Catalytic Hydrogenation in Vapor Phase with Urushibara Nickel Catalyst

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It has been reported[1] that catalytic hydrogenation in vapor phase with Urushibara nickel catalyst (U-Ni in abbreviation) was carried out for the first time and the experimental results were fairly good. In consequence, it has been proved that U-Ni as a catalyst for hydrogenation is able to be used effectively in vapor phase as well as in liquid phase[2]. It is not as troublesome to use U-Ni as to use other catalysts such as Sabatier's reduced nickel catalyst.

From the previous investigations, we got a suggestion of preparing U-Ni from

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[1] K. Hata, K. Watanabe and S. Sato, This Bulletin, **30**, 431 (1957).

[2] Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954); Y. Urushibara, S. Nishimura and H. Uehara, ibid., **28**, 446 (1955); K. Hata et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1405 (1956).

nickel chloride solution and aluminum metal in place of zinc dust. In this paper, we introduce a new study using U-Ni which is made from nickel chloride and aluminum metal. It was found that U-Ni thus made was a more excellent hydrogenation catalyst in vapor phase than any other one because of its activity and convenience in practical use.

At first aluminum powder was used for the precipitating agent, and the precipitated nickel was treated with alkali. The catalyst thus obtained was found to be useful for the reduction of some organic substances. However, aluminum powder did not seem to be entirely suitable for the preparation of the catalyst, although the preparation could be carried out more easily by the addition of some detergent. Then grained aluminum (45 meshes) was chosen instead of aluminum powder. Nickel was precipitated from nickel chloride solution on the surface of aluminum grains, and the precipitated nickel was treated with acetic acid containing inorganic salt such as sodium chloride, whereby the precipitated nickel did not separate from the aluminum grains*. U-Ni catalyst thus prepared, which is called U-Ni-AA** in abbreviation, was proved to be a very convenient catalyst for vapor phase hydrogenation because the grains of aluminum remained undissolved after they were treated with acetic acid, and served as carrier.

A similar catalyst prepared by digesting the precipitated nickel with alkali is called U-Ni-BA**, which is also useful for hydrogenation. U-Ni-BA for the liquid phase hydrogenation must be prepared with grained aluminum[3], but for the vapor phase hydrogenation, it was proved that U-Ni-BA prepared from nickel chloride and commercially available aluminum powder was effective enough. The conditions of preparation of these U-Ni catalysts are shown in Table I.

The results of hydrogenation with these catalysts are summarized in Table II. Nitrobenzene was reduced to aniline, phenol to cyclohexanol. Both styrene and acetophenone were hydrogenated with U-Ni-BA to ethylbenzene (Exp. No. 3 and 4); when U-Ni-AA was used, they were reduced further to ethylcyclohexane (Exp. No. 9 and 10). It is very remarkable that benzene was reduced to cyclohexane[4] with U-Ni-AA, but not with U-Ni-BA (prepared with aluminum powder). Benzonitrile was largely reduced to toluene and ammonia[5], and the result of this cleavage reaction was different from that of previous experiments[1] using U-Ni-A (prepared from nickel chloride and zinc dust).

From these results, it is evident that the aromatic ring is able to be reduced by the use of this new type catalyst U-Ni-AA, while not by U-Ni-A*** or U-Ni-B***. In addition, it is interesting to note that U-Ni-AA can also be used in the hydrogenation in liquid phase under the condition of room temperature and ordinary pressure of hydrogen. For example, nitrobenzene was reduced to aniline in 70% yield in ethanol. Thus U-Ni-AA is shown to be effective for hydrogenation both in vapor and liquid phase as well as reduced nickel catalyst. It may be expected that U-Ni prepared from aluminum will be widely applied in the field of catalytic chemistry.

Experimental

U-Ni-AA.—To 60 g. of grained aluminum (45 meshes), a small amount of water is added. In another vessel, 80 cc. of nickel solution containing 32 g. of $NiCl_2 \cdot 6H_2O$ is heated to 50～60°C, and added to the aluminum with stirring. An exchange reaction occurs and nickel deposits on the surface of the aluminum. The reaction is controlled by cooling with cold water or by heating with hot water. The precipitated nickel is washed with cold water. Then 40% acetic acid solution (385 cc., 70°C) containing 89 g. of sodium chloride is added to the nickel. After 3～7 minutes, the acid solution is decanted, and the residue washed with ca. 2 l. of warm water (50～60°C) and then with methanol. The catalyst thus obtained contains 8 g. of nickel.

U-Ni-BA (for vapor phase hydrogenation).—Ten g. of aluminum powder (200 meshes) is suspended in a small amount of water, and heated on a boiling water bath. Then 10 cc. of warm nickel chloride solution containing 4 g. of $NiCl_2 \cdot 6H_2O$ (ca. 90°C) is added to the aluminum. After a violent exchange reaction ceases, all

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* The procedure of preparing the catalyst and of the hydrogenation was quite different unless the salt was used, and the catalyst thus prepared was not suitable for hydrogenation.

** In abbreviation, the last A means aluminum as precipitating agent, and the first A and B mean acid and base as the digesting solution for the precipitated nickel.

3) K. Hata, S. Taira and I. Motoyama, This Bulletin, **31**, 776 (1958).

4) P. Sabatier and J. B. Senderens, *Compt. rend.*, **132**, 210 (1901).

5) P. Sabatier and J. B. Senderens, ibid., **140**, 482 (1905); K. Hata, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **23**, 224 (1944); M. Tanaka, K. Watanabe and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 1392 (1955).

*** Only phenol was reduced to cyclohexanol in 20～30% yield with U-Ni-A or U-Ni-B (unpublished).

TABLE I

PREPARATION OF CATALYSTS

Catalyst	$NiCl_2 \cdot 6H_2O$ (g.)	Al (g.)	Al (mesh)	Digesting solution	NaCl (g.)	Carrier
U-Ni-AA	32	60	45	40% CH_3CO_2H (385 cc.)	89*	—
U-Ni-BA	4	10	200	20% NaOH (200 cc.)	—	Pumice stone
U-Ni-BA	12	15	45	20% NaOH (350 cc.)	—	" Hyflosupercel "

* The quantity to saturate the acid solution.

TABLE II

VAPOR PHASE CATALYTIC HYDROGENATION WITH U-Ni CATALYSTS

Exp. No.	Catalyst	Compounds	Weight of sample (g.)	Nickel (g.)	Temp. (°C)	Time (hr.)	Flow velocity of sample (g./min.)	Products and Yields (%)	
1	U-Ni-BA	Nitrobenzene	8	1	240[1]	5	0.038	Aniline[2]	(58)
2	U-Ni-BA	Phenol	10	4	185[1]	6	0.034	Cyclohexanol	(79)
3	U-Ni-BA	Styrene	4.3	1	195[1]	4	0.029	Ethylbenzene	(91)
4	U-Ni-BA[3]	Acetophenone	5	3	200	1¾	0.114	Ethylbenzene	(52)
5	U-Ni-AA	Nitrobenzene	5	8	230	2	0.094	Aniline[2]	(65)
6	U-Ni-AA	Phenol	5	8	180	3½	0.111	Cyclohexanol	(66)
7	U-Ni-AA	Benzonitrile	5	8	250	2	0.075	Toluene	(76)
8	U-Ni-AA	Benzene	5	8	176	2⅓	0.046	Cyclohexane[4]	(83)
9	U-Ni-AA	Styrene	5	8	150	2	0.073	Ethylcyclohexane[5]	(94)
10	U-Ni-AA	Acetophenone	5	8	190	2	0.069	Ethylcyclohexane[6]	(71)

1) The temperature of the oil bath.
2) Besides aniline, high molecular amines were obtained as by-products.
3) Grained aluminum (45 meshes) was used, and " Hyflosupercel " was used as carrier.
4) B. p. 80~81.2°C, $n_D^{20}=1.4270$ (lit. 1.4266).
5) B. p. 127~128°C, $n_D^{20}=1.4347$ (lit. 1.4324).
6) B. p. 128~131.8°C, $n_D^{20}=1.4332$ (lit. 1.4324).

the contents are heated to dryness, and 200 cc. of 20% sodium hydroxide solution is added gradually. Since a vigorous exothermic reaction takes place, the contents are stirred well and cooled with running water, and the aluminum is completely dissolved in a short time. Treatment of the nickel precipitate is accomplished by heating for about five minutes. The supernatant solution is decanted, and the residue washed with warm water (50~60°C) until the washing becomes neutral to litmus, and then with methanol thoroughly. The catalyst thus obtained contains about 1 g. of nickel.

Method of hydrogenation.—In the earlier period of these experiments, a special U-tube apparatus was used for hydrogenation reactions, and the reaction tube was heated in an oil bath, as previously reported[1]. In Table II, the experiments, Nos. 1—3, were carried out by the above method.

The U-tube method being somewhat troublesome, the usual hydrogenation method, e. g. with Sabatier's hydrogenation apparatus, has been adopted for convenience. Further experiments, Nos. 4—10, were carried out by such a method in a hard glass reaction tube, 1.8 cm. in diameter and 90 cm. in length, heated in an electric furnace. In experiment No. 4, " Hyflosupercel " (purified kieselguhr) was used as a carrier.

The catalyst was put into the reaction tube, and heated up to an appropriate reaction temperature, while methanol, which was used for washing the catalyst, was expelled by heating. The vaporized sample, together with a large excess of hydrogen, was introduced into the reaction tube. The reaction products flowing out of the tube were collected into the receiver through a condenser, and were isolated by means of fractional distillation. Then each product was identified by preparing an appropriate derivative respectively, except in the case of cyclohexane and ethylcyclohexane.

Summary

Catalytic hydrogenation in vapor phase with new types of Urushibara nickel catalyst was carried out.

1) New types of U-Ni were prepared from nickel chloride and aluminum. U-Ni-BA and U-Ni-AA were respectively obtained by treating the precipitated nickel with alkali or acetic acid.

2) These catalysts are quite easy to prepare and were proved to be useful for hydrogenation. Above all, U-Ni-AA is the most convenient for vapor phase hydrogenation, since it was found to be highly active and the aluminum served as carrier. It was also used in hydrogenation in liquid phase.

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