〔Chem. Pharm. Bull.
13(6) 724~730 (1965)〕

UDC 547.551.04 : 542.941.7 : 543.544.25

97. **Haruhiko Yamamoto, Makoto O'hara, and Takao Kwan** : Application of the Gas Chromatographic Pulse Technique to the Study of the Selective Hydrogenation of Aniline on Acid or Base Supported Metals of Group VIII.

(*Division of Physicochemical Technology, Faculty of Pharmaceutical Sciences, University of Tokyo*[*1])

The hydrogenation of aniline to form cyclohexylamine is one of the important catalytic processes in the pharmaceutical industry. Literatures show that the reaction is accompanied mostly by a few side reactions. The liquid phase hydrogenation by metals produces secondary amines while in the vapor phase the hydrogenolysis of aniline or the fission of the carbon-nitrogen bond takes place. Since the gas chromatographic pulse technique, studied previously,[1] proved to give an useful information, though in a qualitative way, concerning the selectivity of the catalytic hydrogenation and dehydrogenation of cyclohexene, the application of the technique was made further to the study of the selective hydrogenation of aniline on three kinds of transition metals of group Ⅷ, namely reduced nickel, cobalt, and iron, respectively.

The study was performed with particular interest in the acid or the base support. It was considered that the interaction of aniline or of any intermediate or product having amino or imino group with the surface is influenced by the acid or by the base present on the catalyst surface and hence reflected in the selectivity under investigations. A sample of cyclohexene containing about 10% amine was injected to investigate the influence of this kind; the hydrogenation and dehydrogenation activity of cyclohexene was investigated in the presence of amine to see the degree of interaction of amine molecule with the surface.

Our study has led to the following reults : 1) The selectivity for the ring hydrogenation of aniline is best on cobalt among three transition metals. 2) The base supported metal catalysts increase the selectivity for the ring hydrogenation. 3) The acid supported catalysts enhance the formation of secondary amines. Such selectivity data will briefly be discussed.

Experimental

Apparatus and Procedures——The apparatus used for this study was the same with that reported previously.[1] It was confirmed preliminarily that a stainless steel reactor tube is inert toward any reaction of aniline or of cyclohexylamine below 350°. Nickel, cobalt and iron samples in the form of carbonate weighing about 0.4~0.9 g. were put respectively in the reactor tube (3.5~6.0 cm. long) and reduced *in situ* in a stream of hydrogen. Calcined calcium hydroxide and silica-alumina were employed as the base or the acid support respectively. One part of the support was diluted with nine parts of the metal carbonate and well mixed mechanically in an agate mortar. The reduction was carried out at 350° for 6 hr. with respect to nickel and cobalt and at 400° for about 60 hr. with iron. After the reduction, the separation column packed with Apieson grease of 1.5 m. long and PEG 6000 coated celite 1.5 m. was connected to the catalyst tube.

A sample of 10 μl. aniline was usually injected into the flowing hydrogen by means of a microsyringe. The inlet pressure of hydrogen was around 1.5 atm. Preliminary experiment indicated that the distribution of the reaction products on a given catalyst does not change appreciably with varying the flow rate of hydrogen. Therefore, the rate of hydrogen flow was maintained at 100 ml./min. throughout the experi-

---

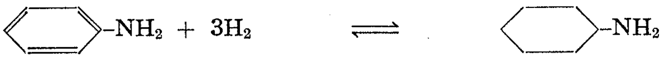
[*1] Hongo, Tokyo (山本晴彦, 小原 誠, 管 孝男).
[1] H. Yamamoto, M. O'hara, T. Kwan : This Bulletin, **12**, 959 (1964).

ment. It corresponded to contact time of 0.3∼0.6 sec. The separation column was always kept at 180°. Consequently, the experimental variables were the temperature of the reaction, the kind of the catalyst and the composition of the sample injected.

Materials——Commercial hydrogen was used as the carrier without special purification. Aniline was the extra pure grade supplied by Osaka Organic Chem. Co. It was purified by the usual distillation. Cyclohexylamine, dicyclohexylamine, cyclohexane, cyclohexene and benzene were respectively of the extra pure grade obtained from Tokyo Kasei Co. The gas chromatographic analysis indicated that the reagents were more than 99% pure except cyclohexane. These samples were used without further purification.

Results

The thermodynamical data for the hydrogenation of aniline to give cyclohexylamine



is only less known as compared with those of the benzene-cyclohexane system. However, judging from the data of Table I, the hydrogenation-dehydrogenation equilibrium of the reaction may be considered not too much different from the benzene-cyclohexane system.

Table I. The Standard Heats of Formation of Benzene, Aniline and their Hydrogenated Products (kcal./mole)

Compound	$-\Delta H_f^\circ$	Compound	$-\Delta H_f^\circ$
Benzene	−19.8[a]	Aniline	−19.7[c]
Cyclohexene	1.7[a]	3-Cyclohexenylamine	−4.1[b]
		1-Cyclohexenylamine	4[d]
Cyclohexane	29.4[a]	Cyclohexylamine	24.3[b]

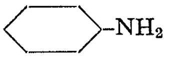
a) G.I. Janz: J. Chem. Phys., **22**, 751 (1954).
b) Calculated by Allen's bond energy scheme on the basis of the data: H.A. Skinner: J. Chem. Soc., **1962**, 4396.
c) Landolt-Börnstein: Physikalisch-chemische Tabellen.
d) Calculated by the aussmed interaction energy (8 kcal./mole) between amino group and double bond.

In the latter case, the average partial pressure of hydrocarbons in the reactor was estimated to be about 0.5 atm. when 5 μl. of the sample was injectd into the 1.5 atm. flowing hydrogen. In the present case, the sample size was twice as much. However, the partial pressure of amine in the reactor would not be so large since the adsorption of amine may be expected to be much stronger.

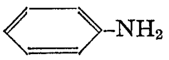
The hydrogenation of aniline was observed first of all over nickel and cobalt respectively in the temperature range 170∼300°. The distribution of the products recorded on the chromatogram may be represented by

A. NH_3, 6-membered hydrocarbons

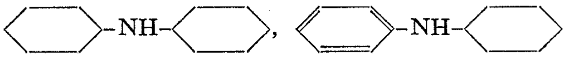
B.



C.



D.



Let us denote A, B, C, and D to be the area under the peak of the corresponding compound respectively. The selectivity for the ring hydrogenation of aniline is defined here by

$$\frac{B}{A+B+D}$$

and those for the hydrogenolysis and the formation of secondary amines by

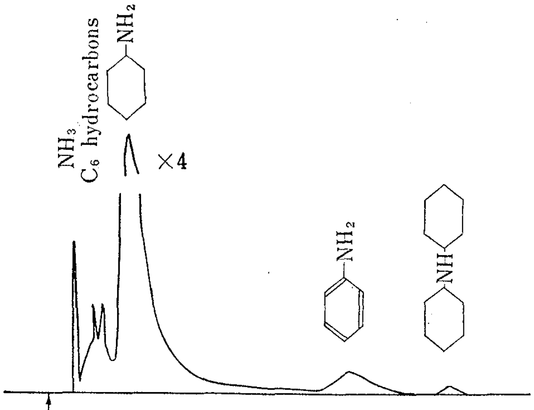
$$\frac{A}{A+B+D} \text{ and } \frac{D}{A+B+D}.$$

On the other hand, the catalytic activity for the hydrogenation will be meant by

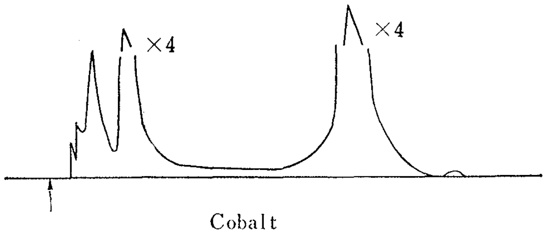
$$\frac{B}{A+B+C+D}.$$

It was noted that iron possesses almost no catalytic activity for the ring hydrogenation below 300° while nickel and cobalt show appreciable activities under the experimental condition used. The hydrogenolysis of aniline took place on iron above 300°, ammonia and benzene being the main products. The selectivity for the ring hydrogenation on three transition metals may be of the order : $Co > Ni \gg Fe$ in the temperature range 175~250°.

The base supported metal catalysts, generally speaking, gave rise to better selectivity for the ring hydrogenation than unsupported catalysts keeping the order of the selectivity unchanged. Typical chromatogram obtained on the calcium oxide supported cobalt is compared with that of the unsupported in Fig. 1. The temperature dependency of the selectivity is also illustrated in Fig. 2 with the supported and unsupported cobalt.



Cobalt-calcium oxide



Cobalt

Fig. 1. The Chromatogram for the Hydrogenation of Aniline on the Reduced Cobalt and the Calcium Oxide Supported Cobalt

Reaction temperature : 212°
Flow rate of hydrogen : 100 ml./min.
Sample size : 10 μl.
Column packing : Apieson grease 1.5 m.+PEG 6000 1.5 m. kept at 180°.

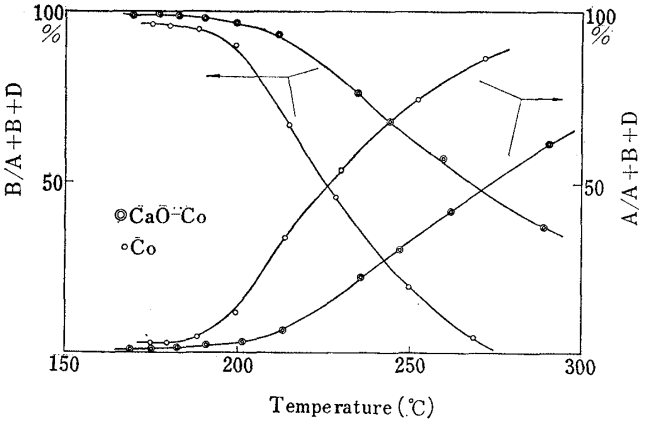


Fig. 2. The Selectivity for the Ring Hydrogenation of Aniline and for the Hydrogenolysis on the Reduced Cobalt and the Calcium Oxide Supported Cobalt

The excellence of the Co-CaO catalyst for the ring hydrogenation of aniline is in accordance with the observations reported earlier.[2~5)] The use of the other alkali

---

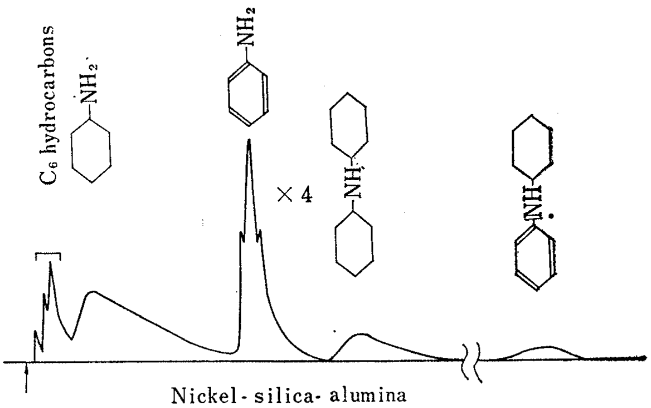
2) C. F. Winans : Ind. Eng. Chem., **32**, 1215 (1940).
3) A. I. Naumov, Z. G. Lateva, M. M. Schumilina : U. S. S. R. Pat., 114,260, 1958.
4) H. Hagiwara, E. Echigoya : Shokubai, **6**, 345 (1964).
5) California Research Corporation : Ger. pat., 1,089,389, 1959.

earth such as barium oxide and magnesia showed similar increases in the selectivity for the ring hydrogenation. The addition of caustic potash gave a good selectivity but the catalyst activity decreased to a greater extent.

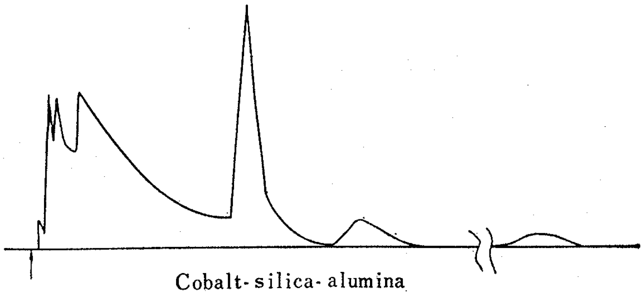
The effect of the acid support on the selectivity was also investigated by using silica-alumina. It was found that the acid supported catalyst of this sort particularly develops the tailing of the peak on the chromatogram. The chromatograms obtained on nickel-silica-alumina and on cobalt-silica-alumina are shown respectively in Fig. 3.

It is apparent that the formation of secondary amines is remarkable on both catalysts. The contrast of the product distribution between the base supported catalyst and the acid supported one should be noteworthy.

The injection of a mixed sample is one of the merits of the present technique; it enables us to follow the reactivity of one component in the presence of the other. A mixed sample of aniline and cyclohexylamine was thus investigated on nickel-silica-alumina. It was found that the formation of dicyclohexylamine (DCA) increases in proportion with the concentration of cyclohexylamine (CA) in the sample.



Nickel-silica-alumina



Cobalt-silica-alumina

Fig. 3. The Chromatogram for the Hydrogenation of Aniline on the Silica-Alumina Supported Nickel and the Silica-Alumina Supported Cobalt

Reaction temperature : 215°(Co), 220°(Ni)

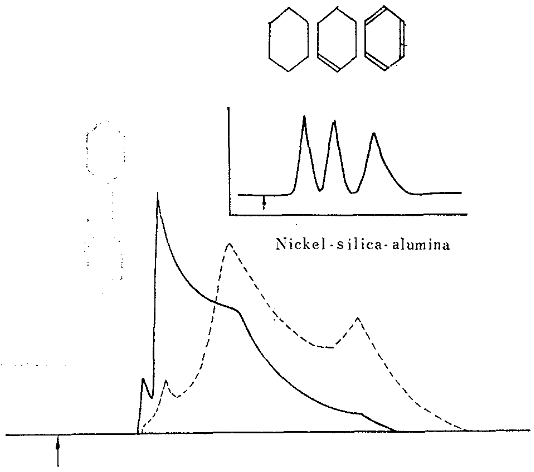
$$\frac{d(\mathrm{DCA})}{dt} \propto (\mathrm{CA})$$

Only dicyclohexylamine was found upon injecting cyclohexylamine while dicyclohexylamine and N-cyclohexylaniline (CHA) appeared upon injecting aniline (A). The yield of N-cyclohexylaniline was proportional to the amount of aniline present in the mixed sample.

$$\frac{d(\mathrm{CHA})}{dt} \propto (\mathrm{A})$$

The presence of benzene, cyclohexene or cyclohexane in the sample showed no effect on the formation of secondary amines, suggesting that dicyclohexylamine and N-cyclohexylaniline were not produced *via* the combination of amine and hydrocarbon. They would probably be formed by the deaminocondensation of amine molecules on the surface.

A sample of cyclohexene containing 10% cyclohexylamine was taken under investigation to see the effect of the latter on the hydrogenating and dehydrogenating activity of cyclohexene on both supported and unsupported catalysts. Cyclohexylamine was found to retard the hydrogenation and dehydrogenation of cyclohexene. The retardation was the greatest on cobalt with the slowest recovery. The phenomena might be correlated with the good selectivity of cobalt mentioned above. Less retardation and quicker recovery resulted however on supported catalysts.



Nickel-Silica-Alumina

Fig. 4. The Chromatogram for the Hydrogenolysis Products for Cyclohexylamine (Solid Curve) and for Aniline (Dotted Curve) on Nickel-Silica-Alumina

Reaction Temperature: 200°
Column temperature: 100°
The annexed figure shows the chromatogram for the hydrogenation and dehydrogenation of cyclohexene.

According to Kemball and Moss,[6] the hydrogenolysis of cyclohexylamine on platinum film gives benzene rather than cyclohexane at the initial stage of the reaction. Such reactions may be studied conveniently by the pulse technique. In Fig. 4 is illustrated the chromatogram of the hydrogenolysis obtained on nickel-silica-alumina. The reaction temperature was 200° and the column temperature was kept in this case at 100° so as to obtain a good separation of 6-membered hydrocarbons.

It is interesting to note that at least three kinds of hydrocarbons appear simultaneously on the chromatogram accompanied by ammonia coming out first. In order to identify the hydrocarbons, cyclohexene was injected, under the same experimental conditions, into the flowing hydrogen. The chromatogram gave cyclohexane, cyclohexene and benzene as shown by the annexed figure in Fig. 4. In view of the similar retention time, three molecular species appeared in the hydrogenolysis of cyclohexylamine may be assigned to cyclohexane, cyclohexene and benzene respectively, although the quantitative evaluation of these hydrocarbons is difficult due to the peak tailing.

The injection of aniline was also investigated and compared with that of cyclohexylamine. The appearance of the hydrogenolysis product was found to be more or less delayed, as shown by the dotted curve of Fig. 4 but the components seemed to be unchanged.

Discussion

The heat of adsorption of aliphatic amine was reported to be as large as 30～40 kcal/mole on reduced iron or even greater on oxidized iron,[7] suggesting that the amino group strongly interacts with the iron atom or ion on the surface. The electron donating nature of nitrogen of the amino group may be considered to play an important role for the formation of the strong nitrogen-iron bond. Little is known however on nickel or cobalt, although it is generally accepted that amine poisons the hydrogenation by metals.

The basicity of ammonia and organic amine is available in the handbook.[8] Accordingly, the order of the basicity is:

$$\text{Cyclohexylamine } (4.4\times10^{-4}) > \text{Ammonia } (1.8\times10^{-5}) > \text{Aniline } (3.8\times10^{-10})$$

Obviously the electron donating ability is the greatest with cyclohexylamine, being comparable with that of aliphatic in its magnitude. The basicity of the amino group can not be the only measure of the strength of the bond of amine with the surface.

---

6) C. Kemball, R. L. Moss: Trans. Faraday Soc., **32**, 154 (1960).
7) Y. Y. Yao: J. Phys. Chem., **67**, 2055 (1963).
8) N. A. Lange: "Handbook of Chemistry," Tenth Ed. McGraw-Hill Book Co., New York. Japan Chemical Society: Kagaku-binran, Maruzen, Tokyo, 1958.

However, in view of the marked difference in the basicity between aniline and cyclohexylamine, it may be quite possible that the progressive hydrogenation favors the formation of the strong bond of amine with the surface.

The work function of three transition metals under investigation is not much different with each other[9] (Fe : 4.48, Co : 4.41, Ni : 4.50 eV.). On the other hand, it is expected to decrease when alkali earth is present on the surface. Thus, the adsorption of amine may be weakened on such a surface. As already mentioned, cyclohexylamine poisoned the hydrogenation of cyclohexene on cobalt. However, the addition of calcium oxide gave rise to less retardation and quick recovery.

The weak adsorption of aniline will probably lead to the efficient hydrogenation of the ring as it was the case for the H_2-D_2 exchange reaction[10] or for the hydrogenation of ethylene on nickel.[11] On the other hand, the hydrogenolysis of amine at the carbon-nitrogen bond will require the formation of the strong bond or the formation of some dehydrogenated complex such as $C_6H_xNH_y$ on the surface. For instance

$$C_6H_{11}NH_2 \longrightarrow C_6H_xNH_y+(13-x-y)H$$

The stronger the adsorption is, x+y will be the smaller. Such evidence was put forward by Tamaru[12] for the decomposition of ammonia on iron and nickel. Reference should be made also to the work by Cimino, Boudart and Taylor[13] who noted, studying the hydrogenolysis of ethane on transition metals with or without added alkali, that the addition of caustic potash to iron causes the stripping of hydrogen from the hydrocarbon to suppress. The reaction was also studied by Yates, *et al.*[14] who found that the surface residue is less hydrogen deficient on cobalt than on nickel.

Let us think of the molecular species at the moment as the precursor of the hydrogenolysis in case of Fig. 4. The hydrogenolysis of aniline occurs to give benzene and ammonia and then benzene is consecutively hydrogenated to form cyclohexene and cyclohexane :

$$\text{I}\begin{cases} C_6H_5NH_2+H_2 \longrightarrow C_6H_6+NH_3 \\ C_6H_6 \longrightarrow C_6H_{10} \longrightarrow C_6H_{12} \end{cases}$$

or the hydrogenolysis of cyclohexylamine occurs, being then followed by the dehydrogenation of cyclohexane to yield cyclohexene and benzene :

$$\text{II}\begin{cases} C_6H_{11}NH_2+H_2 \longrightarrow C_5H_{12}+NH_3 \\ C_6H_{12} \longrightarrow C_6H_{10} \longrightarrow C_6H_6 \end{cases}$$

The experiment indicated that cyclohexane, cyclohexene and benzene appear simultaneously on nickel-silica-alumina. Also neither the hydrogenation of benzene nor the dehydrogenation of cylohexane was found to occur under the experimental conditions. Therefore, the mechanism I or II or both can not account for the experiments.

It is assumed now that the half-hydrogenated state is involved in the hydrogenolysis of aniline or of cyclohexylamine.

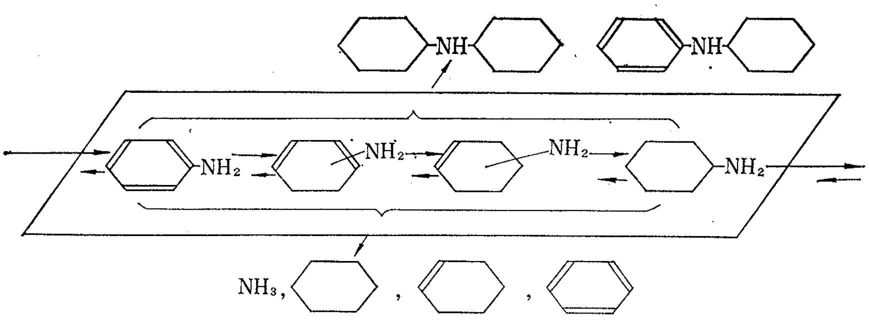
$$\text{III}\begin{cases} \begin{array}{l} C_6H_5NH_2 \searrow \\ \qquad\qquad\quad C_6H_xNH_y \longrightarrow C_6H_{x+1}+NH_3 \\ C_6H_{11}NH_2 \nearrow \end{array} \\ \begin{array}{l} \qquad\qquad \nearrow C_6H_6 \\ C_6H_{x+1} \\ \qquad\qquad \searrow C_6H_{12} \end{array} \end{cases}$$

---

9) G.C. Bond : "Catalysis by Metals," Academic Press, New York, 1962.
10) P. Gundry : "Second International Congress on Catalysis," Paris, 1960.
11) S.J. Thomson, J.L. Wishlade : Trans. Faraday Soc., 58, 1170 (1962).
12) K. Tamaru : Trans. Faraday Soc., **57**, 1410 (1961).
13) A. Cimino, M. Boudart, Hugh Taylor : J. Phys. Chem., **58**, 796 (1954).
14) J.H. Sinfelt, W.F. Taylor, D.J.C. Yates : J. Phys. Chem., **69**, 95 (1965).

Here, C_6H_{x+1} may be either cyclohexene or cyclohexadiene. It readily gives cyclohexane and benzene. Thus, the mechanism III seems to be compatible with the observation at least on nickel-silica-alumina.*2

Finally, mention will be made on the formation of secondary amines. According to Benson and one of the present authors,[15] nickel is completely removed by carbon monoxide from nickel-silica-alumina which is known to be dual-functioning.[16] Undoubtedly, the formation of secondary amines may be due to primarily the acidic nature of silica-alumina support. The over-all reaction of aniline with hydrogen may now be schematically represented by



In conclusion, the ring hydrogenation of aniline is accompanied by two side reactions: one is the formation of secondary amines which is accelerated by the acidic support and the other is the hydrogenolysis at the carbon-nitrogen bond which yields at least three kinds of hydrocarbon and is associated with the formation of half-hydrogenated complex at the surface. The basic support brings about the weak adsorption of amine and results in the good selectivity for the ring hydrogenation of aniline.

The authors wish to express appreciation to Dr. Ken'ichi Sawatari, Yoshitomi Pharmaceutical Ind. Co. for his continuing interest in this work. Thanks are also due to Mr. Takeshi Takagaki for his performance of the flow experiments and the supply of his data. The work was supported in part by a grant from the Ministry of Education.

Summary

The selectivity for the ring hydrogenation of aniline was investigated by the gas chromatographic pulse technique on the acid or base supported nickel, cobalt and iron catalyst respectively. Following results were obtained: 1) The selectivity for the ring hydrogenation was best on cobalt among three metals. 2) The calcium oxide supported catalyst generally suppressed the hydrogenolysis at the carbon-nitrogen bond giving rise to the efficient hydrogenation of the ring. 3) The silica-alumina support enhanced the formation of secondary amines. The selectivity was discussed on the basis of the interaction of amine with the surface and possible mechanism was presented.

(Received March 9, 1965)

---

*2 Benzene was the main product on nickal while it was accompanied by more or less hydrogenated product on cobalt. This may suggest that the precursor of the hydrogenolysis varies depending on the kind of catalyst.

15) J. Benson, T. Kwan: J. Phys. Chem., **60**, 1602 (1956).

16) F. G. Ciapetta, J. B. Hunter: Ind. Eng. Chem., **45**, 147 (1953).