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CATALYTIC ACTIVITY OF $ZnO-SiO_2$ FOR ISOMERIZATION OF BUTENES

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The activity and selectivity of a new mixed oxide, $ZnO-SiO_2$, at several compositions have been examined for the isomerization of butenes. ZnO or SiO_2 alone did not show any appreciable activity, but $ZnO-SiO_2$ (mole ratio : 9) was found to show a very high activity with an interesting selectivity.

Some mixed oxides such as $SiO_2-Al_2O_3$, SiO_2-MgO, $Al_2O_3-B_2O_3$ and TiO_2-ZnO are known to exhibit, in general, high catalytic activity and selectivity[1] which are not found in each component oxide. From this point of view, we have prepared a new type of mixed oxide, $ZnO-SiO_2$ and attempted to test the catalytic action for the isomerization of butenes. A specially made zinc oxide named Kadox was reported recently to be active for the isomerization of cis-2-butene[2], though usually prepared zinc oxides are inactive for this reaction. Therefore, an interesting point of the present work is to see whether an inactive zinc oxide prepared by an usual method may become active upon mixing with an inactive silica gel and to compare the activity of $ZnO \cdot SiO_2$ with the specially made zinc oxide.

The $ZnO-SiO_2$ catalysts were prepared by calcining the coprecipitated mixtures of their hydroxides at 500°C in air for 3 hr after drying at 110°C for 20 hr. The mixtures of the hydroxides were coprecipitated by adding 28% aqueous ammonia to an aqueous solution of zinc nitrate (a guaranteed reagent of Wako Junyaku Co.) and distilled ethyl silicate until the pH of the solution becomes 7~8 and then filtered after washing thoroughly with water. Zinc oxide or silica gel alone was prepared as above. A Kadox 25 ZnO of the New Jersey Zinc Co. was also used as a catalyst for comparison.

The reaction of butenes was carried out at 230-320°C in a chromatographic pulse reactor. The amount of each pulse was 2cc (NTP), helium being used as a carrier gas (flow rate:1.1 ml/sec). The catalysts (0.25g of 20-35 mesh) were pretreated at 500°C for 3 hr under a stream of helium gas before the reaction. Fig. 1 shows the effect of catalyst composition on the conversion percent of 1-butene at 270°C. In the range of reaction temperature from 230 to 320°C, no reaction other than the isomerization took place. As seen in the figure, a silica gel or zinc oxide itself did not show appreciable activity, but the mixed oxides showed high activity, the highest activity being observed for the $ZnO-SiO_2$ (mole ratio:9). The ratio of cis- to trans-2-butene from 1-butene was found to be about 1 (see Table 1), while that of trans-/1-butene from cis-2-butene was about 3.

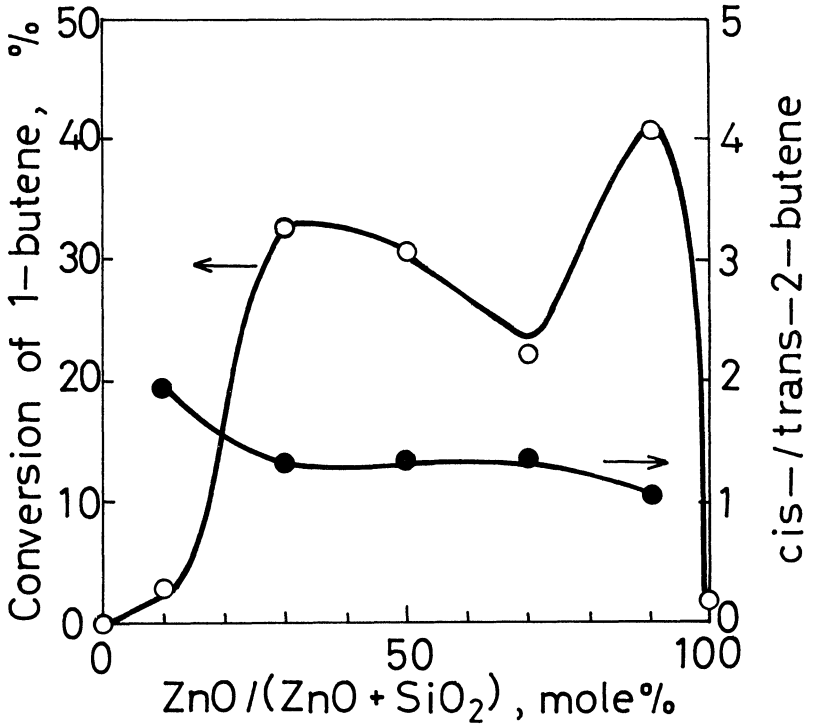

Fig. 1 Isomerization of 1-butene over $ZnO-SiO_2$. Reaction temp., 270°C.

The activity and selectivity of $ZnO-SiO_2$ (mole ratio:9) are compared with that of a Kadox 25 catalyst in Table 1, where the conversion % from 1-butene, cis-2-butene and trans-2-butene are given. Both catalysts showed a comparable activity and similar selectivity, except for the isomerization of trans-2-butene to cis-2-butene. In the latter reaction, the activity of $ZnO-SiO_2$ was found to be five times higher than that of a Kadox 25 catalyst. The present catalyst is highly active for the cis-trans isomerization.

Table 1 Activity and Selectivity of $ZnO-SiO_2$ (mole ratio:9) and Kadox 25. Reaction temperature: 270°C.

Catalysts	Conversion %					
	1- to cis-*	1- to trans-*	cis- to 1-	cis- to trans-	trans- to 1-	trans- to cis-
$ZnO-SiO_2$	21.2	19.6	12.4	41.5	8.8	25.3
Kadox 25	26.1	18.8	17.7	48.4	7.1	5.6

* 1- : 1-butene, cis-: cis-2-butene, trans-: trans-2-butene

References

1) K. Tanabe, "Solid Acids and Bases", Kodansha, Tokyo and Academic Press, New York· London, Chapt. 4 (1970); K. Tanabe, C. Ishiya, I. Matsuzaki, I. Ichikawa and H. Hattori, Bull. Chem. Soc. Japan, 45, 47 (1972).
2) A. L. Dent and R. J. Kokes, J. Phys. Chem., 75, 487 (1971).

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