Studies on the Disproportionation Reaction of Methylnaphthalene

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The disproportionation reaction of toluene and xylene over a silica-alumina catalyst has been studied by several investigators,[1-3] but that of methylnaphthalene (M. N.)[1] has been scarcely studied at all.

This work has been done in order to clarify the promoter action of chromium oxid on the silica-alumina catalyst[4] and also to obtain a kinetic equation for the disproportionation reaction of methylnaphthalene over the catalyst.

Experimental

The reaction was studied by means of the flow method under various pressures. As the reactor for this reaction, a quartz tube (I. D. 2.5 cm.) and a stainless steel tube (I. D. 2.9 cm.), both containing 30 cc. of the catalyst, were used under

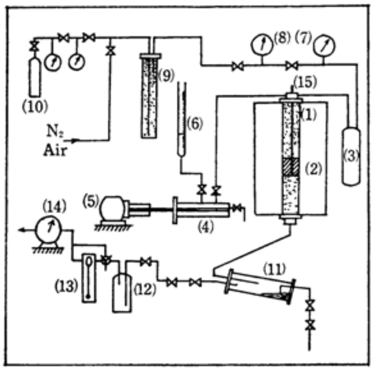

Fig. 1. Flow sheet of the disproportionation reaction of methylnaphthalene.

(1) stainless steel reactor
(2) electric furnace
(3) pressure storage
(4) liquid feed pump
(5) motor
(6) mess cylinder
(7) pressure gauge
(8) pressure gauge
(9) drier (silica gel)
(10) hydrogen cylinder
(11) gas-liquid pa-se rator
(12) dry ice - methanol trap
(13) orifice meter
(14) gas meter
(15) thermocouple

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1) R. C. Hansford, C. G. Myers and A. Sachanen, *Ind. Eng. Chem.*, **37**, 617 (1945).

2) P. M. Pitts, Jr., J. E. Connor, Jr., and L. N. Leum, ibid., **47**, 770 (1955).

3) K. Tarama, S. Teranishi, K. Hattori and M. Shimobayashi, on the 15th Annual Meeting of the Chemical Soceity of Japan.

4) T. Matsuda, T. Takahashi, T. Kakuzen and H. Chiyajima, *J. of the Fuel Soc. Japan*, **41**, 593 (1962).

atmospheric pressure and 3～6 atms. respectively. The flow sheet of this reaction under pressure is shown in Fig. 1. Methylnaphthalene was diluted with hydrogen which was free from oxygen and was introduced into the reactor.

The reaction products from the reactor were caught by methanol - dry ice cold traps and were analyzed by means of the gas chromatographic method.

Raw Material.—The methylnaphthalene employed in these experiments was provided by Mitsui Chemical Industries and was an equiliburium mixture of α and β isomers. (The sulfur content was about 1 wt.%).

Catalysts. — *Nalcat.* — The fine powders (over 100 mesh) of the commercial nalcat silica-alumina cracking catalyst (aluminum oxid content, 12～13 wt.%) were pelletized to a 4 mm. in diameter.

Chromium Oxide - added Nalcat. — Nalcat powders were immersed in a chromic sulfate solution (1 wt.%), and a small amount of dextrin (5 wt.%) was used as a binder in pelletizing.

Chromia - Alumina Gel Mixed Catalyst. — Aqueous gels of alumina and chromia, both prepared by precipitation from nitrate solutions (3 N) with aqueous ammonia, were kneaded well and dried in granules. The Chromium oxide content of this catalyst was 15 wt.%.

Results and Discussion

Reactions under Atmospheric Pressue. — The Effect of Reaction Temperature on the Disproportionation of Methylnaphthalene. — The reaction over the nalcat catalyst was carried out under the following conditions: SV, 600 hr^{-1}; mole ratio of hydrogen to methylnaphthalene, 4.5. The amounts of liquid products (%) recovered varied a little from experiment to experiment. Figure 2 shows that at lower temperatures, 450～520°C, the yield of naphthalene was quite small (about 7%), but that the selectivity of this reaction was excellent (about 100%) ; on the other hand, at higher temperatures, 550～570°C, the yield increased up to 15%, but the corresponding selectivity decreased to about 55% because of the increased demethylation reaction.

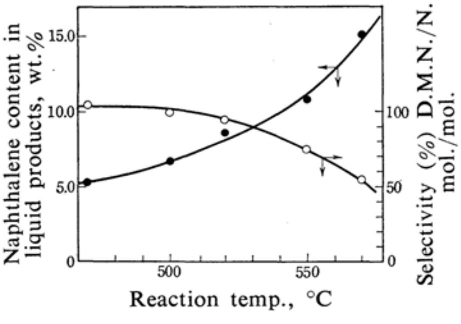

Fig. 2. Activity of SiO_2-Al_2O_3 catalyst for the disproportionation reaction of M. N.
S.V. = 600 (hr^{-1}), H_2/M.N. = 4.5 (mol. ratio)

The Effect of the Chromium Oxide added to the Silicon Oxide - Aluminum Oxide Catalysts on the Disproportionation Reaction. — When several kinds of silica-alumia catalysts were tested, the nalcat was found to give the best result and, therefore, the promoter effect of chromium oxide for this catalyst was examined with nalcat. Figure 3 shows that, as the amount of chromium oxide increased, the yield of naphthalene varied through a maximum, while the selectivity varied through a minimum, in the temperature range of 520～560°C.

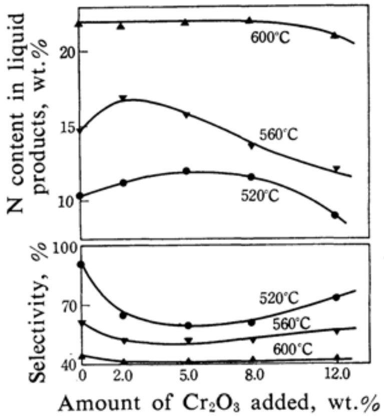

Fig. 3. Effect of addition of Cr_2O_3 on the activity of SiO_2-Al_2O_3 catalysts for the disproportionation reaction of M. N.

The activity of the chromia-alumina catalyst was quite low at 520°C under the same reaction conditions, and the yield of methylnaphthalene was only 4 wt.% even at 560°C. Naphthalene obtained over this catalyst was produced by demethylation, not by disproportionation reaction.

The Structure of Chromium Oxide - added Catalyst.—The nalcat catalyst showed diffuse X-ray patterns, indicating its amorphous structure, while the chromium oxide - added catalyst (5 wt.%) gave markedly sharp diffraction patterns of chromium oxide crystals.

The chromium oxide crystal content was estimated from this pattern to be 3.5 wt.%, amounting to 70% of the chromium oxide added.

The residual 30% of chromium oxide might be in an amorphous state, but its chemical state is not clear.

The mean magnitude of the crystallite of the chromium oxide - added catalyst was calculated by the Scherrer method to be $D_{110}=400$ Å. This crystal might be free from carriers, since this value was almost the same as those found

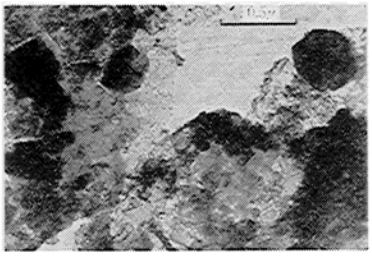

Fig. 4. Electron Micrograph (taken by Mr. A. Kitahara of T. I. T.)
Sample: Cr_2O_3 (5 wt%) on nalcat.

in literature for pure chromium oxide crystals.

Figure 4 shows the electro-micrograph of chromium oxide (5 wt.%)-added nalcat, which was examined by a one-step powder replica method, depositing carbon vapor. This picture shows that many fine crystals (30∼80 Å), besides a few large hexagonal single crystals (2000∼5000 Å), exist in very fine nalcat particles.

On the basis of the above results, it may be concluded that most of the added chromium oxide (about 70%) did not chemically combine with silica-alumina and did not widely disperse on the surface, but rather developed into large crystals. The residual chromium oxide (about 30% which was not observed as crystals in the electro-micrographic picture would be in a very finely-dispersed state and exert a promoter action on this reaction, thus explaining the results of Fig. 3 satisfactorily.

Experiments under Pressure. — The experiments under pressure were carried out to study the kinetics of the disproportionation reaction of methylnaphthalene over the chromium oxide (5 wt.%)-added silica-alumina catalyst.

The change in catalytic activity with reaction time was tested under the following conditions: reaction temperature, 470°C; reaction pressure, 17 atm.; mole ratio of H_2 to methylnaphthalene, 10, and contact time, 11 sec. The selectivity for this reaction was almost 100%, but the conversion decreased as the reaction proceeded.

It was further found that there was little difference between the activity of the nalcat with and without chromium oxide. The former, however, was used for this kinetic study under pressure, with carbon deposit being avoided as much as possible.

A Kinetic Analysis of this Catalytic Reaction Accompanied by Activity Degradation. — The rate of the reaction in the flow system may commonly be obtained from the relationship between the conversion and the time factor (W/F). The catalytic activity, however, decreased gradually as the reaction proceeded. Therefore, the degradation curves as shown in Fig. 5 were prepared; they indicate the change in catalytic activities with the reaction time at the constant value of W/F and at each reaction temperature. The initial activities of the catalyst at each W/F can be obtained by extrapolating each curve to the zero reaction time point.

The following reaction conditions were used: the catalyst, 30 cc. (19.2 g.); reaction temperature, 470∼430°C; mole ratio H_2 to M. N., 10.0; feed rate of M.N., 12 g./hr.∼40 g./hr. (W/F 60∼250 hr. g. cat./mol. M. N.), and reaction pressure range, 3.0∼15.0 atm. The reaction products were collected four times every two hours and were analyzed. The conversion of the disproportionation reaction was assumed to be twice that of the dimethylnaphthalene (D. M. N.) (mol.%) found. The side reaction of destruction, which may be connected with the carbon deposition, occured

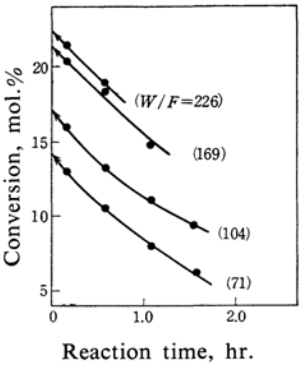

Fig. 5. Chart to read the initial activities of catalysts from the degradation curves.

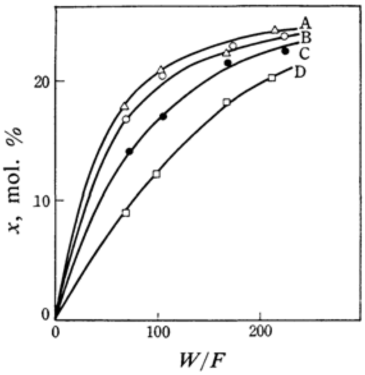

Fig. 6. Relationship between x and W/F under the definite pressures.
H_2/M.N. (mol. ratio), 10.0 Temp., 470°C
π; Total pressure (atm.)
A $\pi=16.0$ atm.
B $\pi=11.0$
C $\pi=6.0$
D $\pi=3.0$

to some extent. Figure 6 shows the experimental results, that is, the relationship between the conversion, x, and the time factor, W/F, under several different pressures.

Analysis of the Experimental Results Obtained. — According to the concept of the Langumuir-Hinshelwood mechanism, three rate-controlling steps: (1) adsorption, (2) surface reaction and (3) desorption, may be considered for this surface reaction.

The initial reaction rates r_0 obtained from Fig. 6 were plotted against the corresponding total pressures, π, as Fig. 7-I shows. The shape of the curve in this figure indicates that step 2, the surface reaction, may be the real rate-controlling step for this reaction.

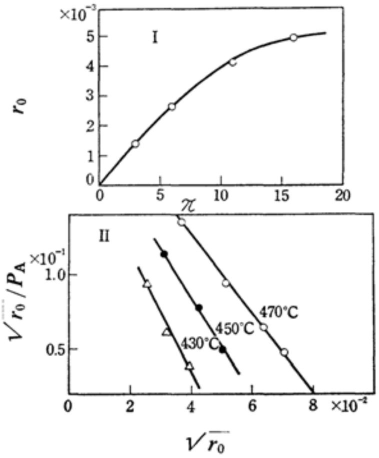

Fig. 7. I: Initial rate vs. total pressure.
II: $\sqrt{r_0}/P_A$ vs. $\sqrt{r_0}$.

Thus, the rate equation (r) and the initial rate equation (r_0) for this reaction may be expressed as follows:

$$r=\frac{k(K_A{}^2P_A{}^2-(1/K)K_RK_SP_RP_S)}{(1+K_AP_A+K_AP_A+K_SP_S+K_IP_I)} \qquad (1)$$

$$r_0=\frac{kK_A{}^2P_A{}^2}{(1+K_AP_A+K_IP_I)^2} \qquad (2)$$

Assuming that K_IP_I would be negligibly small in comparison with K_AP_A,

$$\sqrt{r_0}/P_A=a-\sqrt{r_0}+\sqrt{c} \qquad (3)$$

where a is K_a and c is $k\ K_a{}^2$.

The plots of $\sqrt{r_0}/P_a$ vs. $\sqrt{r_0}$ gave straight lines, as Fig. 7-II shows; from this figure a and c can be estimated, while the rate equation at 470°C is given by the following equation.

$$r=\frac{0.0523(1-x)^2-0.414x^2}{(11.0/\pi+2.55(1-x)+7.71x)^2} \qquad (4)$$

The full lines in Fig. 8, which were calculated using Eq. 4, agree with the experimental data satisfactorily. Figure 9 shows the temperature dependency of k and K_A, from which the activation energy of this reaction and the heat of adsorption of methylnaphthalene can be estimated to be 32.4 kcal./mol. and 12.6 kcal./mol. respectively.

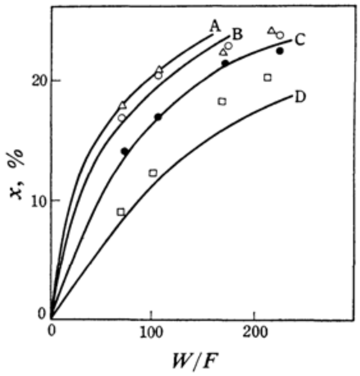

Fig. 8. Test of Eq. 4 with experiments. Full lines indicate the calculated ones after Eq. 4, and all the points indicate the estimated initial activities from the observed conversion-time curves (cf. Fig. 4).
A $\pi=16.0$ atm. C $\pi=6.0$
B $\pi=11.0$ D $\pi=3.0$
React. temp. 470°C

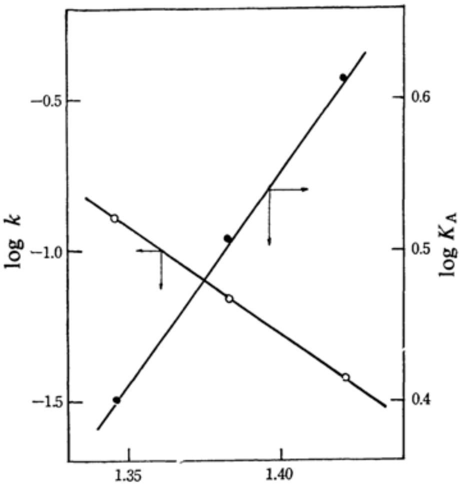

Fig. 6. Temperature dependency of k and K_A.

Summary

The effect of the addition of chromium oxide on the activity of silicon oxide - aluminum oxide for the disproportionation reaction of methylnaphthalene has been studied.

1) As the amount of chromium oxide added increased the yield of naphthalene increased, but the selectivity for this reaction decreased

in the low temperature range of 450~520°C. The 5 wt.%, chromium oxide added catalyst gave the best results.

2) It has been concluded, from the observation of X-ray and electromicrograph of the chromium oxide-added nalcat catalyst, that most of the chromium oxide added developed into large hexagonal crystals which had little activity and that the residue (about 30%), which is supposedly dispersed very finely, is probably responsible for the promotion of the catalytic activity.

3) It has been concluded from the analyses of the experimental data obtained that this disproportionation reaction can be expressed by the kinetic equation based on the surface reaction which is rate-controlling.

Nomenclature

r: reaction rate (mol. M. N./hr. g. cat.)
k: rate constant of surface reaction
K: equilibrium constant
K_A: adsorption equilibrium constant of methylnaphthalene
K_R: adsorption equilibrium constant of naphthalene
K_S: adsorption equilibrium constant of demethylnaphthalene
K_I: adsorption equilibrium constant of hydrogen
P_a: partial pressure of methylnaphthalene (atm.)
P_R: partial pressure of naphthalene (atm.)
P_S: partial pressure of demethylnaphthalene (atm.)
P_I: partial pressure of hydrogen (atm.)
x: conversion of disproportionation reaction (mol.%)
μ: total pressure (atm.)

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