Raney Nickel and Platinized Rany Nickel with Higher Catalytic Activities

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(Received July 8, 1958)

Preparation of Raney Nickel Catalysts. —In a previous paper⁽¹⁾, it was reported that a Raney nickel catalyst with a higher activity can be obtained by adding aqueous sodium hydroxide in portions to the suspension of a Raney alloy in water. To obtain a catalyst of high activity the usual methods of developing the Raney alloy, e. g. the method of Adkins and Billica⁽²⁾, seemed unfavorable for the following reasons.

a) The reaction of the Raney alloy with sodium hydroxide in an aqueous solution is strongly exothermic and it is very difficult to put the alloy into the solution within a short time. Therefore, a catalyst developed uniformly can not be obtained, because the portion of the alloy added at the beginning is treated with the most concentrated sodium hydroxide for the longest time and that added last with the most dilute sodium hydroxide for the shortest time.

The lack of uniformity can not be neglected in such a catalyst as W-7 of Adkins and Billica⁽²⁾, which is prepared with a

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1) S. Nishimura and Y. Urushibara, This Bulletin, **30**, 199 (1957).

2) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

comparatively small quantity of sodium hydroxide and contains a considerable amount of aluminum, or in a catalyst prepared from an alloy containing less nickel.

b) In the preparation of Urushibara nickel catalysts[3,4], which are obtained by treating finely divided nickel, precipitated from a nickel chloride solution by zinc dust, with aqueous caustic alkali or with acetic or propionic acid, it proved harmful to the activity of the catalysts to use a concentrated solution of the developing reagent and mild conditions are favorable so far as the time for the preparation is tolerable. It suggests that use of a strong alkali may be unfavorable also in the preparation of the Raney nickel catalyst.

From this point of view, the author attempted with success to prepare Raney nickel catalyst with a higher activity by adding a sodium hydroxide solution in portions to the suspension of a Raney alloy in water. In the course of this study, it was found that the Raney alloy, after being partly leached with a very dilute sodium hydroxide solution, reacts with, and is developed by, water, forming a large quantity of white aluminum hydroxide, which was confirmed to be bayerite by the X-ray diffraction analysis[5]. After the reaction with water has subsided and the alloy has been covered with grey films of bayerite, the product reacts only very mildly with a concentrated sodium hydroxide solution, which can be added at one time without arousing a violent reaction. Then the digestion is continued to remove the bayerite and to complete the development.

The Raney nickel catalyst prepared in this way (denoted as T-4 when prepared from an alloy containing 40% of nickel) is more active than the W-7 catalyst of Adkins and Billica. The catalyst prepared under the same conditions as W-7 except that a larger quantity of the sodium hydroxide solution of the same concentration was used (denoted as W-7′) was less active than W-7.

It suggests that the W-7′ catalyst was overdeveloped or partly deactivated with the strong alkali in the course of the development. Table I shows the activities of these three catalysts in the hydrogenation of various organic compounds under the ordinary pressure and at 25°C.

TABLE I

TIME (min.) FOR THE HYDROGENATION OF ORGANIC COMPOUNDS WITH RANEY NICKEL CATALYSTS UNDER THE ORDINARY PRESSURE AND AT 25°C

Compound	Amount (g.)	Hydrogen absorbed (mole/mole)	Catalyst		
			T-4	W-7	W-7′
Cyclohexanone	3.93	1	17	21	24
Acetophenone	4.81	1	34	40	50
Cyclohexene	3.29	1	7	9	9
Quinoline	2.58	2	83	84	
Benzonitrile	2.06	2	49	76	80
Cyclohexanone oxime	2.26	2	92	126	

a) The catalyst was prepared from 2 g. of a Raney alloy containing 40% of nickel each time just before the hydrogenation.

b) 20 cc. of 95% ethanol was used as the solvent.

From some apparently similar methods in the literature[6-9] the present method differs in the fact that the Raney alloy is developed mostly with water, but not with an alkali, forming a large quantity of bayerite, which prevents the catalyst from direct contact with a strong alkali and facilitates the later addition of the main portion of the sodium hydroxide solution. The procedure to prepare the T-4 catalyst is given in details in the experimental part.

Preparation of the Platinized Raney Nickel Catalysts. — In many hydrogenations it has been shown that the Raney nickel catalyst is greatly promoted by treatment with chloroplatinic acid. Delépine and Horeau[10,11] showed that a Raney nickel platinized with chloroplatinic acid was effective for the hydrogenation of carbonyl compounds with addition of a little aqueous sodium hydroxide. Lieber, Smith and their co-workers[12-17] showed

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[3] Y. Urushibara and S. Nishimura, This Bulletin, **27**, 480 (1954).

[4] Y. Urushibara, S. Nishimura and H. Uehara, ibid., **28**, 466 (1955).

[5] A small amount of bayerite is also formed in the preparation of the W-7 Raney nickel catalyst. cf. G. W. Watt and S. G. Parker, *J. Am. Chem. Soc.*, **74**, 1103 (1952).

[6] F. Fischer and K. Meyer, *Ber.*, **67**, 253 (1934).

[7] E. B. Maxted and R. A. Titt, *J. Soc. Chem. Ind.*, **57**, 197 (1938).

[8] J. Yasumura, *Science and Ind.*, (*Kagaku to Kogyo*), **22**, 21 (1948).

[9] R. Cornubert and J. Phélisse, *Bull. soc. chim. France*, [5], **19**, 399 (1952).

[10] M. Delépine and A. Horeau, *Compt. rend.*, **201**, 1301 (1935); **202**, 995 (1936).

[11] M. Delépine and A. Horeau, *Bull. soc. chim.* France, [5], **4**, 31 (1937).

[12] E. Lieber and G. B. L. Smith, *J. Am. Chem. Soc.*, **58**, 1417 (1936).

[13] J. R. Reasenberg, E. Lieber and G. B. L. Smith, ibid., **61**, 384 (1939).

that treatment with chloroplatinic acid or with chloroplatinic acid and triethylamine was also effective for many hydrogenations. These methods agree in the fact that the Raney nickel is treated with chloroplatinic acid, and may supposedly have the following disadvantages:

a) The activity of nickel itself may be partly lost on treatment with chloroplatinic acid and the nickel ion then formed may be a catalytic poison[12].

b) The chloride ion and/or the hydrogen ion may be also catalytic poisons[18] and it is not certain if they can be completely removed by mere addition of sodium hydroxide[19] or triethylamine.

Recently Blance and Gibson[20] prepared a platinized Raney nickel from a nickel-aluminum alloy containing 2% of platinum but such an alloy has to be made specially and may not always be readily available.

The present author improved the preparation of the platinized Raney nickel by platinizing and simultaneously leaching the Raney alloy: A chloroplatinic acid solution made alkaline with a little sodium hydroxide is added to the suspension of a Raney alloy in water. The partly leached and platinized Raney alloy reacts with water, forming a large quantity of bayerite, and then can be treated in the same way as in the preparation of the T-4 catalyst. The details of the procedure for the preparation are given in the experimental part.

TABLE II

TIME (min.) FOR THE HYDROGENATION OF ORGANIC COMPOUNDS WITH THE PLATINIZED RANEY NICKEL CATALYSTS UNDER THE ORDINARY PRESSURE AND AT 25°C

Compound	Amount (g.)	Hydrogen absorbed (mole/mole)	Catalyst	
			T-4-Pt	T-4-Pt (D.H.)
Cyclohexanone	3.93	1	10	13
Acetophenone	4.81	1	13	17
Quinoline	2.58	2	27	38
Benzonitrile	2.06	2	11	14
Cyclohexanone oxime	2.26	2	17	19

a) The catalyst was prepared from 2 g. of a Raney alloy containing 40% of nickel and 50 mg. of chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$.

b) 20 cc. of 95% ethanol was used as the solvent.

The platinized T-4 catalyst prepared in this way is more active than the T-4 catalyst platinized by the method of Delépine and Horeau. Table II shows the activities of these two catalysts in the hydrogenation of some organic compounds, T-4-Pt denoting T-4 platinized by the present method and T-4-Pt (D. H.) T-4 platinized by the method of Delépine and Horeau.

Experimental

Preparation of T-4 Catalyst.—To a mixture of 2 g. of a Raney nickel-aluminum alloy containing 40% of nickel[21] and 10 cc. of water, contained in a 30 cc. Erlenmeyer flask with a stirrer and heated in a water bath of 50°C, 0.4 cc. of 20% aqueous sodium hydroxide is added with vigorous stirring, care being taken not to let the reaction become violent, and the mixture is stirred. In about one hour, the partly leached Raney alloy begins to react with water and turns grey in color, and the reaction almost subsides in one hour and a half. Then 6 cc. of 40% aqueous sodium hydroxide is added at one time with continued stirring.

The digestion is continued for one additional hour at 50°C with good stirring, until the upper layer becomes snow-white. The catalyst is washed by stirring and decanting four times with 15 cc. of water of 50°C and then three times with the same volume of ethanol. A specimen of the T-4 catalyst thus prepared contained 13.3% of aluminum and a little aluminum hydroxide.

Preparation of W-7 and W-7′ Catalysts.—W-7 catalyst was prepared from 2 g. of the alloy and 12 cc. of a 20 per cent sodium hydroxide solution exactly as described by Adkins and Billica[2] except that the catalyst was washed as described above for the T-4 catalyst. W-7′ catalyst was prepared from 2 g. of the alloy and 24 cc. of 20 per cent aqueous sodium hydroxide. The W-7 and W-7′ catalysts thus prepared contained 13.3 per cent and 12.5 per cent of aluminum, respectively.

Preparation of Platinized T-4 Catalyst.—To a suspension of 2 g. of the Raney alloy in 10 cc. of water, 50 mg. of chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$, dissolved in 2 cc. of water made alkaline with 0.4 cc. of 20 per cent aqueous sodium hydroxide, was added with vigorous stirring in a water bath of 50°C.

The procedure hereafter is exactly the same as described above for the T-4 catalyst. Incomplete digestion, which is indicated by the grey

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14) S. S. Scholnik, J. R.Reasenberg, E. Lieber and G. B. L. Smith, ibid., **63**, 1192 (1941).

15) D. R. Levering and E. Lieber, ibid., **71**, 1515 (1949).

16) D. R. Levering, F. L. Morritz and E. Lieber, ibid., **72**, 1190 (1950).

17) G. S. Samuelsen, V. L. Garik and G. B. L. Smith, ibid., **72**, 3872 (1950).

18) J. N. Pattison and Ed. F. Degering, *J. Am. Chem. Soc.*, **73**, 611 (1951).

19) S. Watanabe, *Science and Ind.* (*Kagaku to Kogyo*), **31**, 195 (1957).

20) R. B. Blance and D. T. Gibson, *J. Chem. Soc.*, **1954**, 2487.

21) A 50-50% alloy can be used with a somewhat lower activity of the resulting catalyst.

color of the upper layer, does not develop the activating effect by platinum.

Platinization of the T-4 Catalyst by the Method of Delépine and Horeau.—To a suspension of the T-4 catalyst, prepared from 2 g. of the Raney alloy, in 10 cc. of water, 50 mg. of chloroplatinic acid, dissolved in 2 cc. of water, is added with vigorous stirring in a water bath of 50°C. In a few minutes, when the reaction is complete, a little sodium hydroxide solution is added with stirring, and then the catalyst is washed.

Hydrogenation. — After the catalyst, suspended in 15 cc. of ethanol, was saturated with hydrogen at 25°C, the substance dissolved in 5 cc. of ethanol was added and the mixture was shaken with hydrogen at 400—500 oscillations per minute.

Identification of Bayerite.—The snow-white precipitate in the upper layer formed during the digestion with alkali was collected by centrifuging and analyzed by means of the X-ray diffraction. The diffraction pattern shown in Fig. 1 shows that the precipitate is bayerite, one form of aluminum trihydroxide. But the bayerite is different from that formed in the reaction of the alloy with water as shown in Fig. 2. According to Fricke[22], the former is bayerite a and the latter bayerite b.

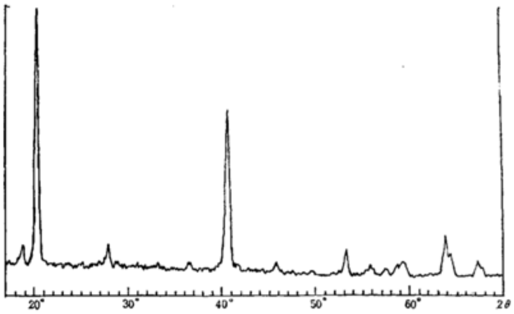

Fig. 1. Diffraction pattern of the precipitate formed during the digestion with alkali.

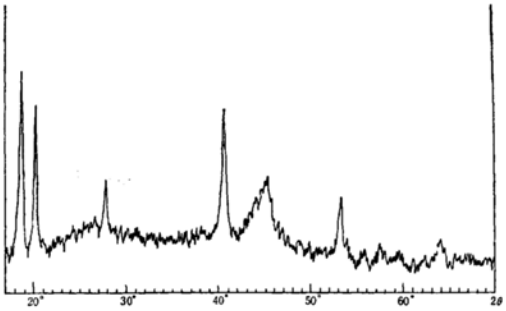

Fig. 2. Diffraction pattern of Raney alloy after the reaction with water.

The patterns were obtained by an X-ray diffractometer with Ni-filtered Cu-K_α radiation.

The author wishes to express his hearty thanks to Professor Yoshiyuki Urushibara for his kind guidance and valuable suggestion given throughout this work. The author is also indebted to Dr. Hiroshi Takahashi and Mr. Haruo Kuroda for their kind help in the measurement of the X-ray diffraction. This study has been supported by the Scientific Research Grant of the Ministry of Education.

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[22] R. Fricke, *Z. anorg. allg. Chem.*, **175**, 249 (1928)