Catalytic Hydrogenation of Cyclic Olefins on Nickel Catalysts*

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The catalytic hydrogenation of cyclic olefins was investigated over various nickel catalysts. The hydrogenation of cyclohexene was promoted by basic reaction conditions and depressed by acidic ones, the hydrogenation of cyclooctene being only slightly influenced by the acidity. The results of competitive hydrogenation indicate that cyclooctene is adsorbed more strongly on nickel catalysts than cyclohexene. The external olefinic bond is preferentially hydrogenated to the internal olefinic bond.

Cycloalkenes show different reactivities in catalytic hydrogenation, depending on the ring size. Jardine and McQuillin found that, over a Pd-charcoal catalyst, the rate of hydrogenation is linear with respect to the heat of hydrogenation, the rates of hydrogenation being of the order: cyclohexene>cyclopentene>cyclooctene.[1] In the case of nickel catalysts, Brown[2] and Brown and Brown[3] reported the order to be: cyclopentene>cyclohexene>cyclooctene (over R-Ni catalyst), cyclopentene>cyclooctene>cyclohexene (over P-1 Nickel Boride catalyst, abbreviated to P-1 Ni_2B).

We have investigated the hydrogenation of cycloalkenes with Urushibara type nickel catalysts, the preparation conditions of which are widely variable. We also studied the effects of added alkali and acid, and the competitive hydrogenation of cycloalkenes. The results were compared with those of other nickel catalysts.

They might provide some insight into the nature of catalysts and the behavior of cycloalkenes in catalytic hydrogenation.

Experimental

Materials. Commercial cyclohexene (Tokyo Kasei, Reagent Grade) and cyclooctene (Wako Pure Chemical Industry, Reagent Grade) were distilled at 83.5 °C and 63 °C/62 mmHg. Reagent Grade cyclopentene, 4-vinylcyclohexene, 1-methylcyclohexene, 3-methylcyclohexene, and 4-methylcyclohexene (Wako Pure Chemical Industry) were used without further purification.

The samples were proved to be pure by gas-chromatography. Trace amounts of methylcyclohexene contaminants were detected by gas-chromatography.

Commercial ethanol was carefully distilled and used as the solvent of hydrogenation.

Catalysts. Urushibara type nickel catalysts were prepared by simplified methods[4] Ppt-Ni was easily prepared by adding 4.04 g of powdered nickel chloride ($NiCl_2 \cdot 6H_2O$) to 10 g of zinc dust suspended in 4 ml of distilled water under vigorous stirring. This was filtered off, washed with about 200 ml of hot distilled water previously degassed by boiling and then with EtOH.

U-Ni-N catalyst was prepared by refluxing ppt-Ni with 30 ml of isopropyl alcohol for two hours under stirring.[5]

Urushibara type nickel catalysts prepared by simplified methods are usually distinguished from ordinary catalysts by the bracketed letter (s) [U-Ni-A (s) or U-Ni-B (s)].[4,6] However, (s) has been omitted in this paper.

R-Ni(W-7 type) catalyst was prepared by the method of Adkins and Billica.[7]

Nickel Boride catalyst (Ni_2B) was prepared as reported by Paul *et al.*, by reducing nickel chloride with sodium borohydride in aqueous solution.[8]

After these catalysts had been subjected to hydrogenation, they were washed throughly with distilled water to completely remove alkali or acid, and several times with ethanol to remove contamination in the water. In particular, U-Ni-B, R-Ni and Ni_2B were sufficiently washed with water until the washings were neutral to phenolphthalein.

The catalysts thus prepared contain about 1 g of Ni.

Hydrogenation. The substrate (0.01 mol) was hydrogenated with various nickel catalysts in 20 ml of ethanol at 30 °C and atmospheric pressure in a glass bottle shaker at 300—350 strokes per minute.

Addition of alkali or acid was carried out before the catalyst was saturated with hydrogen gas. The amounts of alkali and acid added were 0.3 ml of 10% NaOH and 0.5 ml of 13% CH_3COOH, respectively. The amount of alkali added to U-Ni-A was so chosen as to make the solution faintly alkaline to phenolphthalein, as reported by Nishimura.[9]

The rate of hydrogenation was expressed in terms of the initial rate of hydrogen uptake in the region of 0 to about 20% hydrogenation, in which the hydrogen uptake curve was approximately linear.

Analysis of Reaction Mixture. The reaction mixture resulting from the competitive hydrogenation of a mixture of cyclohexene (0.01 mol) and cyclooctene (0.01 mol) was collected at about 100 ml of hydrogen uptake, and subjected to gas-chromatographic analysis as soon as possible. A column of 20% PEG 20M on Celite 545 (column temperature: 56 °C) was used.

Results and Discussion

Effect of Ring Size. In order to investigate the characteristics of nickel catalysts prepared by various methods, the hydrogenation of cyclopentene, cyclohexene, and cyclooctene was carried out at 30 °C under atmospheric pressure. The results are summarized in Table 1. The activities of the catalysts used were compared in terms of the initial rate of hydrogen uptake.

The rates of hydrogenation with U-Ni-A, U-Ni-B, and ppt-Ni were found to be in the order: cyclopentene>cyclohexene>cyclooctene (Nos. 1, 4, and 6,

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TABLE 1. HYDROGENATION OF CYCLOOLEFINS OVER VARIOUS NICKEL CATALYSTS AT 30°C UNDER ATMOSPHERIC PRESSURE

Amount of samples; 0.01 mol, solvent; EtOH 20 ml, Ni content of catalysts; U-Ni-A, U-Ni-B, U-Ni-N, R-Ni, and Ni_2B, 1 g, ppt-Ni 2 g

Entry No.	Catalyst	Initial rate of H_2 uptake (ml/min)			Rate ratio (c-6/c-8)[a]
		Cyclopentene	Cyclohexene	Cyclooctene	
1	U-Ni-A	54	27	15	1.8
2	U-Ni-A+A[b]		7	11	0.6
3	U-Ni-A+B[c]		32	10	3.3
4	U-Ni-B	70	55	16	3.4
5	U-Ni-N(*i*-PrOH)[d]		24	4	6.0
6	ppt-Ni	8	8	2	4.0
7	ppt-Ni(Ni, 1g)		4	1	4.0
8	R-Ni(W-7)		84	46	1.7
9	R-Ni(W-7)+B[c]		45	20	2.2
10	Ni_2B		44	45	0.98
11	Ni_2B+A[b]		14	38	0.37
12	Ni_2B+B[c]		49	44	1.1

a) r_1= (rate of cyclohexene/rate of cyclooctene). b) A: 0.5 ml of 13% CH_3COOH. c) B: 0.3 ml of 10% NaOH. d) Prepared by refluxing ppt-Ni with *i*-PrOH (30 ml) for 2 hr.

Table 1). The order is the same as that with Raney nickel catalyst.[2,3] However, the relative reactivities varied depending on the method of preparation. When the hydrogenation is performed over U-Ni-B, the difference in reactivities is the greatest, while hydrogenation over ppt-Ni gives a rate of hydrogenation of cyclohexene similar to that of cyclopentene.

This could be explained by the change of the catalyst surface by acid and alkali. U-Ni-A catalyst can be subjected to hydrogenation under practically neutral conditions since acetic acid adsorbed on U-Ni-A can be removed easily by washing. On the other hand, sodium hydroxide adsorbed on U-Ni-B cannot be removed completely by washing with water, even if washing is repeated as often as necessary until the washings are no longer alkaline to phenolphthalein.

In order to confirm the role of acid and alkali, the effects of added alkali or acid on the rates of hydrogenation of cyclohexene and cyclooctene were investigated in detail. It was found that the rate of hydrogenation of cyclohexene is remarkably influenced by added acid or alkali, while the hydrogenation of cyclooctene is influenced to a lesser extent (Nos. 2 and 3, Talbe 1). U-Ni-B of basic character exhibited higher activity for cyclohexene than U-Ni-A of neutral character. On the other hand, cyclooctene was hydrogenated by U-Ni-A and U-Ni-B at a comparable rate.

The ratio of the rate of hydrogenation of cyclohexene to that of cyclooctene over U-Ni-A added alkali (abbreviated to U-Ni-A+B) is 3.3, and the value is similar to that of U-Ni-B. This suggests that the behavior of the U-Ni-B catalyst is due to the presence of sodium hydroxide used as the digesting agent. In the case of U-Ni-A added acid (abbreviated to U-Ni-A+A), cyclooctene was hydrogenated more easily than cyclohexene (an inversion in reactivity). Ppt-Ni, the precursor of the Urushibara nickel catalyst, behaves similarly to U-Ni-B. The U-Ni-N catalyst prepared by refluxing ppt-Ni with *i*-PrOH exhibited also a high reactivity to cyclohexene.[5] R-Ni(W-7 type), which was well washed until the washings were no longer alkaline to phenolphthalein, behaved similarly to U-Ni-A. With R-Ni, the effect of added alkali was similar to that with U-Ni-A catalyst.

Nickel boride catalyst (Ni_2B), prepared according to Paul *et al.*[8] by reducing nickel chloride with sodium borohydride in aqueous solution and then washing until the washings were no longer alkaline to phenolphthalein, exhibited approximately the same catalytic activity in the hydrogenation of cyclohexene and cyclooctene.

It was confirmed that the effects of alkali or acid on the rate of hydrogenation of cyclohexene and cyclooctene were the same for Ni_2B as for the U-Ni-A catalyst.

As regards hydrogenation performed over various types of nickel catalysts, the activity for hydrogenation of cyclohexene is promoted by alkali and inhibited by acid, while the hydrogenation of cyclooctene is influenced slightly by alkali or acid.

Apparent Activation Energy. The rates of hydrogenation of cyclohexene and cyclooctene (Table 1) are comparable with the apparent activation energies of the hydrogenation of cyclohexene and cyclooctene in the presence of U-Ni-A, U-Ni-B, and ppt-Ni (Table 2).

TABLE 2. APPARENT ACTIVATION ENERGIES OF HYDROGENATION OF CYCLOHEXENE AND CYCLOOCTENE

Cyclohexene; 0.01 mol, cyclooctene; 0.01 mol, solvent; EtOH 20 ml, Ni content of catalysts; U-Ni-A and U-Ni-B 1 g, ppt-Ni 2 g, hydrogenation temperature; 30—50 °C

Catalyst	E_a (kcal/mol)	
	Cyclohexene	Cyclooctene
U-Ni-A	2.3	2.1
U-Ni-B	1.8	7.6
ppt-Ni	6.9	22.6

The activation energies in the hydrogenation of cyclohexene and cyclooctene over U-Ni-A were practically the same. However, in the presence of U-Ni-B or

TABLE 3. COMPETITIVE HYDROGENATION OF MIXTURE OF CYCLOHEXENE AND CYCLOOCTENE WITH VARIOUS NICKEL CATALYSTS AT 30 °C UNDER ATMOSPHERIC PRESSURE

Amount of samples; cyclohexene (0.01 mol)+cyclooctene (0.01 mol), solvent; EtOH 20 ml, Ni content of catalysts; 1 g

Entry No.	Catalyst	Yield (%)[a]		Product ratio	
		Cyclohexane	Cyclooctane	(c-6/c-8) $=r_2$[b]	(r_2/r_1)[c]
1	U-Ni-A	16.6	22.3	0.74	0.41
2	U-Ni-A+A[d]	6.1	20.0	0.31	0.52
3	U-Ni-A+B[e]	18.8	13.1	1.4	0.42
4	U-Ni-B	24.7	18.3	1.4	0.41
5	U-Ni-N(*i*-PrOH)[f]	11.9	12.7	0.94	0.15
6	ppt-Ni(Ni, 2 g)	21.4	20.3	1.1	0.28
7	R-Ni(W-7)	23.9	25.2	0.95	0.56
8	Ni_2B	16.3	43.8	0.37	0.38
9	Ni_2B+A[d]	4.8	38.1	0.13	0.35
10	Ni_2B+B[e]	18.4	33.2	0.55	0.50

a) yield of hydrogenation products at about 20% of hydrogen uptake. b) r_2= (yield of cyclohexane/yield of cyclooctane). c) [product ratio (r_2)/rate ratio (r_1)]. d) A: 0.5 ml of 13% CH_3COOH. e) B: 0.3 ml of 10% NaOH. f) prepared by refluxing ppt-Ni with *i*-PrOH (30ml) for 1 hr.

ppt-Ni, cyclooctene gave a greater activation energy than cyclohexene. In the case of U-Ni-B, the presence of a small amount of alkali can lower the activation energy of the hydrogenation of cyclohexene. U-Ni-B and U-Ni-N have a similar behavior toward cyclohexene and cyclooctene as regards the rate and activation energy. This suggests a resemblance in the surface character of the catalysts.

Competitive Hydrogenation. The competitive hydrogenation of a mixture of cyclohexene and cyclooctene with various nickel catalysts was carried out in order to obtain further information on the selectivities of catalysts.

Competitive hydrogenation has been reported on olefins[11] and nitrobenzenes,[12] the results of which give information on the selectivity in adsorption.

The selectivity in the competitive reaction was obtained by comparing the product ratio (r_2), that is, yield of cyclohexane/yield of cyclooctane, at about 20% of hydrogen uptake,[13] with the rate ratio (r_1) obtained in individual hydrogenation. The value (product ratio/rate ratio; r_2/r_1) is used as a measure for the strength of adsorption. The results are summarized in Table 3.

We see that cyclooctene is more slowly hydrogenated than cyclohexene (No. 1, Table 1). However, in competitive hydrogenation, cyclooctene which is more strongly adsorbed on the catalyst is preferentially hydrogenated.

Though the rates of hydrogenation of cyclohexene and cyclooctene are dependent upon the catalysts and the addition of acid or alkali, it was found that the values (r_2/r_1) in the adsorption of cyclohexene and cyclooctene is approximately equal in all cases except U-Ni-N. Cyclooctene is twice as strongly adsorbed as cyclohexene. The character of U-Ni-N, which exhibits a different selectivity of adsorption from other catalysts, showed lower double bond migration in the hydrogenation of 1-octene.[5]

Hydrogenation of Methylcyclohexenes. The hydrogenation of methylcyclohexenes was studied in some detail (Table 4).

TABLE 4. HYDROGENATION OF METHYLCYCLOHEXENES (0.01 mol) AT 30 °C UNDER ATMOSPHERIC PRESSURE

Solvent: EtOH 20 ml, Ni content of catalyst: 1 g

	Initial rate of H_2 uptake (ml/min)			
	(Cyclohexene)	4-Me	3-Me	1-Me
U-Ni-A	27	12	8	2
U-Ni-A+A[a]	7	5	3	1
U-Ni-A+B[b]	32	21	20	2
U-Ni-B	55	36		4

a) 0.5 ml of 13% CH_3COOH. b) 0.3 ml of 10% NaOH.

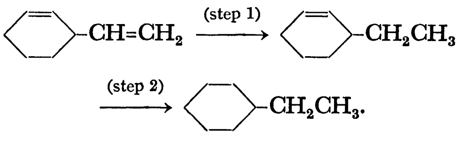
The rate of hydrogenation of cyclohexene was depressed by introducing methyl groups. The effect was in the order: 4-methyl<3-methyl≪1-methyl. 1-Methylcyclohexene could be hydrogenated only at a very small rate. This is probably explained by steric hindrance in the adsorption.

It was found that the rates of hydrogenation of 4-methylcyclohexene and 3-methylcyclohexene are accelerated by added alkali and inhibited strongly by added acid.

Hydrogenation of 4-Vinylcyclohexene (Fig. 1). The difference in reactivity between the internal olefin (cyclohexene ring) and the external olefin (vinyl group) was investigated in the hydrogenation of 4-vinylcyclohexene.

The hydrogen uptake curves at 30 °C under atmospheric pressure are shown in Fig. 1.

Hydrogenation of 4-vinylcyclohexene proceeds stepwise as follows:



The hydrogen uptake curve exhibits a break at an

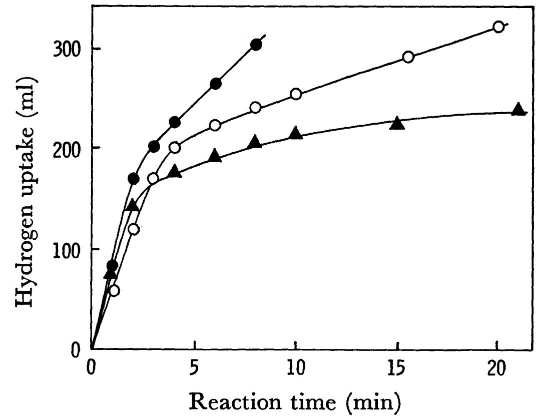


Fig. 1. Hydrogenation of 4-vinylcyclohexene (1 ml) over Urushibara type catalysts in EtOH (20 ml) at 30 °C under atmospheric pressure. Ni content of catalysts: 1 g ●: U-Ni-B, ▲: U-Ni-A, ○: ppt-Ni

uptake of 1.0 mol of hydrogen. After the uptake of 1.0 mol of hydrogen, glc analysis showed that the vinyl group had been almost completely hydrogenated. Brown has reported that the selective hydrogenation of 4-vinylcyclohexene takes palce with the P-1 Ni_2B catalyst.[2]

The rates of hydrogenation at each step are as follows: step 1, U-Ni-B>U-Ni-A>ppt-Ni; step 2, U-Ni-B>ppt-Ni>U-Ni-A.

It is noted that ppt-Ni catalyst differs from U-Ni-A catalyst in the rate of hydrogenation at step 2, *viz.*, at the hydrogenation of cyclohexene ring. The above facts suggest that ppt-Ni exhibits characteristics similar to those of U-Ni-B which exhibits a high activity for cyclohexene owing to its basic character, as is expected from the results of cyclohexene hydrogenation and the apparent activation energy.

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