BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1930—1933 (1967)

The Activity of a Catalyst from Nickel Chloride and Methylhydropolysiloxane in the Hydrogenation of Olefins*[1]

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(Received January 20, 1967)

The reaction of anhydrous nickel(II) chloride with methylhydropolysiloxane has been found to give an active catalyst for the hydrogenation of olefins. These two reagents react readily at 120—170°C, with the evolution of hydrogen, to form a black-colored substance which has been used as the catalyst. The catalytic activity has been found to depend on the amount of hydrogen evolved during the reaction and on the methylhydropolysiloxane : nickel chloride ratio. The most active catalyst has been obtained by using the reagents in the Si : Ni ratio of 25 : 1 and by intercepting the reaction as soon as the hydrogen evolution amounted to 1.0 mol per mole of nickel chloride. Cyclohexane has been successfully used as a solvent. However, the presence of diethyl ether or tetrahydrofuran has considerably deactivated the catalyst. The catalyst deactivated by ether has, though, been highly activated by adding a large excess of water.

In earlier papers[1-6] dealing with several new catalyst systems for the hydrogenation of olefins, it has been shown that these systems can be successfully prepared by the reaction of a salt of transition elements with a variety of reducing agents, such as lithium aluminum hydride,[1-3] the Grignard reagent,[4-6] and other organometallics.[6] In the course of investigating catalysts for hydrogenation, it was found that a catalyst prepared by the reaction of anhydrous nickel(II) chloride with methylhydropolysiloxane has an activity sufficient for the hydrogenation of olefins. In the present paper, several fundamental aspects of the catalytic activity of this catalyst system will be reported on.

Results

Hydrogenation of Styrene. *The Effect of the Amount of Hydrogen Evolved.* Anhydrous nickel chloride reacted readily with methylhydropolysiloxane at 120—170°C,*[2] with the evolution of gas, and gave a black-colored substance. The gas evolved during the reaction was found to be almost pure hydrogen. Although the black-colored substance coluld often be used as an active catalyst for the hydrogenation of styrene under mild conditions (at 0—60°C and at the atmospheric pressure of hydrogen), the reproducibility of the experiments was rather poor. It seems reasonable to consider, by analogy with our earlier work on the catalytic activity of transition metal hydrides, that the catalytic activity was sensitive both to the amount of hydrogen evolved during the preparation of the catalyst and to the methylhydropolysiloxane: nickel chloride ratio. The lack of reproducibility appeared to be due to a difference in the amounts of hydrogen evolved; these amounts were not strictly controlled in the experiments mentioned above. Therefore, first, experiments were undertaken to see the effect of the amount of hydrogen evolved on the catalytic activity, using definite amounts of nickel chloride (1.5 g) and methylhydropolysiloxane (10 ml).

The hydrogen evolved during the preparation amounted to about 1.4 mol per mole of nickel chloride if the heating was continued until the evolution of hydrogen ceased. Although the evolution of hydrogen was rather vigorous, it could be intercepted by cooling the flask quickly in the middle of the evolution. Thus, several catalysts of the different amounts of hydrogen evolved were prepared and used for the hydrogenation of styrene. The hydrogen absorption curves are shown in Fig. 1, where the numerals in parentheses represent the amounts of hydrogen evolved during the preparation of the catalysts. The catalytic activity was quite low when the amount of hydrogen evolved was smaller than 0.5. The activity was

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*[1] Part of this work was reported at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

*[2] The temperature ranged from 120 to 170°C in different lots of anhydrous nickel chloride. The use of coarse anhydrous nickel chloride did not, in most cases, start the reaction.

1) Y. Takegami and T. Ueno, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 246 (1964).

2) Y. Takegami, T. Ueno and T. Fujii, *ibid.*, **67**, 1009 (1964).

3) Y. Takegami, T. Ueno and T. Fujii, This Bulletin, **39**, 1279 (1965).

4) Y. Takegami, T. Ueno and K. Kawajiri, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1068 (1963).

5) Y. Takegami, T. Ueno, K. Shinoki and T. Sakata, *ibid.*, **67**, 316 (1964).

6) Y. Takegami, T. Ueno and T. Fujii, *Catalyst (Shokubai)*, **8**, 54 (1966).

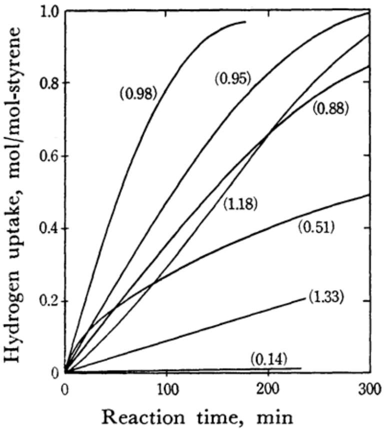

Fig. 1. Hydrogenation of styrene.

Numerals in parentheses represent the amounts of hydrogen evolved during the preparation of the catalyst.

found to rise steadily as the amount of hydrogen evolved rose from 0.5 to 1.0, but, thereafter, it decreased with any further increase. Thus, the activity of the catalyst is closely dependent on the amount of hydrogen evolved, and the heating in the preparation should be intercepted quickly when the amount of hydrogen evolved reaches 1.0 mol per mole of nickel chloride in order to obtain an active catalyst.

Effect of the Methylhydropolysiloxane : Nickel Chloride Ratio. With the amount of hydrogen evolved during the preparation of the catalyst being kept at 1.0 mol per mole of nickel chloride, the effect of the amount of methylhydropolysiloxane used in the preparation on the catalytic activity was also examined with regard to the hydrogenation of styrene. The results are shown in Fig. 2, where the rates of hydrogenation, represented by amounts of hydrogen uptake (mole per mole of styrene) in a reaction period of 50 min, are plotted against the amounts of methylhydropolysiloxane used. As may be seen in Fig. 2, the optimum amount of methylhydropolysiloxane was about 18 m*l* (for 1.5 g of nickel chloride), the Si : Ni ratio being 25 : 1. The catalytic activity gradually decreased when the Si : Ni ratio deviated from this optimum value.

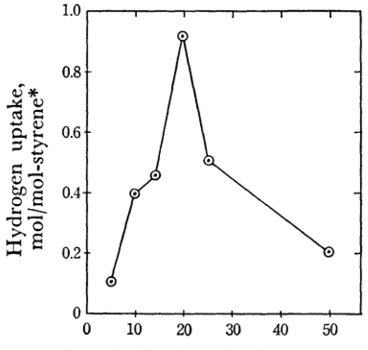

Fig. 2. Activity *vs.* amount of methylhydropolysiloxane used.

* Represented by the amount of hydrogen uptake (mole per mole of styrene) in the reaction period of 50 min.

Hydrogenation of Several Olefins. In order to ascertain the applicability of this catalyst, the catalyst was tested for several types of olefinic linkage. In most of the experiments, 1.5 g of nickel chloride and 10 m*l* of methylhydropolysiloxane (Si : Ni 20 : 1) were used, while the amounts of hydrogen evolved were kept at 1.0 mol per mole of nickel chloride. The hydrogenation was carried out at 0 and 60°C using 5 m*l* of olefin. The hydrogen absorption curves are shown in Fig. 3, where the dotted and solid lines refer to the experiments carried out at 0 and 60°C respectively.

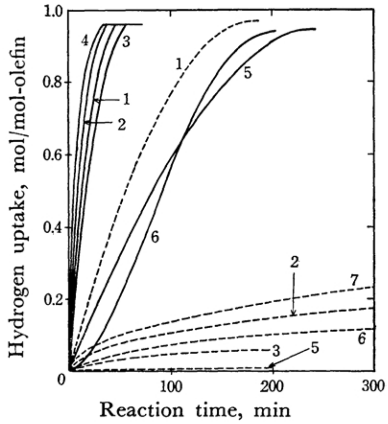

Fig 3. Hydrogenation of olefins.

----: at 0°C, ——: at 60°C
1: styrene, 2: α-methylstyrene, 3: safrole,
4: isosafrole, 5: indene, 6: cyclohexene,
7: isoprene

The hydrogenation was first carried out at 0°C for the convenience of comparison with our earlier works. Styrene was successfully hydrogenated at 0°C, as has been described above. The terminal olefins, such as α-methylstyrene and safrole, were expected to have approximately the same reactivity as styrene; this was in analogy with the results of the hydrogenation with the ferric chloride (or cobaltous chloride)-lithium aluminum hydride catalyst.3) However, α-methylstyrene and safrole, as well as such internal olefins as cyclohexene and indene, were hydrogenated with difficulty; only 5—15% of the olefins (except indene) were hydrogenated in a reaction period of 300 min, and in the case of indene the hydrogenation did not proceed at all. These results appear somewhat unlikely since the conjugated olefin (indene) may be expected to be hydrogenated faster than the nonconjugated one (cyclohexene).

On the other hand, changing the hydrogenation temperature from 0 to 60°C caused the catalytic behavior to differ entirely. Styrene, α-methylstyrene, and safrole were then hydrogenated with great ease; the rates were 3—5 times as large as the rates of styrene obtained at 0°C. The rates for cyclohexene and indene were also greatly increased. It is noteworthy that the tested olefins were all hydrogenated rapidly at 60°C, whereas only styrene was at 0°C; the specificity of the catalyst was thus greatly altered by merely changing the reaction temperature.

In connection with the olefin hydrogenation, the hydrogenation of diethyl ketone was also attempted, but no hydrogen uptake was observed. Furthermore, in the presence of the ketone, not even the hydrogenation of styrene was observed, indicating that the catalyst was poisoned by the ketone.

Although no solvent was used in the hydrogenation described above, the use of a solvent may often be useful in practical application. Therefore, several solvents were added after the preparation of the catalyst had been completed and the activity was examined on the hydrogenation of styrene at 0°C. A hydrocarbon such as cyclohexane was successfully used as a solvent. The presence of this solvent caused no change in the rate of hydrogenation. On the other hand, neither diethyl ether nor tetrahydrofuran could be used as a solvent; the presence of these solvents made the catalyst highly inactive. For example, when diethyl ether was added to the catalyst system in the middle of the rapid hydrogenation, the rate was immediately reduced to one-fifth that in the absence of the ether. The addition of tetrahydrofuran in the same manner resulted in a complete loss of activity.

Catalysts for hydrogenation obtained by the reaction of compounds of ruthenium, rhodium, palladium, iridium, and platinum (*e. g.*, chloroplatinic acid) with compounds having Si–H bonds (*e. g.*, triethoxysilane) have been reported in a recent patent.7) These catalysts were prepared by heating the two reactants in 95% ethanol and were used, after cooling to an ambient temperature, in the hydrogenation of compounds with various functional groups. Although the procedure is quite similar to that employed in this work, the method by which the present anhydrous nickel catalyst was formed seems essentially different from that described in the patent, since the present nickel catalyst was formed only in anhydrous conditions; also, rhodium chloride formed no active catalyst in the present procedure, as will be described below.

Activation of the Inactive Catalysts by the Addition of Water. The nickel catalyst prepared by the present method was rather unstable and lost its activity upon standing for several days. This deactivated catalyst and the catalyst inactivated by the addition of ether or tetrahydrofuran were highly activated by adding a large excess of water (10 m*l* of water to the catalyst prepared from 1.5 g of nickel chloride). The catalyst thus activated will be called the "water-added catalyst" below.

The hydrogenation of olefins were carried out at 0°C with the water-added catalyst.*3 The hydrogen absorption curves are shown in Fig. 4.

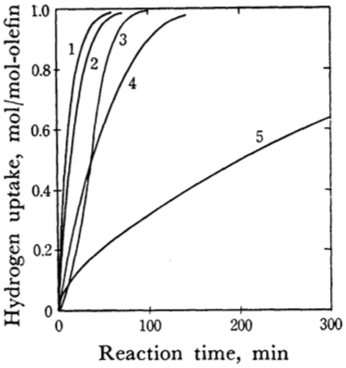

Fig. 4. Hydrogenation with the water-added catalyst.

1: safrole, 2: styrene, 3: indene,
4: α-methylstyrene, 5: cyclohexene

As may be seen in Fig. 4, styrene, α-methylstyrene, safrole, and indene were hydrogenated rapidly at 0°C. These results are incompatible, in part, with the results shown by the dotted lines in Fig. 3, in which only styrene was hydrogenated rapidly at 0°C. The activation by the addition of excess water was effective not only for the deactivated catalyst described above, but also for the relatively less active catalyst prepared by allowing hydrogen to evolve either in smaller than 0.5 or in larger than 1.2 mol per mole of nickel chloride.*4

We have previously reported the similar activation of the nickel catalyst prepared by the use of Grignard reagent or lithium aluminum hydride the addition of water.4,8) It has been postulated that the active species of the water-added catalyst

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7) Union Carbide Corp. (by D. L. Bailey and C. Eaborn), French Pat. 1376744 (1964).

*3 The catalysts used here were prepared by the addition of diethyl ether to the anhydrous catalyst, followed by the addition of water, since the direct addition of water to the anhydrous catalyst often resulted in the solidification of the system (to a black, stick solid).

*4 Regardless of the amount of hydrogen evolved during the preparation, provided that it was larger than 0.1, the catalysts activated by water all hydrogenated styrene at 0°C at almost the same rate as that shown in Fig. 4.

8) Y. Takegami, T. Ueno and T. Sakata, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **68**, 2373 (1965).

differ from those of the anhydrous catalyst. The difference between these catalysts is clearly shown by the fact that the water-added catalyst shows approximately the same activity for the hydrogenation of styrene, whether the ketone is present or not, while the anhydrous catalyst is poisoned by the ketone and is quite inactive in the hydrogenation of styrene in the presence of ketone.

Use of Other Transition Metal Salts. Since anhydrous nickel(II) chloride easily gave a highly active catalyst, other derivatives of nickel, such as nickel(II) chloride hexahydrate, nickel(II) acetate tetrahydrate, nickel(II) nitrate hexahydrate, and nickel(II) acetylacetonate, were tested in combination with methylhydropolysiloxane in the same manner as has been described for anhydrous nickel (II) chloride. These nickel derivatives, however, did not give an active catalyst, but gave unidentified sticky polymers (black in the cases of chloride and acetylacetonate, and white in the cases of acetate and nitrate). In analogy with anhydrous nickel(II) chloride, several anhydrous chlorides of other transition elements, such as cobalt(II), iron(III), manganese(II), chromium(III), rhodium(III), and tungsten(VI), were also used in the preparation of the catalyst. However, the only product of these reactions (except in the case of chromium(III)) was, again, an unidentified, colored polymer; no active catalyst was produced. In the case of chromium(III), no reaction was observed even when the reaction temperature was raised to as high as 270°C.

Use of Dimethylpolysiloxane. When dimethylpolysiloxane was used instead of methylhydropolysiloxane in combination with anhydrous nickel(II) chloride, no reaction was observed even when the reaction temperature was raised to as high as 230°C, indicating that the hydrogen atoms in the methylhydropolysiloxane might be responsible for the formation of the catalyst.

Experimental

Materials. Methylhydropolysiloxane (DC-1107) from the Dow Corning Corp. and dimethylpolysiloxane (KF-96) from the Shin-Etsu Chemical Industry Co. were used without further purification. Anhydrous nickel(II) chloride was obtained from the Maruwaka Chemical Industry Co. The other transition metal salts used were the purest among the commercially-available materials. Diethyl ether, tetrahydrofuran, and cyclohexane, which were used as solvents, were dried over sodium and were freshly distilled just before use. Olefins were distilled under reduced pressure and were used shortly after distillation.

Apparatus and Procedure. The apparatus for the preparation of catalysts and the hydrogenation of olefins consisted of a four-necked flask equipped with a stirrer, a dropping funnel, and a thermometer; it was jointed to a gas burrete by a silica gel tube. This apparatus was flushed with hydrogen. A mixture of anhydrous nickel(II) chloride (1.5 g) and methylhydropolysiloxane (10 m*l*) was placed in the flask and heated gradually. At about 170°C, the mixture turned black or brown-black, and there was an accompanying gas evolution. The mixture was cooled and then used as a catalyst for hydrogenation.

The hydrogenation was carried out by introducing 5 m*l* of an olefin in the catalyst described above. The speed of stirring was kept at 900 rpm during the hydrogenation. After the hydrogenation, the catalyst was destroyed by the addition of 20 m*l* of 15% aqueous hydrochloric acid; the hydrogenation product was extracted with diethyl ether, washed with water, and analyzed by gas chromatography.