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The Preparation of a Highly Active Raney Nickel Catalyst with Formation of a Recoverable Bayerite

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Synopsis. In the presence of a properly prepared bayerite and a small amount of sodium hydroxide, Raney nickel-aluminium alloy is developed with water to give a highly active catalyst with formation of a recoverable bayerite. In hydrogenation of typical organic compounds the catalyst is even more active than the T-4 Raney nickel.

In 1959 one of the authors (S. N.) described a method for the preparation of a highly active Raney nickel catalyst in which the reaction of Raney alloy with water was initiated by partly leaching the alloy with a small amount of sodium hydroxide at 50 °C.[1] After an induction period of about 1 h, the alloy began to react with water violently and was developed extensively to give a product which had been covered with a large quantity of bayerite, a modification of crystalline aluminium trihydroxides. To obtain a highly active catalyst a concentrated sodium hydroxide solution was then added to remove the bayerite from the catalyst and complete the development. The Raney nickel thus prepared (denoted as T-4 when prepared from 40% nickel alloy) was more active than those prepared by usual procedures.[1] It seems that the extensive reaction of Raney alloy with water is promoted by the sodium hydroxide which has been regenerated by the hydrolysis of initially formed sodium aluminate, as suggested by Dirksen and Linden.[2] The violent reaction of Raney alloy with water that occurs after the induction period is probably caused by the transformation of the sodium aluminate into crystalline bayerite which in turn promotes the subsequent crystallization of amorphous aluminium hydroxide[†] and hence the hydrolysis of sodium aluminate, producing continuously sodium hydroxide for further development of the alloy (see Eq. 1). In fact, Taira and Kuroda have shown that the addition of bayerite promotes the reaction of Raney alloy with water and prepared an active catalyst which was supported on bayerite and claimed to be resistant to deactivation, by developing the alloy with addition of bayerite.[3,4]

$$\begin{tikzcd}
NaAlO_2 + 2H_2O \arrow[r, rightleftharpoons] & \text{amorphous } Al(OH)_3 + NaOH \arrow[d, "\text{bayerite}"] \\
& \text{crystalline } Al(OH)_3 \text{ (bayerite)}
\end{tikzcd} \qquad (1)$$

We have intended to improve the T-4 procedure with use of bayerite by which it may be possible to reduce the amount of sodium hydroxide required. In the course of this study it has been recognized that the action of bayerite to promote the reaction in Eq. 1 greatly depends on its preparation as well as reaction conditions, and, by using a properly prepared bayerite and suitable reaction conditions, the catalyst that is not combined with the bayerite formed can be prepared. Under these conditions the alloy can be developed extensively at a low temperature with use of only a small amount of sodium hydroxide to give a highly active catalyst, and at the same time the bayerite initially added as well as newly formed can easily be separated from the resulting catalyst merely by decantations. The bayerite thus recovered has been found to become reusable after treatment with a dilute hydrochloric acid. Whether the bayerite formed is deposited on the catalyst or not appears to depend on the nature of bayerite initially added as well as on the mode of the addition of sodium hydroxide. As described in the experimental part, the bayerite that promotes efficiently the reaction in Eq. 1 and gives the catalyst not combined with bayerite is prepared by the reaction of CO_2 gas with a rather concentrated solution of sodium aluminate at 40 °C. Such conditions suggest that the contamination of amorphous aluminium hydroxide or gelatinous boehmite should be avoided.[5] Further, to prepare a catalyst free from bayerite it is advisable to add the bayerite prior to the addition of sodium hydroxide. If we add the bayerite to the alloy after partly leached with sodium hydroxide, a catalyst which is firmly combined with bayerite tends to result, just as in the T-4 preparation where it is necessary to use a concentrated sodium hydroxide solution to remove the bayerite from the catalyst.[1]

As an example of the preparation, 0.5 g of Raney alloy powder (40% Ni) and 1 g of the bayerite prepared by the procedure given in Experimental are stirred in 10 ml of water at 40 °C. To this 0.03 ml of 20% sodium hydroxide is added and the mixture stirred for 30 min in which a violent reaction of the alloy with water almost subsides. At this stage the alloy is already developed to the extent of *ca.* 70% and the catalyst is sufficiently active for most hydrogenations (see the example in Table 1). To obtain the catalyst of the highest activity 0.3 ml of 20% sodium hydroxide is then added and the mixture stirred for 1 h at 40 °C. With one preparation the degree of oxidation of the aluminium in the alloy was estimated to be 81% at the final stage.[6] The catalyst thus prepared (denoted as N-4) has been more active than the T-4 catalyst in typical hydrogenations (Table 1). With benzonitrile, however, treatment with a larger amount of sodium hydroxide was

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[†] The transformation of sodium aluminate to bayerite has been shown to occur according to the following scheme: sodium aluminate solution →amorphous hydroxide→gelatinous boehmite→bayerite [B. C. Lippens, "Structure and Texture of Aluminas," Uitgeverij Waltman, Delft (1961), p. 15].

TABLE 1. HYDROGENATION OF TYPICAL ORGANIC COMPOUNDS WITH N-4 AND T-4 RANEY NICKEL CATALYSTS[a]

Compound	Amount mmol	Catalyst	Rate of H_2 uptake[b] ml at STP min^{-1}	Time for hydrogenation min
Cyclohexene	15	N-4	20.0	20
		T-4	18.0	26
Cyclohexanone	15	N-4	12.4	36
		N-4[c]	11.1	41
		N-4[d]	12.1	38
		T-4	9.4	45
Nitrobenzene	10	N-4	14.1	62
		T-4	11.1	90
Benzonitrile	5	N-4[e]	4.4	130
		T-4	4.4	130

a) The catalyst was prepared from 0.5 g of Raney alloy (40% Ni) each time before use. The compound was hydrogenated in 10 ml of methanol at 25 °C and atmospheric pressure. b) Average rate from 0 to 50% hydrogenation. c) The catalyst was prepared with use of 0.03 ml of 20% sodium hydroxide. d) The catalyst was prepared with the bayerite recovered two times. e) The catalyst was prepared with use of 0.5 ml of 20% sodium hydroxide.

favorable for the activity and both N-4 and T-4 catalysts showed the same activity.

The bayerite becomes grey in its color during the preparation. By treatment of the bayerite with a dilute hydrochloric acid, the bayerite turns almost white and becomes reusable for the N-4 preparation to give the catalyst of the same activity (see Table 1). Since the hydrochloric acid after the treatment was found to contain only a trace amount of nickel, the grey color of the bayerite after the preparation is presumed mostly due to the presence of fine particles of aluminium.

The procedure for the preparation of Raney nickel catalyst described here is advantageous not only for the use of only a small amount of sodium hydroxide but also for the easiness in controlling the highly exothermic reaction of aluminium oxidation which is often too violent to control in the reaction with a concentrated sodium hydroxide solution or in a sudden reaction with water after an induction period in the T-4 procedure. Further, it is also advantageous in that the degree of the development of the alloy can readily be controlled to a desired extent by the amount of sodium hydroxide employed and/or the reaction time. The present method is also recommended for obtaining a catalyst of reproducible activity.

Experimental

Preparation of the Bayerite Suitable to the Development of Raney Alloy. Twenty grams of aluminium grains are dissolved into a sodium hydroxide solution prepared from 44 g of sodium hydroxide and 100 ml of water. The solution is diluted to 200 ml and CO_2 gas is bubbled into the solution at 40 °C until small amounts of white precipitates are formed. The precipitates are filtered off and more CO_2 gas is bubbled into the filtrate. Then the solution is gradually cooled to room temperature under good stirring and left overnight with continued stirring. The precipitates thus formed (20—24 g) are collected, washed with warm water, and dried *in vacuo* over silica gel.[7]

Preparation of N-4 Raney Nickel and Recovery of Bayerite. In a 10 ml conical flask are placed 0.5 g of Raney alloy powder (40% Ni) and 1 g of the bayerite prepared by the procedure described above. To this 10 ml of distilled water is added and stirred well at 40 °C. Then 0.03 ml of 20% sodium hydroxide solution is added and the mixture stirred for 30 min at 40 °C in which a violent reaction almost subsides. Further 0.3 ml of 20% sodium hydroxide is added and the mixture stirred for 1 h at 40 °C. The upper layer is decanted with care not to let the catalyst flow away. The catalyst is washed three times with each 10 ml of distilled water and then three times with the same volume of methanol. The bayerite suspensions are combined and acidified with a dilute hydrochloric acid, and then warmed to 50—60 °C, when the grey color of the bayerite turns almost white. The bayerite is collected, washed well which water, and then dried *in vacuo* over silica gel. The bayerite thus recovered amounts to 1.4—1.6 g and can be reused repeatedly for the catalyst preparation. A specimen of the catalyst contained 0.192 g of nickel, 0.050 g of aluminium, and 0.036 g of acid insoluble materials.

Hydrogenation. All hydrogenations were performed in a small glass apparatus driven vibrationally at 25 °C and atmospheric pressure. After the catalyst had been shaken with hydrogen in methanol for 5 min, the compound to be hydrogenated was added with a syringe through a silicone rubber septum.

References

1) S. Nishimura, *Bull. Chem. Soc. Jpn.*, **32**, 61 (1959).

2) H. A. Dirksen and H. R. Linden, *Res. Bull. Inst. Gas Technol. Chicago*, **31**, 32 (1963).

3) S. Taira and A. Kuroda, Japan Patent 15059 (1968).

4) S. Taira and A. Kuroda, Japan Patent 9459 (1969).

5) G. Yamaguchi, K. Sakamoto, and K. Shirasuka, *Kogyo Kagaku Zasshi*, **61**, 307 (1968).

6) The degree of aluminium oxidation was determined from the amounts of evolved hydrogen (293 ml at STP) and adsorbed hydrogen (13.4 ml at STP, estimated from the hydrogenation of cyclohexanone in *t*-BuOH under an atmosphere of argon), on the basis that the alloy contained 39% of nickel.

7) The bayerite thus prepared usually contains a small amount of gibbsite as observed by an X-ray diffraction analysis. The bayerite recovered from the catalyst preparation has been found less contaminated with gibbsite.