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Decomposition of Methylamine over Ruthenium Black

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The decomposition of methylamine over Ru black was investigated in the presence and absence of hydrogen, and the dependence of reaction rate on the pressures of reactants was also examined. Methylamine decomposes rapidly to gaseous ammonia and deposited carbon species (CH_x(a)) over clean Ru black in the absence of hydrogen. The hydrogenation of CH_x(a) after the decomposition of amines produced hydrocarbons in the range C_1—C_4 whose distribution was dependent on the way CH_x(a) was accumulated.

The reactions of aliphatic amines over some evaporated metal films (Ni, Fe, Pd, Pt, W, Co, V) were studied previously by Kemball and Moss,[1–3] and by Anderson and Clark.[4] Two most important reactions of methylamine have been considered to be (i) simple hydrocracking and (ii) disproportionation involving two amine molecules, which leave considerable amount of carbon on the catalysts.[1,4] On the other hand in the presence of hydrogen thermodynamics indicates that methylamine should be decomposed readily to methane and ammonia.

In the present work, ruthenium was chosen as a catalyst because of its high activity for ammonia synthesis and Fischer-Tropsch reaction, and the decomposition of methylamine over a ruthenium black was investigated in the presence and absence of hydrogen. The reaction mechanism has been discussed on the basis of the reaction kinetics and the nature of the carbon species deposited from amines.

Experimental

The catalytic reaction of amines was carried out in a conventional closed-circulation system, whose dead volume was 336 cm^3. The analysis of gas mixture was carried out by gas chromatography using Chromosorb 103 (3 m, 110—120 °C) for ammonia and amines, Molecular Sieve 5 A column (1.5 m, room temperature) for hydrogen and methane, and active alumina column (2 m, room temperature) for C_2—C_4 hydrocarbons.

The ruthenium black was purchased from Nippon Engelhard and was used as a catalyst after hydrogen reduction at 300 °C. After this treatment, no impurity was observed on the surface of ruthenium black by X-ray photoelectron spectroscopy. Methylamine was obtained from its hydrochloride solution and potassium hydroxide, followed by drying, purifying by vacuum distillation and out-gassing by freezing and pumping. Dried ethylamine (>99%) was purchased from Tokyo Kasei and was out-gassed before use. Hydrogen was purified by passing through a Deoxo catalyst (room temperature) and a liquid nitrogen cold trap.

Prior to each run of the reaction, the catalyst was reduced by hydrogen for 2 h and was evacuated for 1.5 h at 300 °C. The reaction temperature was fixed at 120±2 °C in order to prevent a secondary reaction. The exchange reaction with deuterium was investigated by IR, mass spectrometry, and gas chromatography (alumina+2% $MnCl_2$ column).

Results and Discussion

Decomposition of Methylamine. The decomposition of methylamine over ruthenium black was investigated in the presence and absence of hydrogen, which are shown in Figs. 1 and 2, respectively. In the presence of hydrogen (Fig. 1a) ammonia and methane were produced simultaneously, but the amount of ammonia was more than that of methane. This indicates that carbon is deposited on the catalyst during the reaction. (The deposited carbon may be partially hydrogenated in the presence of hydrogen, which will hereafter be designated as CH_x(a).) The rate of reaction became slower as the reaction proceeded, and small amounts of hydrocarbons in the range of C_2—C_4 were also produced in the later stage if the reaction was prolonged. (The ratio of ethane to methane was ≈0.07.) After evacuation for about 5 min, the gas mixture of methylamine and hydrogen was introduced again to the catalyst on which CH_x(a) had been accumulated (Fig. 1b). Rapid production of ammonia was not observed this time, but ammonia and methane were produced proportionally and almost stoichiometrically. The formation of higher amines over ruthenium black was not observed although the production of larger amounts of higher amines have been reported over Pd, Pt, and W films.[1,4]

The decomposition of methylamine occurred readily even in the absence of hydrogen (Fig. 2a), producing ammonia and hydrogen, whereas the production of methane was not detected under this reaction condi-

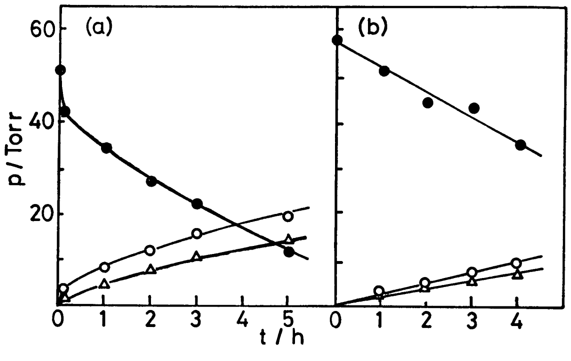

Fig. 1. (a) Reaction of CH_3NH_2 (51 Torr, 1 Torr = 133.3 Pa) and H_2 (241 Torr) over a Ru black at 120±2 °C; (b) reaction of CH_3NH_2 (58 Torr) and H_2 (241 Torr) over CH_x deposited Ru black at 120±2 °C; ●: CH_3NH_2, ○: NH_3, △: CH_4.

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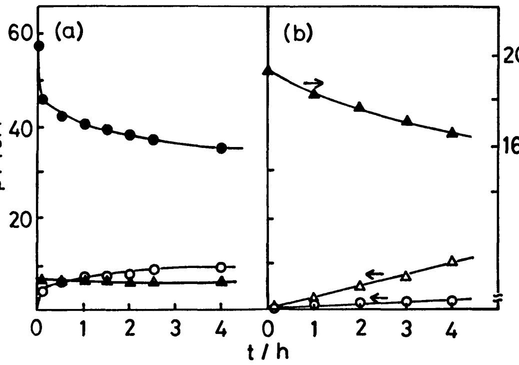

Fig. 2. (a) Decomposition of CH_3NH_2 (57 Torr) over clean Ru black at 120±2 °C; (b) hydrogenation (H_2, 200 Torr, 120 °C) of surface species after decomposition of CH_3NH_2; ●: CH_3NH_2, ○: NH_3, △: CH_4, ▲: H_2.

tion, and the reaction was almost stopped after 1 h. After evacuation for 5 min, only hydrogen was introduced onto the catalyst (Fig. 2b). A large amount of methane was produced, whose rate of formation was almost equal to that of steady-state conditions.

The exchange reaction of ammonia or hydrogen with deuterium and the hydrogenation of olefins during hydrogenolysis of methylamine were very fast and finished within 10 min, which indicates that chemisorption of hydrogen is not inhibited even in the presence of methylamine.

The dependences of the formation of methane and ammonia on the pressures of methylamine and hydrogen were examined. The formation of methane and ammonia was independent of the pressure of methylamine, but increased with increasing the pressure of hydrogen. The dependence of the formation of methane on hydrogen pressure was determined to be 0.9±0.1, but that of ammonia could not be estimated because of the scatter of data. The independency of amine pressure suggests that the surface must be substantially covered by adsorbed amine under the experimental conditions. The increase of the reaction rate with increasing hydrogen pressure suggests that the removal of CH_x(a) from the surface with hydrogen may be an important process.

On the basis of the above mentioned experimental results, the reaction mechanism is considered as shown in Fig. 3. The decomposition of methylamine occurs rapidly over freshly reduced ruthenium black even in the absence of hydrogen (step (i)), and then CH_x(a) is hydrogenated to methane slowly (step (ii)).

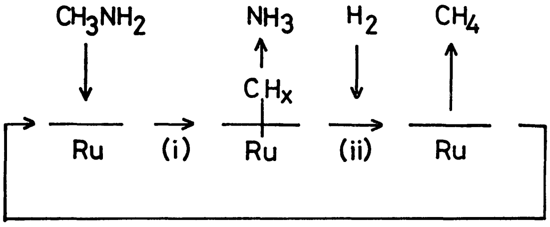

Fig. 3. Mechanism of hydrogenolysis of CH_3NH_2.

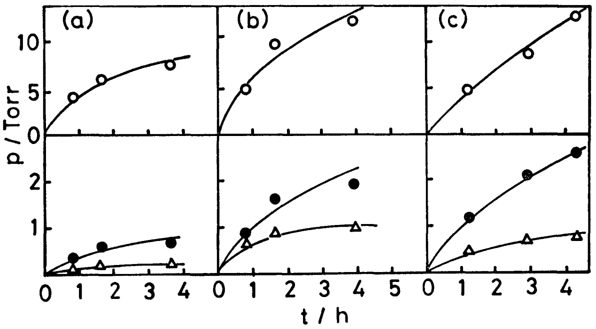

Fig. 4. Hydrogenation of surface hydrocarbon species after various of amines over 3 g Ru black at 120 °C; (a) $CH_3NH_2+H_2$ (20 h), (b) CH_3NH_2 decomposition (4.5 h), and (c) $C_2H_5NH_2$ decomposition (4.5 h); ○: CH_4, ●: C_2H_6, △: C_3H_8.

Hydrogenation of CH_x(a) after Various Reactions of Amines over Ruthenium Black. In order to investigate the nature of CH_x(a) produced from amines, the hydrogenation of CH_x(a) was carried out after various reactions of amines. The results are shown in Fig. 4 and Table 1. Main hydrogenation product was methane in all the cases, but the ratios of higher hydrocarbons to methane and the production rates were dependent on the way CH_x(a) was formed. The ratios of higher hydrocarbons to methane were larger in the hydrogenation of CH_x(a) produced from methylamine decomposition than that produced from the reaction of methylamine and hydrogen. This fact suggests that the CH_x(a) species produced from the reaction of methylamine and hydrogen is more easily hydrogenated to form methane than that from methylamine decomposition.

In the decomposition of methylamine and ethyl-

Table 1. HYDROGENATION OF SURFACE SPECIES AFTER VARIOUS REACTIONS OF AMINES OVER RU BLACK (120 °C, 3 g-catalyst)

Reactions	Products of the hydrogenation of surface species						
	C_1	C_2	C_3	C_4	C_2/C_1	C_3/C_1	C_4/C_1
	Torr						
$CH_3NH_2+H_2$ (20 h)[a]	4.2	0.3	0.1	0.07	0.07	0.03	0.02
CH_3NH_2 decomp (4.5 h)[b,c]	5.0	0.9	0.7	0.2	0.18	0.14	0.04
$C_2H_5NH_2$ decomp (4.5 h)[b,d]	4.8	1.2	0.5	0.3	0.25	0.1	0.06

a) The time of hydrogenation is 50 min. b) Production of ammonia is almost stopped after 4.5 h. c) Amount of evolved ammonia is 28.7 Torr, and the time of hydrogenation is 50 min. d) Amount of evolved ammonia is 28.3 Torr, and the time of hydrogenation is 70 min.

amine, the same amount of ammonia was evolved, but when these CH_x(a) species were hydrogenated, smaller amount of methane and larger amount of ethane were produced in the case of ethylamine. Consequently, it is considered that CH_x(a) produced from the decomposition of ethylamine preserves the C–C bond to some extent. In the reaction of ethylene and hydrogen over clean ruthenium black at 120 °C, the hydrogenation of ethylene occurred rapidly and only a small amount of methane was produced. Therefore, the C–C bond is much more stable than the C–N bond over ruthenium black. Since CH_x(a) produced from amines has reactivity to produce C–C bonds, it may be similar to CH_x(a) species accumulated during CO–H_2 reaction over ruthenium metal.

References

1) C. Kemball and R. L. Moss, *Proc. R. Soc. London, Ser. A*, **238**, 107, (1956).
2) C. Kemball and R. L. Moss, *Proc. R. Soc. London, Ser. A*, **244**, 398, (1958).
3) R. L. Moss and C. Kemball, *Trans. Faraday Soc.*, **56**, 154, (1960).
4) J. R. Anderson and N. J. Clark, *J. Catal.*, **5**, 250, (1966).