

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

Akira SATOH, Hideshi HATTORI*, and Kozo TANABE

Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

Zirconium oxide catalyzed elimination of ammonia from 2-butan-amine to yield 1-butene as the major product. The selective formation of 1-butene was also observed for ZnO, La₂O₃, ThO₂, and MgO, though considerable formation of C₂ and C₅ 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 ZrO₂, and that the similar tendency was observed for other basic catalysts.

Zirconium oxide, La₂O₃, and ThO₂ were prepared from aqueous solutions of ZrOCl₂, La(NO₃)₃, and Th(NO₃)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 ThO₂, La₂O₃, 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 SiO₂-Al₂O₃ which is also included 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

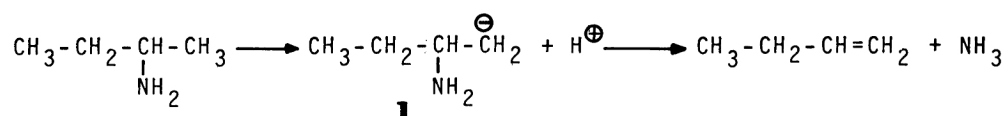
Catalyst	Reaction temp. /°C	Conversion to hydrocarbons* /%	% each hydrocarbon						
			Ethane	Ethene	Propane (Propene)	1-Butene	trans-2-Butene	cis-2-Butene	C ₅ -Olefins
ZrO ₂	350	2.3	1.9	1.1	1.9	61.1	8.6	12.5	12.9
ThO ₂	450	1.6	32.5	12.7	(9.4)	8.4	1.2	0	35.8
La ₂ O ₃	450	2.0	29.8	6.3	(5.1)	33.6	15.4	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. **SiO₂-Al₂O₃

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⁾

The selective formation of 1-butene from 2-butanamine is considered to occur by a similar 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 mechanism⁵⁾ or carbanion mechanism⁶⁾ 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.



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.*, 3G₂09 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).

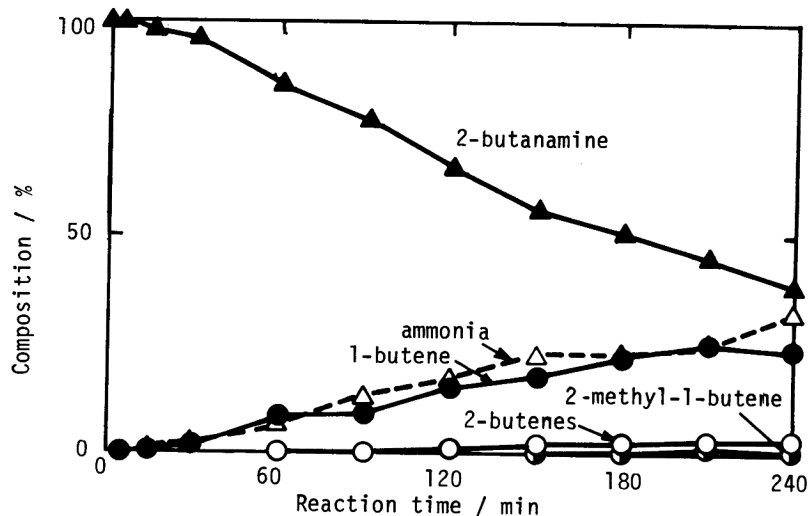


Fig. 1 Decomposition of 2-butanamine at 300°C over ZrO_2 which was pretreated at 350°C

(Received February 14, 1983)