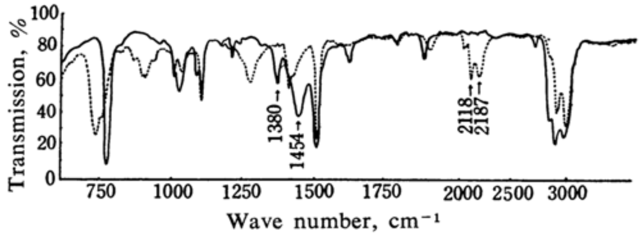

Fig. 3. IR spectra for the liquid samples.
—— Normal *p*-xylene, ---- Partially deuterated *p*-xylene on Ni catalyst (No. 0) prepared from nickel formate (NaCl prism)

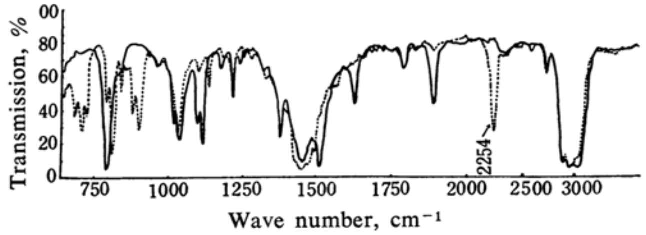

Fig. 4. IR spectra for the liquid samples.
—— Normal *p*-xylene, ---- Partially deuterated *p*-xylene on D_2SO_4 catalyst (NaCl prism)

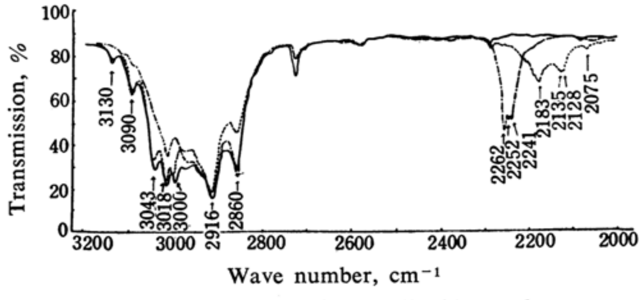

Fig. 5. IR spectra for the liquid samples.
—— Normal *p*-xylene, ---- Partially deuterated *p*-xylene on Ni catalyst, —·—· Partially deuterated *p*-xylene on D_2SO_4 catalyst (LiF prism)

TABLE I. EXPERIMENTAL CONDITIONS

Exp. No.	Catalyst	Weight of samples			Conditions of the reaction	
		Catalyst	*p*-Xylene	D_2O	Temp., °C	Time, hr.
1	Raney Ni	2.06	0.544	0.611	100	150
2	Ni-kieselguhr (1 : 1)	10.1	0.587	0.576	〃	〃
3	Ni-SiO_2 (1 : 10)	22*	0.616	0.666	〃	〃
4	Ni-$Al_2O_3{}^a$ (1 : 1)	10*	0.458	0.446	〃	〃
5	〃 (1 : 3)	20*	0.527	0.547	〃	〃
6	〃 (3 : 1)	6.7*	0.525	0.582	〃	〃
7	Ni-$Al_2O_3{}^b$ (1 : 1)	10*	0.525	0.523	〃	〃
8	$Al_2O_3{}^a$	5.1	0.660	0.475	〃	〃
9	$Al_2O_3{}^b$	5.0	0.449	0.477	〃	〃
10	Pt black	0.64	0.534	0.520	〃	285
11	〃 〃	〃	0.757	0.725	80	300
12	Pd black	0.99_4	0.568	0.741	100	150

* These numerals denote the estimated values of the produced catalyst after the decomposition of $Ni(HCO_2)_2$-Al_2O_3.

precipitation of nickel formate on alumina, acetone was added to the solution. Two kinds of alumina were used as the carrier: (a) $Al_2O_3{}^a$: commercial activated γ-alumina (Wako Co. (Osaka)); (b) $Al_2O_3{}^b$: pure alumina obtained by dehydration of alumina gel, which was made by adding ammonia solution to aluminium nitrate and letting dry air flow over it for 10 hr. at 500°C. Nickelformate-silica was prepared by the same method as in the case of nickelformate-alumina, by the use of commercial silica gel (Mallinckrodt Chemical Works) in this case instead of alumina.

Platinum black was prepared by reducing chloroplatinic acid made from platinum with formaldehyde and potassium hydroxide.

Commercial palladium black was used (Mitsuwa Kagaku Yakuhin Co.).

Procedure. — Since the procedure has been described in detail in previous reports1), only the essential points will be mentioned. The catalyst was always prepared in a reaction tube, in which *p*-xylene and deuterium oxide were charged by distillation from their store vessels. The tube was kept at the reaction temperature in a thermostat. After the reaction both *p*-xylene and deuterium oxide were separated from the catalyst by distillation. Paraxylene was pipetted out from the upper part of the distillate, which formed two liquid layers; the paraxylene was then dehydrated with calcium chloride and distillated into another vessel. By infrared spectrometry the deuterated positions of the *p*-xylene molecules were determined, but quantitative analysis of the degree of deuteration was made by resorting to the NMR method. The mass-spectrometric method was also adopted for the same purpose.

The experimental conditions of all the runs are summarized in Table I, where the ratios in parentheses denote those in weight. Infrared spectra were obtained by using Hilger H 800 and Hitachi EPI-2 spectrophotometers equipped with sodium chloride or lithium fluoride prism. The NMR analysis was made by resorting to a high resolution spectrometer (Varian 4300 B; 40 Mc/sec.). The mass-spectrometric analysis was conducted with a Hitachi RMU-5 mass-spectrometer.

Results and Discussion

Difference of Activity among Nickel Catalysts, Platinum Black and Palladium Black.— Before the particular discussion on all the runs, it will be convenient to explain the general tendency of the differences in catalytic activity, taking the runs of Raney nickel (No. 1) and platinum black (Nos. 10 and 11) as examples.

The infrared spectra of the reaction products of Nos. 1 and 11 are shown in Figs. 1 and 2 respectively. The former is quite similar to the one shown in Fig. 3, which was the spectrum of the product when a nickel catalyst prepared from nickel formate was used1). It will be evident from a comparison of Figs. 1 and 3 that only hydrogen molecules of the methyl group were catalytically exchanged by nickel, while a new band appeared at 2252 cm^{-1} in the spectrum (Fig. 2) of the sample after the exchange reaction in the presence of platinum at 80°C (No. 11*). The same band was observed in the spectrum of No. 10 when the reaction was carried out at 100°C. It perfectly coincides with that of the deuterated product3) of *p*-xylene with deuterosulfuric acid D_2SO_4, as is shown in Fig. 4. Since it is a well-known fact that only ring hydrogen can be exchanged with deuterium oxide by an acid catalyst4), this new band must be due to the stretching vibration of the C–D bond in the

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* A similar conclusion has been obtained recently by A. Ozaki et al., (Abstr. Papers of the 14th Annual Meeting of Chem. Soc. Japan, p. 185 (1961)) in the system of toluene and deuterium oxide.

3) T. Ueda, *Catalyst* (*Tokyo*), **1**, 1 (1959).

4) C. K. Ingold et al., *J. Chem. Soc.*, **1946**, 222.

ring. Two other bands, which appear at 2192 and 2124 cm^{-1} by deuteration, seem to coincide with those appearing at 2187 and 2118 cm^{-1} in Figs. 1 and 3, i. e., in the samples catalyzed by nickel. (When a lithium fluoride prism was used, the 2187 and 2118 cm^{-1} bands were found to be at 2183 and 2128 cm^{-1} respectively (Fig. 5).) These bands therefore can be ascribed to those of the stretching vibrations of the methyl C–D bond.

The characteristics of the activities of all the catalysts investigated in this research are summarized in Table II, with No. 0 indicating the previous data on nickel prepared by the decomposition of nickel-formate. It will be noted that the activity of palladium black (No. 12) is similar qualitatively to that of platinum, but lies between those of nickel and platinum. The above conclusion can be derived quantitatively from the data of the mass-spectrometric method shown in Table III, where deuterium distribution in the reacted samples was tabulated as d_i (=% of *p*-xylene molecules containing *i* deuterium atoms). The existence of highly deuterated xylene in the cases of platinum and palladium catalysts indicates that all the hydrogen molecules in *p*-xylene are exchangeable, and especially so in the case of platinum.

TABLE II. CHARACTERISTICS OF CATALYSTS ON HYDROGEN EXCHANGE OF PARAXYLENE WITH DEUTERIUM OXIDE

Exp. No.	Catalyst		Benzene ring	Methyl group
0	Ni powder		−	+
1	Raney Ni		−	+
2	Ni-kieselguhr		−	+
3	Ni-SiO$_2$		−	+
4	Ni-Al$_2$O$_3$^{a}	(1 : 1)	+	+
5	〃	(1 : 3)	+	+
6	〃	(3 : 1)	+	+
7	Ni-Al$_2$O$_3$^{b}	(1 : 1)	+	+
8	Al$_2$O$_3$^{a}		−	−
9	Al$_2$O$_3$^{b}		−	−
10	Pt black		+	+
11	〃 〃		+	+
12	Pd black		+	+

N. B. + Exchangeable, − Not exchangeable

TABLE III. MASS-SPECTROMETRIC ANALYSIS OF THE REACTED SAMPLES, WHEN Ni, Pt AND Pd CATALYSTS WERE USED

Catalyst	Exp. No.	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	ϕ
Ni powder	0	0.2	2.0	9.0	23.5	32.6	24.7	7.9	0.1	—	—	—	39.0
Pt black	11	29.1	2.2	2.7	5.8	10.2	14.1	15.7	11.5	6.1	2.2	0.4	38.4
Pd black	12	7.2	3.9	12.0	21.6	25.7	20.1	10.8	3.9	0.8	0.3	—	39.5

$\phi=(1/10)\sum_{i=1}^{10} id_i$ (average deuterium content %)

TABLE IV. DEUTERIUM DISTRIBUTION IN THE REACTED SAMPLES

A. MASS-SPECTROMETRIC ANALYSIS

Exp. No.	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	ϕ
6	1.4	4.1	14.2	27.7	29.9	17.7	4.8	0.2			35.4
4	3.1	9.7	21.1	28.7	21.5	11.1	3.8	0.9	0.1		30.9
5	0.1	7.2	15.4	25.7	25.4	16.3	7.1	2.2	0.5	0.1	36.1
7	1.3	4.9	14.7	23.7	25.3	17.8	8.8	2.8	0.7		37.4

$\phi=(1/10)\sum_{i=1}^{10} id_i$ (Average deuterium content %)

B. NMR METHOD ANALYSIS*

Exp. No.	Catalyst		Deuterium fraction in benzene ring, %	Deuterium fraction in methyl groups, %
6	Ni-Al$_2$O$_3$^{a}	(3 : 1)	1	34
4	〃	(1 : 1)	7	24
5	〃	(1 : 3)	11	25
7	Ni-Al$_2$O$_3$^{b}	(1 : 1)	13	25
11	Pt black		15	23
12	Pd black		9	30

* Both fractions were determined by allotting ϕ proportionally to the height of NMR signals of methyl and ring hydrogens.

Another point to be mentioned here is the fact that nickel has no activity with the hydrogen atoms of benzene ring. This is apparently in contradiction to the finding of Horiuti and Polanyi⁵⁾ that benzene can exchange hydrogen with heavy water in the presence of nickel powder. According to our experiment²⁾, where nickel powder was prepared by the procedure adopted in the case of xylene, a similar degree of exchange could be found in the case of benzene under the same experimental conditions. Therefore, it must be considered that the activity of ring hydrogen is decreased by the introduction of methyl groups. Such a decrease may be explained by the "geometric" factor rather than by the "electronic" factor, because if it is assumed that the exchange of methyl hydrogen can be realized by dissociative chemisorption of the methyl group ($-CH_3 \rightarrow -CH_2 + H$) on a nickel surface, it will be difficult from the structural reason that a part of the benzene ring is chemisorbed simultaneously. However, the reason why platinum and palladium have the catalytic activity with both hydrogen atoms cannot be answered at the present state of investigation.

Effect of Carriers on Nickel.—As shown in Table II, in the presence of Ni-kieselgulr (No. 2) or $Ni-SiO_2$ (No. 3) the catalytic exchange of methyl hydrogen occurred in a way similar to the case when no carrier was used (Nos. 0 and 1); i. e., no qualitative effect of these carriers could be found in the infrared spectrum. On the other hand, the results obtained on the $Ni-Al_2O_3$catalysts (Nos. 4～7) were the same in nature as those obtained on the platinum and palladium catalysts (Nos. 10～12); i. e., both kinds of hydrogen atoms were exchanged, though no exchange could be observed in two runs of the alumina catalyst (Nos. 8 and 9). It is interesting that the catalytic activities of $Ni-Al_2O_3{}^a$ (No. 4) and $Ni-Al_2O_3{}^b$ (No. 7) were nearly the same, irrespective of the differences in their methods of preparation. In order to confirm quantitatively the above results obtained by the IR method, both mass-spectrometric and NMR methods were utilized, the results being shown in Tables IV A and B.

It must also be mentioned regarding Table IV B that the activity of the nickel-alumina catalysts obviously changes according to the ratio of the two components. From a comparison of Nos. 4, 5 and 6, it can be noted that No. 5, the catalyst of the least nickel content, shows the largest activity with ring hydrogen and that the degree of activity is similar to that of platinum black.

Such peculiar effects of alumina as a carrier make it difficult to classify this oxide in the same category as silica and kieselguhr, because it cannot be explained by the difference in surface area between these catalysts. According to Rubinishtein et al. and Morikawa et al.⁶⁾, when alumina coexists with nickel, it interacts with nickel more strongly than silica gel⁶⁾ does. If so, it is not surprising that nickel catalyst can change its activity when supported on alumina. Another explanation is the change in the valency state of nickel, as proposed by Selwood et al.⁷⁾ in the case of nickel oxide-alumina. From their magnetic susceptibility measurement, they concluded that the valency of some nickel atoms changes into +3 in the presence of alumina. Considering the infrared measurement of Eischens⁸⁾ that the chemisorbed state of carbon monoxide on platinum-alumina differs from that on platinum-silica, a valency change due to carriers may be possible. Such being the situation, it will be required hereafter to investigate the change in activity from the standpoint of the electronic factor.

Summary

It has been confirmed that nickel can exchange catalytically only hydrogen atoms of methyl groups of paraxylene with deuterium oxide, irrespective of the method of preparation, while platinum and palladium can exchange hydrogen atoms of both methyl groups and benzene ring under similar experimental conditions.

It has been found that the catalytic activity of nickel becomes similar to that of platinum and palladium if nickel is supported on alumina, but remains unchanged if it is supported on silica or kieselguhr.

It has been shown to be difficult to explain these two findings perfectly.

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