CHEMISTRY LETTERS, pp. 1017-1018, 1973. Published by the Chemical Society of Japan

HIGH SELECTIVITIES OF ZIRCONIUM OXIDE CATALYST FOR ISOMERIZATION OF 1-BUTENE AND DEHYDRATION OF sec-BUTANOL

Tsutomu YAMAGUCHI, Hiroshi SASAKI, and Kozo TANABE
Department of Chemistry, Faculty of Science, Hokkaido University
Sapporo-shi 060

Zirconium oxide catalyst gave a high product ratio, 7.3, of cis-2-butene/trans-2-butene from 1-butene and 90.2 % of 1-butene in butenes formed from sec-butanol. Poisoning effect of n-butylamine or carbon dioxide on the reactions suggested that the catalyst has both acidic and basic character.

The catalytic actions of zirconium oxide have been reported for dehydration of alcohols and other reactions.[1] However, since the selective formation of butene isomers in two title reactions is not known, the present work has been done.

Zirconium oxide was prepared by calcining zirconium hydroxide in air at 500°C for 6 hr after drying at 100°C for 24 hr. The hydroxide was precipitated by adding 28 % aqueous ammonia to an aqueous solution of zirconium oxychloride and washed thoroughly with water until no chloride ion was detected in the filtrate. Alumina used for comparison was prepared by calcining the hydroxide in air at 500°C for 3 hr which was precipitated by the hydrolysis of aluminium nitrate with 28 % aqueous ammonia. The surface areas of zirconium oxide and alumina were 57 and 349 m^2/g, respectively. 1-Butene of 99 % purity was redistilled in vacuo. sec-Butanol was fractionally distilled and degassed by repeated freeze-thaw cycles over molecular sieve 3A in vacuo.

The isomerization of 1-butene was carried out in a closed circulation system. After 100 mg of the catalyst was activated by evacuating at 500°C for 4 hr, the reaction was started at 100°C under 100 mmHg of 1-butene. The dehydration of sec-butanol was carried out in a usual flow system at 200°C and atmospheric pressure, using nitrogen as a carrier gas. The products of the isomerization and dehydration were analyzed by gas chromatography.

The catalytic activities, k, and selectivities of zirconium oxide are shown in Table 1, where those of alumina are given for comparison. In the case of isomerization, the catalytic activity and selectivity of zirconium oxide were 2 and 2.5 times as much as those of alumina, respectively. The value of selectivity (the ratio of cis-2-butene/trans-2-butene) was 7.3, which was much larger than 1 - 2 observed for many solid acid catalysts.[2] The high value is comparable to the values (ca. 8 and 10) observed for basic catalysts such as calcium oxide[3] evacuated at 400°C and magnesium oxide[4] evacuated at 450°C, respectively. Thus, zirconium oxide seems to have a basic character. In fact, zirconium oxide lost its catalytic activity when it was contacted with 20 mmHg of carbon dioxide and evacuated at 100°C

for 1 hr.

For the dehydration reaction, zirconium oxide produced 90.2 % of 1-butene, though its activity was less than that of alumina. The reaction products were only butenes. The unusual selectivity of the catalyst for the formation of 1-butene is comparable to that of thorium oxide which has been known as the selective catalyst.[5] The catalytic activity of zirconium oxide was slightly decreased by introducing 10 - 50 μl of n-butylamine into the reactant gas during the reaction, but recovered readily by a continuous flow of the sec-butanol vapor, while the activity of alumina was markedly decreased by the same treatment and the activity was not recovered. The reversible adsorption of the base on zirconium oxide seems to indicate that zirconium oxide possesses a weak acidic character.

Table 1 Catalytic activity and selectivity of zirconium oxide for isomerization of 1-butene and dehydration of sec-butanol

Catalysts	Activity and selectivity	Isomerization	Dehydration
ZrO_2	k	6.42×10^{-4} a)	4.46×10^{-7} a)
	1-butene	———	90.2 %
	cis-2-butene	5.65×10^{-4} a)	7.4 %
	trans-2-butene	0.77×10^{-4} a)	2.4 %
	cis/trans	7.3	3.1
Al_2O_3	k	3.0×10^{-4} a)	4.33×10^{-5} a)
	1-butene	———	26.9 %
	cis-2-butene	2.25×10^{-4} a)	62.2 %
	trans-2-butene	0.75×10^{-4} a)	10.9 %
	cis/trans	3.0	5.7

a) mol/g. min.

References

1) A. A. Balandin, A. A. Tolstopyatova and V. A. Ferapontov, Dokl. Akad. Nauk, SSSR, 103, 611 (1955); A. D. Mokorov, Yu. S. Tarasevich and Y. M. Schchekochkhin, Metody Issled. Katal. Reacts., Akad. Nauk, SSSR, Sib. Otd., Inst. Katal., 1, 34 (1965); "Shokubai Binran", ed. by A. Ozaki et al., Chijin Shokan, Tokyo (1967), p.273.
2) G. C. Bond and P. B. Wells, Adv. in Catalysis, 15, 91 (1964); J. W. Hightower and W. K. Hall, Chem. Eng. Prog., 63, 122 (1967).
3) K. Tanabe, N. Yoshii and H. Hattori, Chem. Commun., 464 (1971).
4) H. Hattori, N. Yoshii and K. Tanabe, 5th Intern. Congr. Catalysis, Preprint No. 10, 1972, Palm Beach.
5) A. J. Lundeen and R. Van Hoozer, J. Amer. Chem. Soc., 85, 2180 (1963).

(Received July 16, 1973)