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SELECTIVE FORMATION OF 1-BUTENE IN ELIMINATION OF AMMONIA FROM 2-BUTANAMINE CATALYZED BY ZIRCONIUM OXIDE

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Zirconium oxide catalyzed elimination of ammonia from 2-butanamine to yield 1-butene as the major product. The selective formation of 1-butene was also observed for ZnO, La_2O_3, ThO_2, and MgO, though considerable formation of C_2 and C_5 hydrocarbons occurred.

Primary amines undergo decomposition to yield ammonia and olefins over acidic catalysts.[1)] 2-Alkylamines decompose to give a mixture of olefins rich in 2-olefins, which is produced by the mechanism involving alkyl cation intermediates.[2)] We wish to report that 1-butene was selectively formed in the decomposition of 2-butanamine over ZrO_2 , and that the similar tendency was observer for other basic catalysts.

Zirconium oxide, La_2O_3, and ThO_2 were prepared from aqueous solutions of $ZrOCl_2$, $La(NO_3)_3$, and $Th(NO_3)_3$, respectively, by precipitation with aqueous ammonia, followed by washing,drying and calcining. Magnesium oxide was obtained by decomposition of $Mg(OH)_2$(Kanto Chem. Co.) at 500°C in He stream. Zinc oxide was purchased from Kanto Chem. Co. Silica-Alumina(Nikki Chem., N-631L) was used for comparison. A microcatalytic pulse reactor was employed for most of the runs. For some experiments, a closed recirculation reactor was used.

Results obtained with the pulse reactor are given in Table 1.[3)] Produced butenes were considered to form by elimination of ammonia from 2-butanamine. Besides butenes, ethane and isomers of pentene were produced in considerable amount especially over ThO_2, La_2O_3, MgO, and ZnO. It is noted that butenes consisted mainly of 1-butene. This is in contrast to the predominant formation of 2-butenes over SiO_2-Al_2O_3 which is also includes in Table 1. As the hydrocarbons other than butenes might be produced by the successive reactions or by the processes different from butene formation, the reaction was carried out at a low temperature in the recirculation reac-

Table 1 Distribution of hydrocarbon produced in elimination of ammonia from 2-butanamine

Catalyst	Reaction temp. /°C	Conversion to hydrocarbons* /%	% each hydrocarbon						
			Ethane	Ethene	Propane (Propene)	1-Butene	trans-2-Butene	cis-2-Butene	C_5-Olefins
ZrO_2	350	2.3	1.9	1.1	1.9	61.1	8.6	12.5	12.9
ThO_2	450	1.6	32.5	12.7	(9.4)	8.4	1.2	0	35.8
La_2O_3	450	2.0	29.8	6.3	(5.1)	33.6	15.4	14.8	0
ZnO	450	1.4	6.2	7.1	0	65.6	0	0	21.1
MgO	450	0.3	74.3	24.2	0	1.5	0	0	0
S-A**	250	0.7	0	0	0	15.3	36.9	47.8	0

*Calculated on the base of the amount of reactant injected. **SiO_2-Al_2O_3

tor to avoid the processes other than the elimination of ammonia. Time dependence of composition in the reaction over ZrO_2 is shown in Fig. 1. At the reaction temperature of 300°C, 1-butene was exclusively produced in addition to ammonia.

The selective formation of 1-butene from 2-butanamine over ZrO_2 is reminiscent of the dehydration of 2-butanol over ZrO_2, in which 1-butene was selectively formed.[4)] Furthermore, selective formation of 1-butene from 2-butanol was observed over La_2O_3 and ThO_2.[5)]

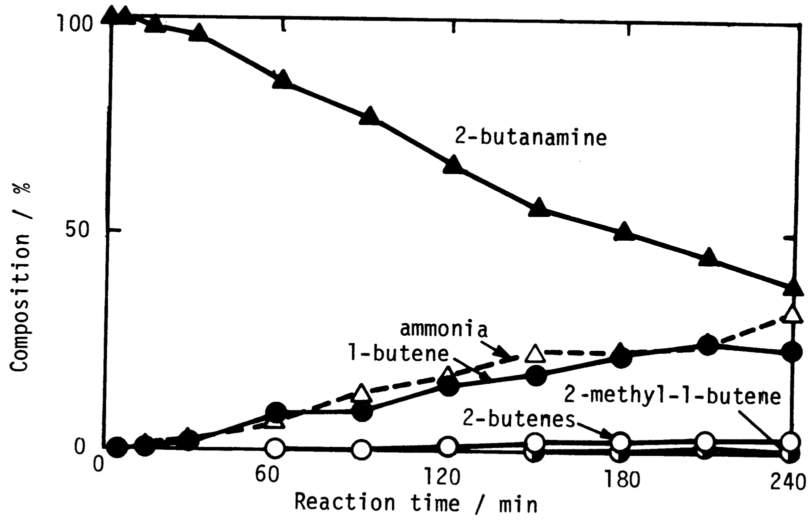
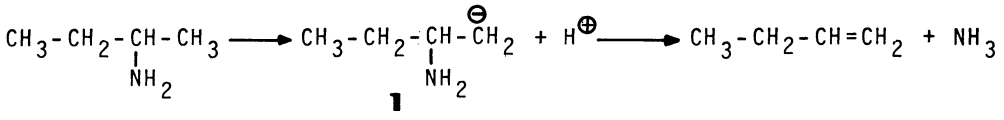


Fig. 1 Decomposition of 2-butanamine at 300°C over ZrO_2 which was pretreated at 350°C

The selective formation of 1-butene from 2-butanamine is considered to occur by a silmilar mechanism to the selective formation of 1-butene from 2-butanol. For the dehydration, the reaction is explained to occur by the process in which either concerted mechanism[5)] or carbanion mechanism[6)] is involved. Considering that ZrO_2, ZnO, La_2O_3, ThO_2, and MgO possess basic sites on the surfaces, it seems more likely that the selective formation of 1-butene from 2-butanamine proceeds by the carbanion mechanism as shown below.



$$CH_3\text{-}CH_2\text{-}\underset{NH_2}{\underset{|}{CH}}\text{-}CH_3 \longrightarrow \underset{\mathbf{1}}{CH_3\text{-}CH_2\text{-}\underset{NH_2}{\underset{|}{CH}}\text{-}\overset{\ominus}{CH_2}} + H^{\oplus} \longrightarrow CH_3\text{-}CH_2\text{-}CH{=}CH_2 + NH_3$$

The reaction is initiated by abstraction of an H^+ from carbon atom 1 by basic sites on the catalyst surface to form carbanion **1**.

References

1) W. S. Brey, Jr., and D. S. Cobbledick, Ind. Eng. Chem., 51, 1031(1959).
2) A. Satoh, H. Hattori, and K. Tanabe, Prep. 50th Disc. Catal., $3G_209$ Niigata,1982.
3) Analysis for all products has not been complete. Material balance has not been established in the pulse reactor. Condensation appeared to occur to some extent.
4) T. Yamaguchi, H. Sasaki, and K. Tanabe, Chem. Lett., 1973,1017.
5) A. T. Lundeen, and R. V. Hoozer, J. Org. Chem., 32, 3386(1967).
6) T. Tomatsu, T. Yoneda, and H. Otsuka, Yukagaku, 17, 236(1972).

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