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A NEW TYPE OF URUSHIBARA NICKEL CATALYST (U-Ni-N). ACTIVATION OF THE PRECIPITATED NICKEL (PRECURSOR OF URUSHIBARA NICKEL CATALYSTS) BY REFLUXING WITH ALCOHOLS

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A new method of activation of ppt-Ni by refluxing with alcohols is described. The ppt-Ni activated in this way (U-Ni-N) exhibits high catalytic activity corresponding to U-Ni-A. The catalyst performs selective reactions in the hydrogenation of 1-octene (low isomerization) and of cycloolefins.

It has been reported that the precipitated nickel (abbreviated to ppt-Ni), prepared by the reaction of nickel chloride with zinc dust, is not active for catalytic hydrogenation, unless it is digested with acid or alkali (U-Ni-A and U-Ni-B).[1)]

It was found, however, that ppt-Ni exhibits catalytic activity for hydrogenation at ordinary temperature, when it is refluxed in alcohols such as i-PrOH and sec-BuOH.

The authors denote the ppt-Ni thus activated by refluxing with sec-alcohols as "Urushibara nickel N", abbreviated to U-Ni-N, after the nomenclature of Urushibara catalysts, because the developing reagents are neutral.

The experimental procedure is as follows; Ppt-Ni is easily prepared by adding 4.04 g of commercial nickel chloride crystals ($NiCl_2.6H_2O$) to 10 g of zinc dust suspended in 4 ml of water under vigorous stirring.[2)] U-Ni-N was prepared by refluxing ppt-Ni with 0.4 mol of various organic reagents for one or two hours under stirring. Then, the catalyst was washed with EtOH, and submitted to hydrogenation.

The catalytic activities of U-Ni-N were examined in the hydrogenation of cyclohexanone at moderate temperature (30-40 °C) under high pressure (50 kg/cm^2). The results are shown in Table 1. The activities are compared in terms of the yield of cyclohexanol for one hour of hydrogenation. As is shown in Entry No.1 of Table 1, ppt-Ni is almost inactive as a catalyst in the hydrogenation of cyclohexanone at moderate temperature. However, U-Ni-N prepared with i-PrOH or sec-BuOH exhibits high catalytic activity even at moderate temperature (Entry Nos.2 and 3 of Table 1).

From the results of Table 1, the dependence of the catalytic activity on the developing reagents was as follows; i-PrOH > sec-BuOH > EtOH > n-PrOH >> t-BuOH, n-Hexane, Cyclohexane, H_2O, MeOH. This order was approximately parallel to the hydrogen donating ability of reagents with the exception of water and methanol which deactivated ppt-Ni.

The apparent activation energies of the hydrogenation of cyclohexanone with ppt-Ni and U-Ni-N were 15.6 and 11.5 kcal/mol, respectively. In view of the activation energy, ppt-Ni is activated by refluxing with i-PrOH.

The optimum conditions for the preparation of U-Ni-N catalyst were investigated in the hydrogenation of ethyl crotonate at 30 °C under atmospheric pressure. The results are shown in Table 2. The ability of reagent to provide catalytic activity in this case was parallel to that in the hydrogenation of cyclohexanone.

Table 1. Hydrogenation of cyclohexanone at 30-40 °C under high pressure with ppt-Ni treated for two hours with various organic reagents. cyclohexanone, 0.05 mol; solvent, EtOH 20 ml; initial hydrogen pressure, 50 kg/cm^2; Ni content of catalyst, 1 g; hydrogenation time, 1 hr

Entry No.	Developing Reagent (0.4 mol)	Hydrogenation Temperature (°C)	Cyclohexanol Yield (%)
1	----- -------	31-----40	10
2	i-PrOH	30-----38	100
3	sec-BuOH	30-----40	84
4	EtOH	30-----42	73
5	n-PrOH	30-----40	71
6	MeOH	30-----40	trace
7	t-BuOH	30-----38	15
8	H_2O	30-----39	2
9	n-Hexane	32---- 50	10
10	Cyclohexane	34-----42	6

Table 2-1. Hydrogenation of ethyl crotonate at 30 °C under atmospheric pressure with ppt-Ni treated with various organic reagents. ethyl crotonate, 0.01 mol; solvent, EtOH 20 ml; Ni content of catalysts, 1 g

Entry No.	Developing Reagent (0.4 mol)	Reflux Time (hr)	Initial Rate of H_2 Uptake (ml/min)
1	ppt-Ni		23
2	U-Ni-A		84
3	U-Ni-B		113
4	i-PrOH	0.5	49
5	i-PrOH	1	95
6	i-PrOH	2	77
7	i-PrOH	2 (74 °C)	49
8	i-PrOH	2 (100 °C)[a]	49
9	sec-BuOH	1	81
10	n-PrOH	1	71
11	EtOH	1	53
12	n-BuOH	1	44
13	MeOH[b]	3	4
14	n-Hexane	2	11
15	H_2O	1	7

a: in autoclave
b: 30 ml

As is seen in Entry Nos.5, 6 and 7 of Table 2-1, U-Ni-N(i-PrOH) exhibited the highest activation when ppt-Ni was heated under reflux. In other alcohols, the activation was also most favorable under reflux. The highest activity of U-Ni-N(i-PrOH) was obtained when ppt-Ni was refluxed with i-PrOH for one hour (Table 2-1).

A comparatively small amount of water added had no influence on the activation of ppt-Ni (Table 2-2). The catalyst treated with i-PrOH containing water has less zinc, and is convenient for practical use. However, the activity of U-Ni-N decreased when the amount of water exceeded a certain limit, that is, about 1 ml of water for 30 ml (0.4 mol) of i-PrOH.

Ppt-Ni treated with water showed hardly any activity (Entry No.15 of Table 2-1). The catalyst, once deactivated with water, could not recover its activity on re-treatment with i-PrOH. In the case of prim-alcohols, the presence of a small amount of water was liable to accelerate the activation of ppt-Ni, compared with sec-alcohols.

Table 2-2. The influence of H_2O added to alcohols on the activation of ppt-Ni. Hydrogenation of ethyl crotonate (0.01 mol) in 20 ml of EtOH at 30 °C under atmospheric pressure; Ni content of catalyst, 1 g

Entry No.	Developing Reagent (0.4 mol)	H_2O Added (ml)	Reflux Time (hr)	Initial Rate of H_2 Uptake (ml/min)	
1	i-PrOH	1	1	73	
2	i-PrOH	0.5	2	87	
3	i-PrOH	1	2	83	
4	i-PrOH	3	2	31	
5	sec-BuOH	1	1	85	
6	n-PrOH	1	1	82	
7	EtOH	1	1	81	
8	n-BuOH	1	1	54	
9	MeOH[a]	1	1	19	a: 30 ml

A low isomerization in the hydrogenation of 1-olefin is one of the characteristics of the U-Ni-N catalyst. The proportion of isomerization was determined with [2-octene/(octane + 2-octene)] x 100 at 20 % hydrogenation. The ratio of isomerization on various nickel catalysts was found to decrease in the following order: U-Ni-B (45 %) > U-Ni-A (34 %) > ppt-Ni(containing 2 g of Ni) (23 %) > U-Ni-N(i-PrOH) (15 %).

An interesting selectivity was found in the hydrogenation of cycloolefins. The hydrogenation of cyclohexene and cyclooctene at 30 °C under atmospheric pressure was investigated. The results are shown in Table 3. In the hydrogenation of cyclohexene, U-Ni-N(i-PrOH) exhibits high catalytic activity comparable to U-Ni-A, while the activity of U-Ni-N for cyclooctene is very low compared with U-Ni-A and U-Ni-B. The above facts suggest that U-Ni-N catalyst is effective in selective hydrogenation.

It is also noteworthy that hydrogenation with U-Ni-N can be performed under practically neutral conditions.

The change of composition of ppt-Ni treated with various reagents was investigated by X-ray diffraction. Ppt-Ni contains zinc, zinc oxide, and zinc hydroxide chloride, the last of which has been assumed to be a poison for hydrogenation. The X-ray diffraction patterns of the ppt-Ni treated with alcohols for two hours, except with MeOH, show only the lines due to zinc and zinc oxide, and the lines of

Table 3. Hydrogenation of cyclohexene and cyclooctene at 30 °C under atmospheric pressure.
amount of samples, 0.01 mol; solvent, EtOH 20 ml; Ni content of catalysts, 1 g

Entry No.	Catalyst	Initial Rate of H_2 Uptake (ml/min)	
		Cyclohexene	Cyclooctene
1	U-Ni-N(i-PrOH)[a]	24	4
2	ppt-Ni	4	1
3	U-Ni-A	27	15
4	U-Ni-B	55	16

a: refluxed in i-PrOH (0.4 mol) for 2 hrs

zinc hydroxide chloride disappear. In the case of MeOH and n-Hexane, the X-ray diffraction patterns are similar to that of ppt-Ni itself, and the lines of zinc hydroxide chloride remain. In spite of a high hydrogenation activity of the ppt-Ni treated with i-PrOH containing H_2O, zinc hydroxide chloride was found to be still present in it.

It has been considered that the activation of ppt-Ni with a base or an acid consists in exposing the active nickel surface of ppt-Ni by the removal of zinc hydroxide chloride.[1)] However, the above facts suggest that zinc hydroxide chloride which was considered to cover originally the active nickel surface of ppt-Ni in some way might have been transformed by refluxing with alcohols containing a small amount of water into a form which does not inhibit the activity of the ppt-Ni for hydrogenation.

At present, the authors are further exploring the mechanism of the activation of ppt-Ni by treatment with alcohols.

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