Catalytic Hydrogenation in Vapor Phase Using Urushibara Nickel as Catalyst

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Urushibara nickel (U-Ni in abbreviation), a new catalyst made from nickel choride and zinc dust, has been reported to show excellent behavior in the catalytic reduction of many organic compounds[1-5].

In this paper, we introduce a new idea applying this catalyts to vapor phase hydrogenation. The procedure of the vapor phase hydrogenation with U-Ni as catalyst is not so troublesome as that with other catalysts, and efficient reduction was observed except in special cases. U-Ni-A, which was used in these experiments, was prepared by treating precipitated nickel with acetic acid as previously reported[4].

Nitrobenzene was reduced to aniline, styrene and acetophenone to ethylbenzene respectively, and benzonitrile to primary and secondary amines together with some toluene. However, benzene could not be reduced by this method. The conditions of the reaction and products are shown in Table I.

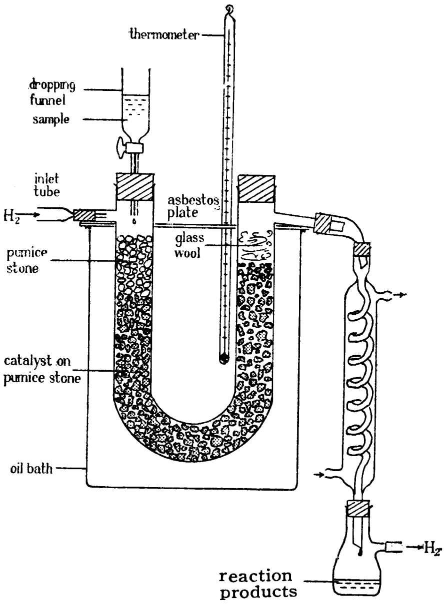

Fig. 1. Apparatus for the hydrogenation.

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TABLE I

VAPOR PHASE HYDROGENATION USING U-Ni-A AS CATALYST

Compound	Weight of Sample (g.)	Nickel (g.)	Temp. (°C)	Time (hr.)	Flow Velocity of Sample (g./min.)	Weight of Product (g.)	Product and Yield (%)	
Nirobenzene	10	4	220	3	0.08	9.7	Aniline	(81)
Benzene	10	4	180	4	0.06	9.0	(Benzene recovered)	
Styrene	10.4	4	165	3	0.08	9.3	Ethylbenzene	(88)
Acetophenone	9.9	4	200	3½	0.06	9.1	Ethylbenzene	(90)
Benzonitrile	8.0	4	250	3	0.07	6.5	Toluene	(14)
							Benzylamine	(29)
							Dibenzylamine	(41)
							Ammonia	(50)

The hydrogenating apparatus used in these experiments is shown in Fig. 1. A hard glass U-tube, 3 cm. in diameter and about 50 cm. in total length, was used as a reaction tube. Small grains of pumice stone were put in the U-tube to fill about three quarters of its content. Freshly prepared U-Ni-A catalyst was washed with alcohol, and was poured on the pumice stone in the U-tube together with a small quantity of alcohol. The catalyst settled over the surface of the pumice stone when treated by this method. Then, other pieces of pumice stone were added to fill up the U-tube, and the tube was set in an oil bath after the greater part of the alcohol was decanted away. A small dropping funnel to introduce the liquid sample was fitted on the top of the U-tube over the hydrogen inlet tube. A condenser and a receiver were connected with the other branch of the U-tube. The reaction tube was heated and hydrogen was passed through the tube to expel the vapor of alcohol. Now the receiver was changed to catch the reaction products, and the temperature of the bath was suitably controlled for the hydrogenation. The liquid sample was then slowly dropped into the U-tube. The liquid was vaporized on the upper grains of pumice stone and was hydrogenated on the nickel catalyst, the reaction products being distilled into the receiver.

Each sample was hydrogenated under the suitable temperature with a large excess of hydrogen. After all the sample had been supplied, more hydrogen was passed through for 30-60 minutes to expel the hydrogenation products throughly. After the reaction was over, each product in the receiver was fractionally distilled, and then identified by preparing an appropriate solid derivative.

From these experiments, it was proved to be very convenient to use U-Ni in the vapor phase catalytic hydrogenation. For the preparation of the catalyst, it is not necessary to reduce the nickel compound at high temperature such as by Sabatier's method; all procedures are simple and quick, and the yields of the hydrogenation products are pretty good.

Different results from the hydrogenation with Sabatier's reduced nickel were obtained in the hydrogenation of benzene and benzonitrile. Benzene nucleus could not be hydrogenated with U-Ni by any way, though Sabatier's reduced nickel converts benzene into cyclohexane[6]. Benzonitrile can be hydrogenated almost perfectly to toluene and ammonia with reduced nickel catalyst at 250°C[7], but with U-Ni, the formation of toluene was largely depressed alternatively yielding primary and secondary amines.

The further investigation on the activity of Urushibara nickel in vapor phase hydrogenation is now in progress.

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