BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1663—1667 (1969)

The Hydrogenation Catalysts Prepared from Transition Metal Chloride and Triethylaluminum[*1]

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(Received October 4, 1968)

Catalysts composed of anhydrous iron(III) chloride, cobalt(II) chloride, or nickel(II) chloride plus triethylaluminum have been used for the hydrogenation of olefin. The catalytic activity has changed with the $Al(C_2H_5)_3/MCl_n$ ratio. The optimum ratios for the hydrogenation of styrene have been found to be 1—7 for the iron catalyst, 0.2—1 for the cobalt catalyst, and 0.3—2 for the nickel catalyst. Cyclohexane has been used satisfactorily as a solvent. Tetrahydrofuran could be used for the nickel catalyst, but its presence was unfavorable for the iron and cobalt catalysts. The gas evolved in the reaction of the transition metal chlorides with triethylaluminum has been found to be essentially ethane, and sluggish gas absorption was observed when the atmosphere was switched to hydrogen. Ethylbenzene was formed in the treatment of the catalyst with styrene under nitrogen; the amount increased considerably if the catalyst was pre-treated with hydrogen. Ethane was formed in the hydrogen-treatment of the reaction mixture of nickel chloride and triethylaluminum. On the basis of these results, it has been assumed that metal hydride has been formed by the hydrogenolysis of metal - ethyl bonds.

Breslow and his co-workers[1] have reported Ziegler-type soluble catalysts composed of acetylacetonates or alkoxides of transition metals plus triethyl- or tri-isobutylaluminum. They hydrogenated various olefins at 30—50°C and at 3.7 atm. They postulated that the active sites for the hydrogenation are transition metal - hydrogen bonds. Lapporte and Schuett[2] have reported the hydrogenation of aromatic hydrocarbons with catalysts composed of nickel(II) 2-ethylhexanoate plus triethylaluminum at 150—210°C and at 1000 psi, and they assumed that finely-divided transition metal is responsible for the hydrogenation. Analogous catalyst systems have also been patented.[3,4]

As part of their investigation of the synthesis and the catalysis of transition metal hydrides prepared by the use of Grignard reagents[5-8] or lithium aluminum hydride,[9-12] the present authors have

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[*1] The Preparation of Heavy Metal Hydride and Its Catalystic Activity. XI. Part X: Ref. 11.

1) M. F. Sloan, A. S. Matlack and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963).

2) S. J. Lapporte and W. R. Schuett, *J. Org. Chem.*, **28**, 1947 (1963).

3) California Reserch Corp., French Pat. 1390570 (1965).

4) W. R. Kroll, U. S. Pat. 3323902 (1967).

5) Y. Takegami, T. Ueno and K. Kawajiri, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **64**, 1068 (1963).

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

7) Takegami, T. Ueno and K. Kawajiri, *Shokubai (Catalyst)*, **4**, 13 (1962).

8) Y. Takegami, T. Ueno and K. Kawajiri, This Bulletin, **39**, 1 (1966).

studied the activity of the catalysis prepared by the reaction of iron(III) chloride, cobalt(II) chloride, or nickel(II) chloride with triethylaluminum. In this paper, some novel aspects of the natures of these catalysts and of the mechanism of catalyst formation will be reported.

Experimental

Materials. Triethylaluminum was obtained from the Ethyl Co. Anhydrous iron(III) chloride was prepared by the dehydration of a hexa-hydrate (from Merck) with thionyl chloride.[13] The solvent, tetrahydrofuran and cyclohexane, were dried over sodium and distilled just before use. The other reagents used were the purest among the available commercial materials.

The Preparation of the Catalysts and the Hydrogenation. The apparatus consisted of a four-necked flask (100 m*l*) equipped with a stirrer, a dropping funnel, and a thermometer; it was jointed to a gas buret through a silica gel tube. To a solution of 40 m*l* of cyclohexane containing 0.003 — 0.005 mol of transition metal chloride, a desired amount of triethylaluminum solution in cyclohexane was added through the dropping funnel. The solution immediately turned black or brown-black, and there was an accompanying gas evolution. The mixture was then stirred for an additional hour until the gas evolution ceased.

The hydrogenation of olefin was carried out by introducing 2 m*l* of olefin into the catalyst solution prepared above. The speed of stirring was kept constant (900 rpm) during the hydrogenation. After the hydrogenation, the reaction mixture was poured into cold aqueous hydrochloric acid in order to destroy the catalyst. The hydrogenation product was extracted with ethyl ether, washed with water, concentrated by the evaporation of ether, and gas-chromatographed.

Determination of Ethane. Anhydrous nickel(II) chloride (0.005 mol) was placed in a 300 m*l* two-necked flask equipped with a magnetic stirrer, and the flask was flushed with nitrogen. The triethylaluminum solution was added slowly. When the gas evolution ceased, the reaction mixture was degassed completely by evacuating the flask until a half of the solvent had been distilled. Then, the atmosphere was switched to hydrogen. Gas samples (2—5 m*l*) were removed periodically by the use of a syringe and subjected to gas chromatography. The amount of ethane was determined by the use of the absolute calibration curve prepared for a hydrogen - ethane mixture.

Results and Discussion

The Reaction of Transition Metal Chlorides with Triethylaluminum. The reaction of anhydrous transition metal chlorides with triethylaluminum was carried out under a nitrogen atmosphere and at 0°C. A black-colored substance (suspended in the solvent)was formed immediately, and there was an accompanying gas evolution. The amount and composition of the gas are represented in Table 1. A great portion of the evolved gas was ethane, but its amount was relatively small. When the atmosphere was switched from nitrogen to hydrogen after the reaction, a diminution in the gas volume was observed. However, the rate was quite sluggish; the gas-volume diminutions represented in the last columm of Table 1 are those observed during reaction periods of 5—15 hr.

Hydrogenation of Olefin. Using a black-colored suspension as a catalyst, the hydrogenation of styrene was carried out at 0 or 35°C. For most of the experiments, about 0.003 mol of transition metal chlorides and 3 m*l* of styrene were used. Cyclohexane was used as the solvent. Figures 1—3 show the hydrogen absorption curves for the hydrogenation with iron, cobalt, and nickel catalysts respectively. The numerals attached to

TABLE 1. PREPARATION OF THE MCl_n-$Al(C_2H_5)_3$ CATALYSTS[a]

Run	MCl_n	Solvent	$AlEt_3/MCl_n$	Amt. of gas evolved[b]	Ethane %	Gas vol. dimin. on H_2-treatment[c]
1	$NiCl_2$	C_6H_{12}-THF	1.08	0	—	0
2[d]	$NiCl_2$	C_6H_{12}-THF	2.08	0.02	100	0.14
3	$NiCl_2$	C_6H_{12}-THF	2.00	0.34	97.3	0.03
4	$NiCl_2$	C_6H_{12}	2.06	0.34	96.3	0.43
5	$FeCl_3$	C_6H_{12}	2.13	0.29	94.5	—
6	$FeCl_3$	C_6H_{12}	2.11	0.22	93.4	0.35
7	$CoCl_2$	C_6H_{12}	2.08	0.52	98.3	0.31

a) MCl_n: 0.005 mol; reaction temp.: 35°C. b) Represented by mol/mol MCl_n.
c) Gas volume diminution observed during the hydrogen-treatment of the catalyst component (mol/mol MCl_n).
d) Reaction temp., 0°C.

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

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

11) Y. Takegami, T. Ueno and T. Fujii, *ibid.*, **69**, 1467 (1966).

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

13) "Inorganic Synthesis," Vol. V, p. 153 (1957)

each curve represent the $Al(C_2H_5)/MCl_n$ ratios (abbreviated as "molar ratio" below further description). As may be seen in Figs. 1—3, the catalytic activity of these catalysts is dependent on the molar ratio; the optimum molar ratios for iron, cobalt, and nickel catalysts are 1—7, 0.2—1, and 0.3—2 respectively.

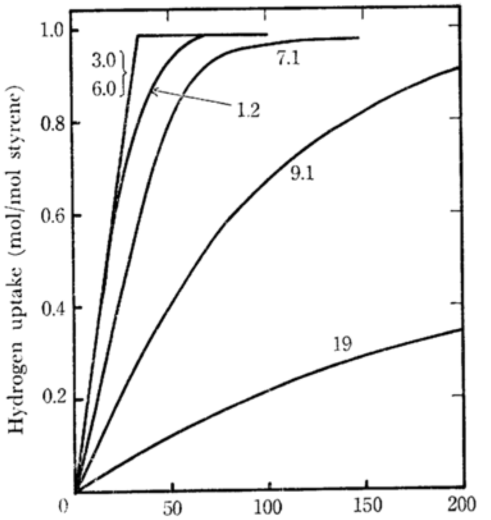

Fig. 1. Hydrogenation of styrene with the $FeCl_3$-$AlEt_3$ catalyst.
At 35°C and in cyclohexane solvent.
Numerals attached to the curves represent the $AlEt_3/FeCl_3$ ratios.

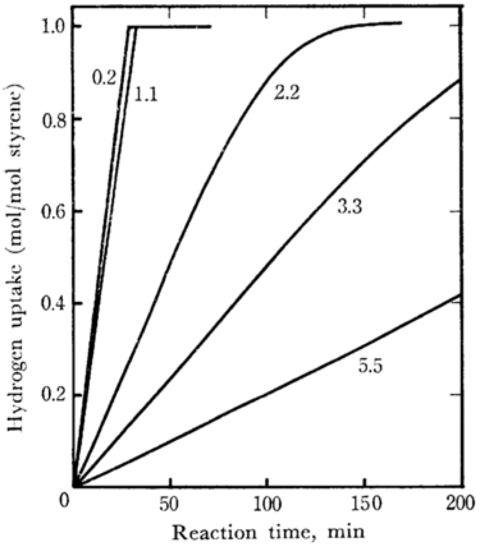

Fig. 2. Hydrogenation of styrene with the $CoCl_2$-$AlEt_3$ catalyst.
At 35°C and in cyclohexane solvent.
Numerals attached to the curves represent the $AlEt_3/CoCl_2$ ratios.

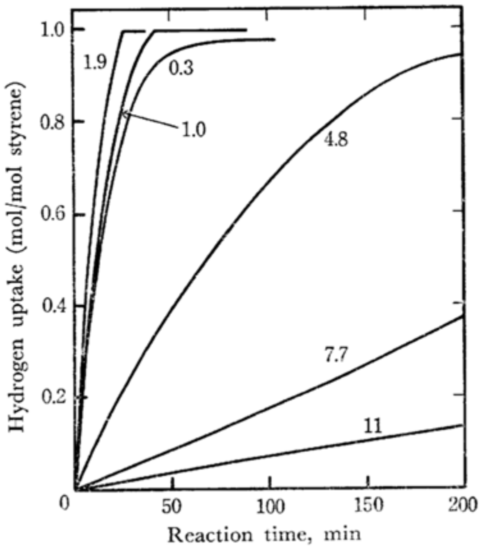

Fig. 3. Hydrogenation of styrene with the $NiCl_2$-$AlEt_3$ catalyst.
At 35°C and in cyclohehexane solvent.
Numerals attached to the curves represent the $AlEt_3/NiCl_2$ ratios.

Several other olefins were tentatively hydrogenated using the iron catalyst (the molar ratio was 3); the ease of hydrogenation was found to vary in the order; styrene>indene>cyclohexene>safrole>*d*-limonene>isosafrole. Actually, the rate of the hydrogenation of isosafrole was nearly zero. Acetophenone and ethyl vinyl ether could not be hydrogenated with this catalyst; furthermore, in the presence of the ketone or ether, the hydrogenation of styrene was considerably depressed.

In the runs shown in Figs. 1—3, cyclohexane was used as the solvent. When a cyclohexane-tetrahydrofuran (1 : 3—10) mixture was used as the solvent, the catalysts was quite different in nature from those observed in the cyclohexane solvent. In the cases of the iron and cobalt catalysts, no active catalyst for the hydrogenation of styrene could be obtained at any molar ratio of 1—12. Furthermore, when a small amount of tetrahydrofuran was added the halfway through the rapid hydrogenation carried out in the cyaclohexane solvent, the rate of hydrogenation was considerably lowered, showing the presence of tetrahydrofuran to be unfavorable for the iron and cobalt catalysts. In the case of the nickel catalyst, on the other hand, an active catalyst was prepared in the cyclohexane-tetrahydrofuran solvent. As may be seen in Fig. 4, the optimum molar ratio for the hydrogenation of styrene was 1—12; this was a very much wider range than the optimum ratio of 0.3—2 observed in the cyclohexane solvent (Fig. 3).

Centrifugation of the Catalyst. Breslow and his co-workers[1)] have pointed out that the use of halogen derivatives of transition metals leads,

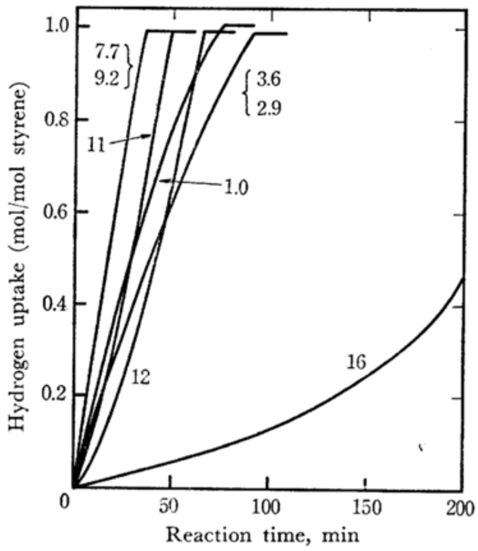

Fig. 4. Hydrogenation of styrene with the $NiCl_2$-$AlEt_3$ catalyst.
As 0°C and in cyclohexane/tetrahydrofuran solvent.
Numerals attached to the curves represent the $AlEt_3/NiCl_2$ ratios.

in general, to insoluble catalyst systems. In our experiments, the black-colored substance suspended well in a solvent and the black-colored substance did not separate from the solvent even when the mixture stood for several days. When the catalyst system was centrifuged (2800 rpm), a black-colored precipitate was isolated, while the solvent was still black-colored. The precipitate and the solution were assumed to constitute the soluble and insoluble parts of the catalyst system respectively. The precipitate and the solution were then tested for the hydrogenation of styrene. The rates were taken as the reaction periods for 50% hydrogen uptake and are listed in Table 2. In general, both the solution and the precipitate were active in the hydrogenation, while there was a trend for the activity of the former or the latter to be predominant in the case of the nickel or the cobalt catalyst respectively. In the case of the nickel catalyst prepared in the cyclohexane - tetrahydrofuran solvent, only the solution was active, as may be seen in run 7. Since, in these experiments, the amount of the precipitate decreased with an increase in the molar ratio, and since only a small amount of the precipitate was isolated in runs 2, 4, and 6, the rate of the hydrogenation catalyzed by precipitates may depend on both the catalytic activity and the amount of the precipitate. However, the rate of the hydrogenation seems to be affected by the catalytic activity, rather than the amount, of the precipitate, since it was found in a preliminary experiment that the rate of the hydrogenation was very slightly affected by changing the amount of catalyst (1—0.1 times), and since a rapid hydrogenation occurred with a very small amount of the precipitate in runs 2 and 4.

Table 2. ACTIVITIES OF THE SOLUTION AND THE PRECIPITATE[a]

Run	Catalyst	Molar ratio[b]	Solution[c]	Precipitate[c]
1	Fe	1.00	29	51
2	Fe	3.60	51	10
3	Co	1.01	63	15
4	Co	3.58	(585)	34
5	Ni	1.02	18	24
6	Ni	5.99	240	(3900)
7	Ni[d]	4.63	124	e)

a) For the hydrogenation of styrene. MCl_n: 0.003 mol; Reaction temp.: 35°C
b) $Al(C_2H_5)_3/MCl_n$
c) Activities are represented by reaction periods (min) for 50% hydrogen uptake.
d) In cyclohexane-tetrahydrofuran solvent.
e) Only 1% of hydrogen was absorbed during the reaction period of 300 min.

Styrene-treatment of the Nickel Catalyst. In the previous publications,[8,10] it has been reported that, when the catalyst prepared by the use of a Grignard reagent or lithium aluminum hydride was treated with styrene under a nitrogen atmosphere, ethyl benzene was formed by the hydrogen migration from the catalyst to styrene. We applied this styrene-treatment to the nickel catalysts prepared in the cyclohexane - tetrahydrofuran solvent at the molar ratio of 6.0. 1) One of the catalysts was treated with styrene under nitrogen (at 35°C, for 8 hr) immediately after the preparation of the catalyst; 0.08 mol of ethylbenzene was formed per mol of nickel chloride. 2) The other catalyst was stirred under hydrogen for 20 min[*2] after the preparation of the catalyst. Thereafter, the atmosphere was switched to nitrogen and the catalyst was treated with styrene; 0.35 mol of ethylbenzene was thus formed per mole of nickel chloride.

Formation of the Catalyst. It is felt that the strict dependence of the catalytic activity on the molar ratio is strong evidence that metallic component does not furnish an active sites. If the catalysts are finely-divided metal, as Lapporte reported,[2] the fact that a higher molar ratio lowers the catalytic activity can not be explained. In fact, however, Lapporte operated under conditions which were not as mild as ours. The agreement in the molar ratio dependence between the present catalysts and the transition metal hydride catalysts prepared by the use of a Grignard reagent or lithium aluminum hydride suggests that the active sites of the present catalysts are, at least in part, transition-metal-hydride in character.

[*2] No gas absorption was observed during the treatment.

Three processes for the transition metal hydride formation are possible: (a) the elimination of ethylene from the transition metal-ethyl bonds; (b) the absorption of hydrogen on the transition metal, and (c) the hydrogenolysis of the transition metal-ethyl bonds. However, the elimination of ethylene to give transition metal hydride is improbable, since the greater part of the gas evolved during the preparation of the catalyst was ethane, as may be seen in Table 1. Ethylene might not be observed if it polymerized immediately, but the catalyst was found to be inactive in the polymerization of ethylene under the conditions employed. When the reaction of transition metal chloride with triethylaluminum was carried out under nitrogen and the atmosphere was switched to hydrogen, a sluggish gas absorption was observed if cyclohexane was used as the solvent, while no gas absorption occurred if a cyclohexane-tetrahydrofuran mixture was used as the solvent. The gas absorption might result from the reaction of the transition metal with hydrogen to form transition-metal-hydride sites, but in view of the sluggishness of the gas absorption, it appears improbable that the hydride sites thus formed can be intermeditaes in the relatively rapid hydrogenation of olefin which we observed.

The hydrogenolysis of metal-ethyl bonds to give transition-metal hydride and ethane seems to offer the most probable explanation for the formation of transition-metal-hydride sites without any apparent gas absorption, and for the fact that the amount of ethylbenzene formed in the styrene-treatment of the nickel catalyst increased considerably if the catalyst was pre-treated with hydrogen.

$$\text{M-Cl} \xrightarrow{\text{Al}(\text{C}_2\text{H}_5)_3} \text{M-C}_2\text{H}_5 \xrightarrow{\text{H}_2} \text{M-H} + \text{C}_2\text{H}_6 \uparrow$$

In order to establish the hydrogenolysis process, the ethane which was formed in the hydrogen-treatment of the catalyst component was determined. As may be seen in Fig. 5, ethane was formed rapidly.

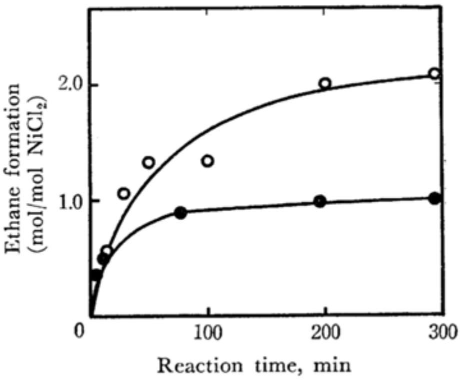

Fig. 5. Ethane formation in the hydrogen-treatment of the $NiCl_2$-$AlEt_3$.
○: molar ratio=2.2, at 35°C, in cyclohexane solvent.
●: molar ratio=2.2, at 35°C, in cyclohexane-tetrahydrofuran solvent.

Although no gas absorption was observed during the hydrogen-treatment of the nickel catalyst in the cyclohexane-tetrahydrofuran solvent (Expt. 1 in Table 1), about 2 mol of ethane was formed per mole of nickel chloride, confirming the hydrogenolysis process described above.