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The Classification of Metal Catalysts in Hydrogenolysis of Hexane Isomers

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The hydrogenolysis of hexane isomers has been studied on various supported metal catalysts (Fe, Co, Ni, Pd, and Pt) in the presence of hydrogen. The previous conclusion that there are two different mechanisms in the hydrogenolysis of saturated hydrocarbons on nickel and platinum catalysts has been found to hold generally on the above metal catalysts. From the product patterns in catalytic hydrogenolysis of hexane isomers, the catalysts could be classified into two groups, one containing Fe, Co, and Ni and the other containing Pd and Pt. This distinct difference cannot be explained by an intensive factor, but must be attributed to some more intrinsic property of these metals, because this contrast between the two groups is generally observed among several metal-catalyzed reactions.

The effect of the support on the hydrogenolysis of hexane isomers was also investigated in the case of platinum and nickel catalysts. It was found that the differences observed between nickel and platinum were preserved on all supports used.

INTRODUCTION

It was concluded in a previous work (*1*) that the hydrogenolytic mechanism of saturated hydrocarbons on nickel catalysts can be differentiated from that on platinum catalysts in terms of the detailed analysis of the initial reaction products. On nickel catalysts, the reaction intermediates in hydrogenolysis were presumed to be normal alkyls, $—CH_3(CH_2)_nCH_3$, which are selectively hydrocracked by successive α-scission, giving methane as a main product. On the other hand, a carbonium ion mechanism was proposed for platinum in order to interpret both the characteristic initial hydrogenolytic product distribution and the considerable skeletal isomerization during hydrogenolysis. This sharp contrast in catalysis between nickel and platinum for hydrogenolysis and related reactions of saturated hydrocarbons was ascribed to the differences in magnitude of the inherent *softness* of these metals as acids.

From the relationship between the specific activities of the Group VIII metals for ethane hydrogenolysis and the percentage *d* character of metals, Sinfelt and Yates (*2, 3*) classified metals into two groups, the *noble* metals (Pd, Rh, Ru, Pt, Ir, and Os) and the *nonnoble* metals (Fe, Co, and Ni). They suggested the possibility of a secondary geometric factor which influences the catalytic activity, in addition to the electronic factor, since the lattice spacings of the non-noble metals of Group VIII are significantly smaller than those of the noble metals (*4*). In the case of ethane hydrogenolysis, however, the simple molecular structure restricts catalytic tests merely to the catalytic activities. As demonstrated by Boudart and Ptak (*5*) for neopentane and by Anderson and Baker (*6*) for isobutane, neopentane, and neohexane, the selectivities or the product patterns

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provide much more information when larger saturated hydrocarbons are adopted as reactants. It is possible to classify catalyst metals on the basis of the product patterns which are obtained from larger hydrocarbon molecules in the presence of hydrogen. In order to interpret the classification, some intrinsic properties of the metals should be taken into account, as the geometric factor seems to be unsuitable to differentiate the reaction characteristics. Since the product patterns from hexane isomers under hydrogen atmosphere on nickel and platinum catalysts are reflecting the mode of the carbon–hydrogen splitting, homolytic or heterolytic, at the stage of adsorption (*1*), some Group VIII metals other than nickel and platinum have been investigated in the present work. From the viewpoint of inherent *softness* of catalyst metals as acids, the product patterns are expected to be different for one group (Fe, Co, and Ni) than from the other (Pd, Pt).

The effect of support materials on hydrogenolysis of hexane isomers has also been investigated for both platinum and nickel catalysts. Although the main role of catalyst supports may be to disperse the metal and to maintain high surface area, the specific activity per metal surface in ethane hydrogenolysis for nickel (*3*, *7–9*) and platinum (*3*, *9–10*) catalysts depends on the support material. The influence of the supports on catalysis will be complex. As far as the reaction mechanism on a certain metal catalyst is concerned, however, support effects are scarcely to be anticipated, since the reaction mechanism is concerned with the inherent nature of the metal component. The support material used in the previous work was silica gel, prepared carefully to avoid acidic properties (*1*). In the present work, the same reactions have been examined also on alumina- and charcoal-supported platinum and zirconia-supported nickel.

EXPERIMENTAL METHODS

Apparatus and Procedure

The catalytic reactions were carried out with a pulse technique in a microcatalytic reactor using hydrogen as carrier gas. A dose of 1 μl of a given liquid reactant, at about 0.1 atm partial pressure, was injected into the hydrogen stream. The apparatus and the procedure for the hydrogenolysis of hexane isomers have been previously described (*1*).

Materials

Five hexane isomers were used as the reagents. Nonacidic silica gel (60–150

TABLE 1

METAL CATALYSTS USED

			Amount of supported metal	
Symbol	Catalysts	BET surface area (m^2/g)	Supported (wt %)	Estimated by analysis (wt %)
Pt–S	Pt–SiO_2^{a}	661		
Pt–A	Pt–Al_2O_3^{b}	148	0.375	
Pt–C	Pt–Charcoal^c		5.0	
Ni–S	Ni–SiO_2^{a}	650	4.15	3.17
Ni–Z	Ni–ZrO_2^{d}	94		
Pd–S	Pd–SiO_2^{e}	660	4.83	3.55
Co–S	Co–SiO_2^{e}	660	4.19	3.51
Fe–S	Fe–SiO^e	660	3.89	

[a] Described in the previous paper (*1*).

[b] Reforming catalyst.

[c] Nippon Englehard catalyst.

[d] Girdler G-60 hydrogenating catalyst.

[e] See text.

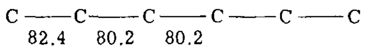
mesh) was prepared by hydrolysis of ethylorthosilicate at 90°C as stated previously (*1*). The cobalt, iron, and palladium catalysts were prepared by impregnating the silica gel with aqueous solutions of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$, ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$, and palladium nitrate $Pd(NO_3)_2$, respectively. These catalysts were dried overnight and heated at 550°C for 4 hr. Prior to reaction, they were reduced in the hydrogen stream for more than 4 hr at 450°C. The amount of catalyst metal supported on silica was determined by means of EDTA titration using Murexide or Eriochrome Black T as indicator in the case of nickel and cobalt, after solution of the supported catalyst in HNO_3–3HCl. The amount of palladium was also determined by gravimetric analysis using dimethylglyoxime as a precipitant after solution, see Table 1. Some commercial supported catalysts of platinum and nickel are also summarized in Table 1.

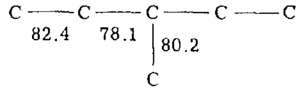
RESULTS AND DISCUSSION

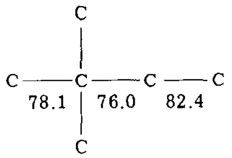
Palladium Catalyst

During the hydrogenolysis of hexane isomers on the silica-supported palladium catalyst, the side reactions, i.e., isomerization and cyclization, took place simultaneously as shown in Table 2. It may be worthwhile to point out that the hydrogenolytic products at low conversions exhibited quantitative coincidence between the couple of either methane and pentanes or ethane and butanes. Both the reaction pattern of side reactions and also the product pattern of hydrogenolysis at low conversion level are similar to the case of the platinum catalyst reported previously (*1*). It is to be noted, however, that a slightly different feature was observed for palladium in the distribution of hydrogenolytic products. The couple of methane and pentanes amounted to 80 or 90 mol % on palladium catalyst among the hydrogenolytic initial products of any hexane isomer, in contrast to the case of platinum catalyst which extended from 25 to 80 mol % (*1*). Analogous features are reported by Anderson and Avery (*11*), whose results are included in Table 2. They compared the hydrogenolytic products on evaporated palladium films to those on platinum films for *n*-butane, isobutane, neopentane, and isopentane, and coincidentally observed isomerization during hydrogenolysis for both catalysts. Interestingly enough, the prevailing initial product was methane on palladium. Furthermore, their results strongly suggest that saturated hydrocarbons are more difficult to isomerize on palladium than on platinum in accord with the present results obtained on supported catalysts for hexane isomers, see Table 2.

The larger amount of methane produced on palladium in hydrogenolysis of all hexane isomers suggests that bond splitting easily occurs at the terminal carbon–carbon bonds of molecules on this catalyst. Although the experiments were carried out at 405°C because of its low activity, it is certain that the bond splitting is not performed thermally but catalytically, since the bond energies of hexane isomers are largest at the terminal carbon–carbon bonds in all isomers, according to the calculation of Hirota and Fueki (*12*) by the bond orbital method, which was useful for the interpretation of the *G′* values of mass spectrometry (*13*). Examples are as follows:







(unit: kcal mol)

The catalytic behavior of palladium is different from that of nickel. First, the side reactions, isomerization, and cyclization, did not occur on nickel. Second, the hydrogenolytic products other than methane and pentanes, i.e., ethane, propane, and butanes, were found as the primary products on palladium; there exists quantitative

TABLE 2
THE HYDROGENOLYSIS OF HEXANE ISOMERS ON PALLADIUM

Reagents	Temp (°C)	Selectivity (%)			The hydrogenolytic products (mol %)								Mass balance $\sum_{n=1} n \times C_{6-n}$
		Cracking	Isomerization	Cyclization	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	isoC_5	n-C_5	
n-Hexane	405	39.8	17.5	42.7	42.8	5.78	4.78		5.26			41.5	89.48
2-Methylpentane	405	23.4	26.4	50.2	47.2	3.08	3.92	2.18			20.6	22.8	71.84
3-Methylpentane	405	24.8	13.5	61.7	47.0	3.94			3.72		38.7	6.9	68.80
2,2-Dimethylbutane	405	89.8	10.2	0.0	36.0	13.1		13.7			37.3		117.1
2,3-Dimethylbutane	405	96.1	3.9	0.0	43.4		7.35				49.2		71.25
Palladium evaporated film (8)													
n-Butane	276–310	99	1.0	—	45	13	41	1	—				
Isobutane	270–311	97	3.0	—	49	1	47	—	3				
Neopentane	310	100	0.0	—	49	3	6	35	7	—	0	0	
Isopentane	310	97	3.0	—	42	7	7	16	25	0	—	3	
Platinum evaporated film (8)													
n-Butane	256–300	89	11.0	—	32	29	28	11	—				
Isobutane	265–299	50	50.0	—	24	6	20	—	50				
Neopentane	239–295	36	64.0	—	14	5	4	10	3	—	59	5	
Isopentane	278	80	20.0	—	31	13	13	14	9	1	—	19	

coincidence within the couple of either ethane and butanes or methane and pentanes at low conversions. In order to verify the successive α-scission mechanism of the adsorbed species on nickel catalyst, the amount of produced methane was calculated from the mass-balance equation (*1*),

$$C_1 = \sum_{n=1} n \times C_{6-n}$$

The calculated values were in excellent quantitative correspondence with the observed ones for nickel catalyst (Table 6) (*1*), but not for palladium catalyst as shown in Table 2. Third, 2,2-dimethylbutane was subject to the selective hydrocracking into methane and neopentane on nickel (*1*, *14*, *15*), whereas on palladium methane was formed as a couple with isopentane during reaction.

All of these features found on palladium are similar to those on platinum, which, therefore, strongly suggests that the carbonium ion mechanism proposed for platinum (*1*) is operative for palladium as well. The carbon–hydrogen heterolysis, i.e., hydride abstraction, at the stage of adsorption on palladium would give a carbonium ion, which may be easily followed by isomerization or cyclization and thereafter β-scission at the carbon–carbon bond of the carbonium ions. According to the soft acid parameters of palladium ions (*16*), palladium-hydride coordination may not be so stable as expected for platinum hydride, whereas the assumption of hydride abstraction from saturated hydrocarbons on the surface of either platinum or palladium seems more likely, as far as the reaction features in catalysis are concerned.

Cobalt and Iron Catalysts

Hexane isomers were selectively hydrocracked on cobalt and iron catalysts without any side reaction, as was the case on nickel catalysts (see Tables 3 and 4). However, the quantitative coincidence within the couple of methane and pentanes obtained on nickel was not found on these catalysts, even at low conversions. Nearly 90 mol % was methane among hydrogenolytic products on the iron catalyst at a conversion as low as 0.5%, whilst pentanes or butanes were scarcely observed or not observed at all from any hexane isomers. It seems reasonable that the secondary splitting of produced pentanes and butanes occurs rapidly on these catalysts before their desorption back to the gas phase (*deep hydrogenolysis*). As suggested by Anderson and Baker (*6*), the rate controlling step in the hydrogenolysis may vary with metals. With regard to cobalt and iron catalysts, the desorption process of the products seems to be the rate-determining step from the present work. The selective hydrocracking on cobalt and iron seems to proceed along with the mechanism of the successive α-scission at the coordinated terminal carbon on the metal surface as the case on nickel, although the rate-determining step probably differs.

The contrast between two groups of metals is thus clearly demonstrated in hydrogenolysis of hexane isomers, one group comprising Fe, Co, and Ni and the other group Pd and Pt. The mode of the carbon–hydrogen splitting, homolytic or heterolytic, at the stage of adsorption of saturated hydrocarbons seems to be substantially different for these two groups. These modes are understandable from the viewpoint of inherent *softness* of catalyst metals as acids, as described previously (*1*).

Classification of Metal Catalysts

The hydrogenation activities of olefins on Group VIII metals have been related to the strength of olefin adsorption (*17*). The selectivity for hydrogenation of diolefins and acetylenes has also been well explained in terms of the intensive factor of these metals (*17*). However, the catalytic patterns in hydrogenolysis of hexane isomers may not be interpreted only by the intensive factor. In the studies of ethane hydrogenolysis on the Group VIII metals, Sinfelt and Yates compared the specific activities of these metals (*2*–*4*). Among *noble* metals (Pd, Rh, Ru, Pt, Ir, and Os) the specific activity increases with increasing percent-

TABLE 3

THE HYDROGENOLYSIS OF HEXANE ISOMERS ON COBALT

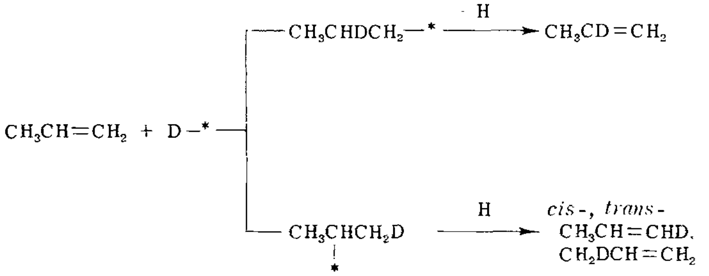
Reagents	Temp (°C)	Conversion (%)	Selectivity (%)			The hydrogenolytic products (mol %)							
			Cracking	Isomerization	Cyclization	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	isoC_5	n-C_5
n-Hexane	233	3.00	100	0	0	72.2	10.1	6.4					6.2
2-Methylpentane	233	2.18	100	0	0	67.4	7.4	5.98	5.47	1.73		4.59	7.62
3-Methylpentane	233	3.10	100	0	0	65.0	8.0	3.12	1.84	6.62		9.69	5.78
2,2-Dimethylbutane	233	0.85	100	0	0	62.1	2.5		3.46		32.1		
2,3-Dimethylbutane	233	2.58	100	0	0	68.1	6.4	3.86	6.89	3.46		11.5	

TABLE 4
THE HYDROGENOLYSIS OF HEXANE ISOMERS ON IRON

Reagents	Temp (°C)	Conversion (%)	Selectivity (%)			The hydrogenolytic products (mol %)							
			Cracking	Isomerization	Cyclization	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	neoC_5	n-C_5
n-Hexane	250	0.45	100	0	0	87.4	8.8	3.8					
2-Methylpentane	250	0.50	100	0	0	87.0	8.6	2.8				1.6	
3-Methylpentane	250	0.47	100	0	0	88.0	9.2	2.8					
2,2-Dimethylbutane	250	0.08	100	0	0	88.0					12.0		
2,3-Dimethylbutane	250	0.48	100	0	0	87.6	9.3	3.1					

age *d* character of the metal bonds. However, the values for *non-noble* metals (Fe, Co, Ni) did not fall on the same correlation line, and this discrepancy was attributed to a geometric factor. Indeed, the present classification of metals into two groups, one group (Fe, Co, Ni) and the other (Pd, Pt), is the same as the above one. However, their geometrical explanation is inapplicable to the hydrogenolysis of hexane isomers in the present work. Some intrinsic factor might have an essential role in differentiation of these two groups of metals, but which could not be demonstrated by the hydrogenolysis of ethane because of its simple molecular structure.

Hirota *et al.* (*18*) studied the reaction intermediates in the hydrogen exchange reaction between deuterium and propylene by means of microwave spectrometry. The distribution of deuterium in monodeuteropropylene was characteristic to catalyst metals (Ni, Cu, Pd, Rh, and Pt). On nickel and copper, the methine hydrogen was the most exchangeable (CH_3—CD=CH_2), leading to the interpretation of the intermediate of the normal alkyl type adsorbed species,



This information supports the idea that the normal alkyl type species will also be the reaction intermediates in hydrogenolysis of saturated hydrocarbons on nickel, in addition to the ir evidence of adsorbed species on nickel under the hydrogenating conditions of olefins (*19*, *20*). On the other group of metals (Pd, Rh, Pt), no characteristic exchangeability of the methine hydrogen was recognized. All the hydrogen atoms were nearly equal in the exchangeability on palladium and *trans*-CH_3CH=CHD was obtained more than *cis*-CH_3CH=CHD on platinum (*18*).

The hydrogenolysis of many benzylic alcohols was reported by Mitsui *et al.* (*21*–*25*) and Breste (*26*) to proceed with retention of configuration on Raney nickel, Raney cobalt, and Raney copper, in contrast with inversion on palladium catalyst. It was also reported by Mitsui *et al.* (*27*) that *trans*-alcohols are selectively produced on Raney nickel in contrast with the selective formation of *cis*-alcohols on Pd–charcoal, PtO_2, and Rh–charcoal in the hydrogenation of 3-hydroxycycloalkenes in ethanol. The stereoselectivity on these catalysts was interpreted in terms of the differences of adsorbed state of reactants, where the affinity of the metal surface toward the hydroxy group was assumed strong for nickel, cobalt, and copper catalysts but weak for palladium, platinum, and rhodium. Thus the catalyst metals are also separated into the same two groups, one group (Ni, Co, Cu) and the other (Pd, Pt, Rh).

Support Effect

In Table 5 the results on alumina- and charcoal-supported platinum catalysts, together with silica-supported platinum catalyst are shown. The catalytic patterns for all platinum catalysts are similar, judging from the side reactions, isomerization and cyclization, which proceeded considerably during hydrogenolysis. The hydrogenolytic products on these supported platinum catalysts are rather complex even at a low conversion, although the quantitative coincidence within the couple of either methane and pentanes or ethane and butanes was evident for any hexane isomer. When the support material was changed from silica to alumina, there was scarcely any variation except for preference to isomeri-

TABLE 5

THE SUPPORT EFFECTS FOR PLATINUM CATALYSTS IN HYDROGENOLYSIS OF HEXANE ISOMERS

Reagents	Catalyst symbol	Temp (°C)	Conversion (%)	Selectivity (%)			The hydrogenolytic products (mol %)							
				Cracking	Isomerization	Cyclization	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	isoC_5	n-C_5
n-Hexane	Pt-S	295	1.84	15.9	39.1	45.0	12.5	18.3	42.9		15.1			11.2
	Pt-A	285	4.18	16.4	38.2	45.4	18.8	16.9	30.6		15.5			18.2
	Pt-C	386	4.68	27.8	45.8	26.4	41.1	7.2	4.5		6.6			40.6
2-Methylpentane	Pt-S	295	2.55	11.0	58.4	30.6	23.1	12.1	31.6	13.5			9.5	10.3
	Pt-A	285	5.38	25.2	66.5	8.3	31.2	12.2	13.4	11.4			15.7	16.1
	Pt-C	386	3.96	23.7	29.4	46.9	46.9	6.7	0.9	4.5	1.5		23.4	23.1
3-Methylpentane	Pt-S	295	2.86	19.0	63.8	17.2	28.7	22.0			19.9		22.1	7.3
	Pt-A	285	3.81	12.3	70.7	17.0	35.9	10.3			9.1		35.6	9.1
	Pt-C	386	3.55	27.8	18.0	54.4	47.1	2.3			3.1		37.0	10.5
2,2-Dimethylbutane	Pt-S	295	1.04	27.0	73.0	0.0	12.6	38.8		36.2			12.4	
	Pt-A	285	2.31	22.0	78.0	0.0	26.1	24.6		20.7			28.6	
	Pt-C	386	0.52	32.0	68.0	0.0	46.9						53.1	
2,3-Dimethylbutane	Pt-S	295	1.30	30.3	69.7	0.0	39.8		20.6				39.6	
	Pt-A	285	3.46	54.3	45.7	0.0	43.3		11.7				45.0	
	Pt-C	386	1.84	91.0	9.0	0.0	48.4		4.4				47.2	

TABLE 6

THE SUPPORT EFFECTS FOR NICKEL CATALYSTS IN HYDROGENOLYSIS OF HEXANE ISOMERS

Catalyst symbol	Temp (°C)	Conversion (%)	Selectivity	The hydrogenolytic products (mol %)								Mass balance
			Cracking (%)	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	isoC_5	n-C_5	$\sum_{n=1} n \times C_{6-n}$
n-Hexane												
Ni-S	250	0.47	100	53.2							46.8	46.8
	235	5.24	100	58.3	0.80	3.10		7.20			30.6	57.5
Ni-Z	250	1.10	100	54.3		1.20		6.70			37.8	52.8
2,2-Dimethylbutane												
Ni-S	250	0.16	100	55.6					44.4			44.4
	235	3.45	100	52.2			2.20		40.0	5.6		50.0
Ni-Z	250	0.21	100	52.3					47.7			47.7

zation during hydrogenolysis on the latter. On the other hand, the product distribution on charcoal-supported platinum is different from those on silica- and alumina-supported platinum; it is rather similar to that on the palladium catalyst.

In Table 6 are shown the results on zirconia- and silica-supported nickel catalysts for hydrogenolysis of 2,2-dimethylbutane and *n*-hexane. In both cases they can be well explained by the mechanism of successive α-scission from the terminal carbon–carbon bonds, proposed earlier for nickel catalyst (*1*).

As reported by Maxted and Akhtar (*28*), a remarkable effect of the supports on the catalytic activity has been often recognized. In order to compare the catalytic activities of supported metals, it is necessary to discuss the specific catalytic activities (rates per unit metal area), as was done by Sinfelt, Taylor, and Yates (*3, 7, 8*), in the catalytic hydrogenolysis of ethane on supported metals, the surface areas of which were determined by hydrogen chemisorption. The specific activity of nickel varied over 50-fold for the various supports from the highest activity for the silica support to the lowest for the silica-alumina support (*4*). The activation energies in ethane hydrogenolysis were also reported to vary markedly with the support; 54 kcal/mole for platinum–silica and 31 kcal/mole for platinum–alumina catalysts (*10*). These facts indicate that the properties of metals are sensitive to the support material. However, the differences observed between nickel and platinum in the hydrogenolysis of hexane isomers was unchanged on any support as shown in the present work. The hydrogenolytic mechanisms on nickel and platinum proposed in the previous paper (*1*) are certainly applicable for the supported metal catalysts used. Therefore, the reaction mechanism on a given metal catalyst is little affected by the support materials, but the catalytic activities are considerably influenced by them.

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