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SUPERBASICITY OF RUBIDIUM OXIDE AND CAESIUM OXIDE, AND THEIR REACTION PROFILES OF ISOMERIZATION OF BUTENES

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The superbasic sites on a rubidium oxide and a caesium oxide have been revealed by means of the benzoic acid titration method. The double-bond-migration and the cis-trans isomerization of butenes took place over the rubidium oxide and the caesium oxide; but the skeletal isomerization was not observed.

Great attention has been paid on the superacidity and the superbasicity of the various catalysts.1) However, relatively little investigation on the superbasic catalyst has been reported. The superbasic catalysts so far reported are magnesium oxide,2) and doped magnesium oxide, e.g. MgO-Na.3) The superbasicity of any alkali metal oxide and of alkaline earth metal oxides, have not been measured.1,4,5) The present work has been carried out in order to find other kind of superbase and to investigate on its catalytic properties, the rubidium oxide and the caesium oxide being employed.

A closed circulating system (370 ml) connected to a gas chromatograph was used to follow the reaction. The reaction employed is the isomerization of butenes, since the reaction has often been employed as a model reaction and extensively investigated over solid acids and bases. The reaction mixtures were occasionally analyzed by means of gas chromatograhy

The rubidium oxide and the caesium oxide supplied from Alfa Division Ventron Co., were employed as catalysts. They were evacuated under ca. 10^{-3} Pa either at 573 K or at 643 K for 6 h. The 1-butene, cis- and trans-2-butene used as the reactants were obtained from the Tokyo Kasei Kogyo Co., Ltd., and were purified by repeated distillation to be more than 99%.

The amount and the strength of basic sites were measured by means of the benzoic acid titration method.[1,6] The indicators employed are 4-nitroaniline (H_-=1.84), diphenylamine (H_-=22.3), 4-chloroaniline (H_-=26.5), aniline (H_-=27.0), triphenylmethane (H_-=33.0) and diphenylmethane (H_-=35.0). The oxides samples (ca. 0.10 g), which have been evacuated beforehand, were weighed in separate glass tubes (18 cm long, 0.6 cm in ontside-diameter). Then, the solution of benzoic acid (0.005 mol·dm^{-3}) in benzene and of appropriate indicator in benzene (0.2 ml) were introduced with microsyringes (1 ml) to each sample. The amount of benzoic acid added might differ among samples in steps of 0.005 to 0.1 mmol per g of sample, depending on the expected base-strength distribution. All the operations for the measurement were conducted under the dry argon atmosphere. The sample tubes were cooled with liquid-nitrogen trap, and evacuated for 30 min. Then, the tubes were sealed off. From the resultant color changes of indicators after two days, where basic color just disappear, the end point of titration was visually determined.

Before each run of the isomerization, the catalyst was evacuated under ca. 10^{-3} Pa for 4 h at 573 K for the repeating use, and the experimental results were well reproducible.

Figure 1 shows the amount of base per weight of catalyst plotted against the base strength for rubidium oxide and caeseium oxide. The surface areas of these oxide were so small (<0.5 m^2·g^{-1}) that they could not be accurately measured by means of nitrogen-adsorption method. The very strong base sites ($H_- \geq 26$) were found on the surfaces of rubidium oxide evacuated at 643 K and of caesium oxide evacuated at 573 K. According to the Tanabe's definition,[1)] these sites are superbasic sites. Although the superbasic property of the alkali metal oxides has been expected,[1)] this is the

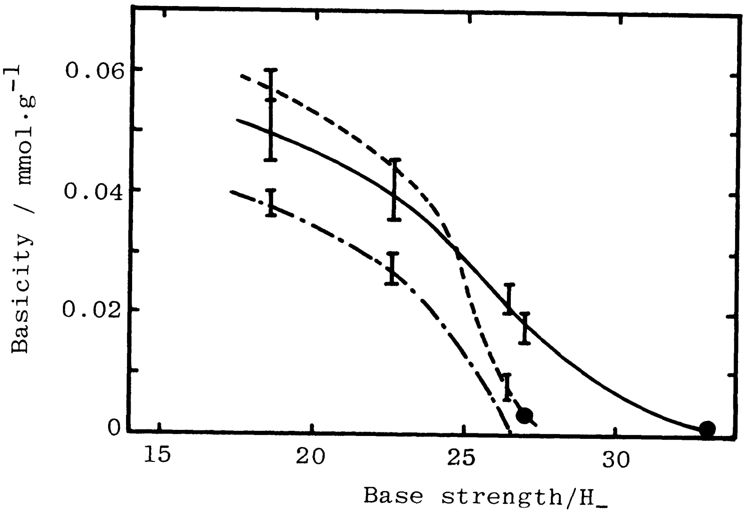
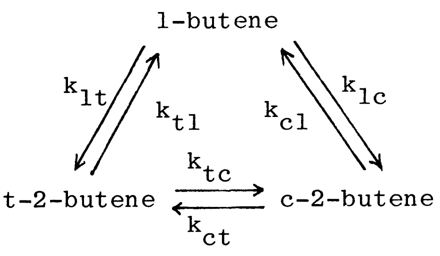


Fig. 1. Basicity vs. Base strength.
—— Rb_2O evac. at 643 K
—·— Rb_2O evac. at 573 K
--- Cs_2O evac. at 573 K

first observed evidence. Malinowski and Kijenski, however, consider that the basic strength of a superbase should lie in the range $40>H_->33$.$^{3)}$ The results on rubidium oxide suggest that the evacuation at higher temperature increase the basicity and the strength of bases. For calcium oxide and magnesium oxide, the basicity and the strength of base have been reported.$^{1-3,6)}$ It may be suggested that the rubidium oxide and the caesium oxide are more basic than the calcium oxide, but that they are not very much different from magnesium oxide.

The isomerization of butenes has been investigated over the rubidium oxide and the caesium oxide; the double-bond migration and the cis-trans isomerization of butenes took place over these oxides. No gaseous hydrocarbon other than butenes could be detected in the reaction mixtures; the skeletal isomerization could not be observed.

The rate of the isomerization of butenes was almost ploportional to the pressure of the reactant. From the initial rates of reaction and the selectivity, all six of the rate constants expressed by Scheme 1 have been determined. The results of isomerization over the oxides with superbasic sites are shown in Table 1.



Scheme 1.

Table 1. Rate Constants of Isomerization of Butenes at 413 K

	Rate Constant Caesium Oxide$^{a)}$	k_{ij}/min·g Rubidium Oxide$^{b)}$
k_{1t}	8.61×10^{-5}	1.28×10^{-4}
k_{tc}	2.51×10^{-6}	1.51×10^{-5}
k_{c1}	1.19×10^{-4}	2.33×10^{-4}
k_{t1}	9.69×10^{-6}	1.59×10^{-5}
k_{1c}	4.97×10^{-4}	9.03×10^{-4}
k_{ct}	5.19×10^{-6}	3.15×10^{-5}

a) evacuated at 573 K.
b) evacuated at 643 K.

Figure 2 shows the reaction profile of isomerization of butenes at 413 K over the rubidium oxide evacuated at 643 K, which was obtained in a manner similar to that described previously.$^{7)}$ The profile is entirely different from that obtained in the isomerization over a H_2SO_4-graphite.$^{8)}$ The high cis-convex profiles were obtained for both oxides. The results may suggest that the high cis-convex type profile is obtained for the isomerization of butenes over the superbase. The acid-base property of catalyst has been characterised by the product ratio, cis-2-/trans-2-butene, formed from 1-butene. Because the shape of profile shown on the triangular graph depends not only upon the ratio, k_{1c}/k_{1t}, but also upon the ratio, k_{ct}/k_{1t}, the catalytic characteristics can be more clearly expressed by the profile than by the cis-2-/trans-2-butene ratio.

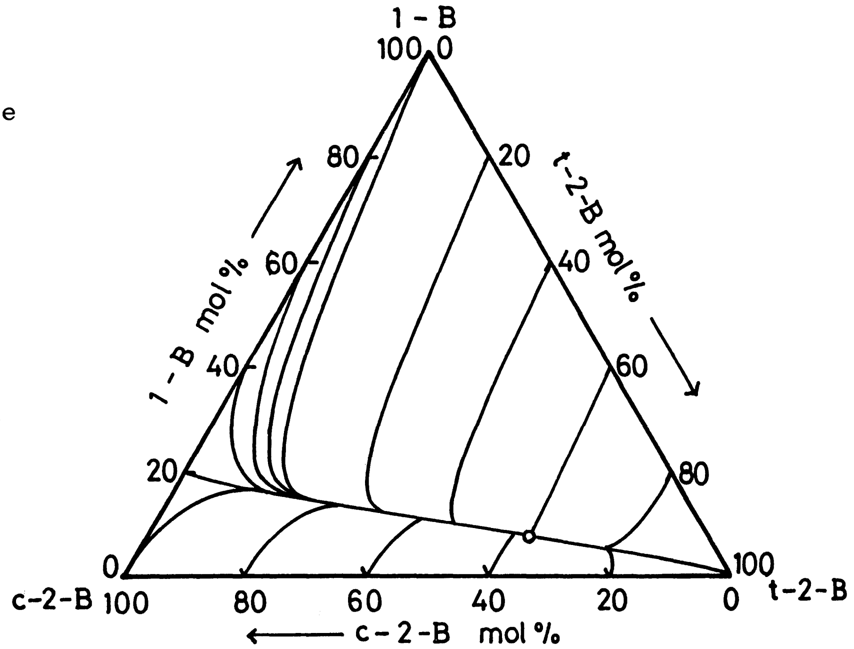


Fig. 2. Reaction profile of isomerization of butenes over Rb_2O at 413 K.

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