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HIGH-TEMPERATURE EVACUATED HYDROXYAPATITE AS A BASE CATALYST FOR THE ISOMERIZATION OF 1-BUTENE

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Hydroxyapatite calcined in air did not show any catalytic activity for the isomerization of 1-butene even at 573 K, but hydroxyapatite evacuated above 773 K catalyzed the isomerization at 273 K selectively to form cis-2-butene by an intramolecular hydrogen rearrangement.

A number of metal phosphates are recognized as solid acid catalyst,$^{1)}$ however, little attention has been paid to the basic properties of metal phosphates. Hydroxyapatite is one of the most well-characterized phosphate compounds.$^{1)}$ Kibby and Hall$^{2)}$ reported that there exist both acidic and basic sites on its surface, but little is known about the surface acid-base properties of high-temperature pretreated one. We wish to report the pronounced catalytic behavior of a hydroxyapatite evacuated above 773 K for the isomerization of 1-butene.

Hydroxyapatite was prepared by the precipitation method of J. A. S. Bett et al.,$^{3)}$ and was activated by evacuating at 573-1173 K for 1 h prior to reaction. X-Ray diffraction pattern of the catalyst sample evacuated at 1073 K showed a sharp crystalline pattern with the lines attributed to hydroxyapatite in the ASTM classification. No lines attributable to CaO and/or tricalcium phosphate were observed. Isomerization reactions were carried out in ca. $4.9 \times 10^{-4} m^3$ of a closed circulation reactor at 273 K with an initial pressure of 13 kNm^{-2} of 1-butene. Coisomerization of cis-2-butene-d_0/d_8 was carried out in a pulse reactor.

When only 0.05 g of hydroxyapatite evacuated at 973 K was used, 50% of 1-butene isomerized to 2-butene at 273 K in 30 min. On the other hand, when calcined in air at 973 K for 2 h, no reaction occured even at 573 K in 120 min. The catalytic activity, represented by % conversion at the initial stage of the reaction, begins to appear following evacuation at 773 K, and increases sharply to a maximum at 973 K, above which a rapid decline occurs up to 1173 K (Figure). Initial cis to trans-2-butene ratio-evacuation temperature curve has the minimum value (ca.7) at 1073 K, and the large ratios of ca. 14 are observed on evacuation at both 773 K and 1173 K (Figure). These large cis to trans ratios are characteristic of the base-catalyzed reaction, which are presumed to involve π-allyl carbanion mechanism.$^{4)}$

The poisoning experiment with CO_2 was carried out using hydroxyapatite evacuated at 973 K to elucidate the nature of the active sites. The isomerization was completely retarded when the catalyst was exposed to CO_2 at a room temperature and subsequently evacuated at the same temperature. As the adsorbed CO_2 was removed, Table. Isotopic Distribution of Butene Isomers in the Coisomerization of cis-2-Butene-d_0/d_8 over Hydroxyapatite Evacuated at 973 K.[a]

Pulse no.[b]	Product	% each product	% each isotopic species						Atom exchanged/ molecule[c]	Light material/ heavy material[d]
			d_0	d_1	d_2	$d_3 \sim d_6$	d_7	d_8		
Reactant	c	97.2	57.6	0	0	0	2.2	40.2	0.022	1.36
2	1	4.2	54.1	0.7	0.4	0	2.8	42.0	0.043	1.23
3.8 μmol	t	37.6	69.0	1.5	0	0	2.8	26.7	0.043	2.40
	c	58.2	48.7	0.6	0	0	3.0	47.7	0.036	0.97
4	1	7.9	44.9	0.9	0.6	0	4.0	49.6	0.061	0.87
3.2 μmol	t	30.1	79.6	1.1	0	0	1.6	17.7	0.027	4.18
	c	62.0	45.9	0.9	0	0	3.7	49.5	0.046	0.88

a) 0.05 g of catalyst; reaction temp., 0°C and 25°C for pulse no.2 and 4 respectively.
b) He carrier flow rate, 100 ml/min and 30 ml/min for pulse no.2 and 4 respectively.
c) Calculated from $\sum_{i=1}^{4} iN_i + \sum_{i=5}^{8} (8-i)N_i$, where N_i represents the mole fraction of isotopic species containing i deuterium atoms. d) Calculated from $(\sum_{i=0}^{3} N_i + \frac{1}{2}N_4)/(\sum_{i=5}^{8} N_i + \frac{1}{2}N_4)$.

however, the catalytic activity was gradualy restored. Fractions of the activity restored after desorption at 573, 873, and 973 K were 0.1, 0.7, and 1.0, respectively. These results indicate that the active sites are of basic property and are probably generated by the removal of CO_2 strongly held on the surface.

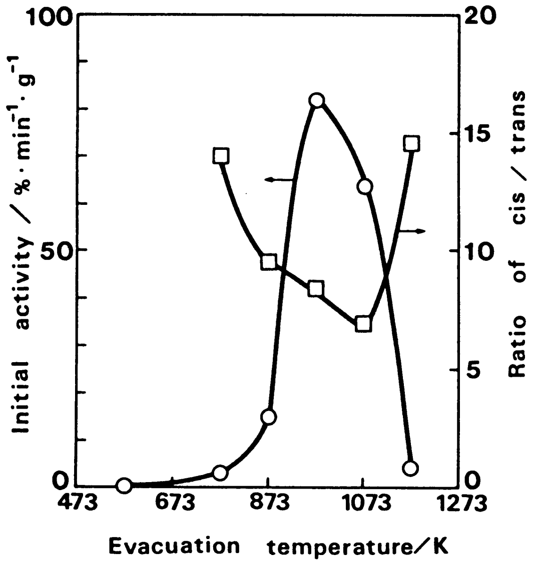

Fig. Catalytic activity and selectivity of hydroxyapatite for the isomerization of 1-butene as a function of evacuation temperature.

Results of coisomerization of cis-2-butene-d_0/d_8 over hydroxyapatite evacuated at 973 K are given in the Table. Since the numbers of H (or D) atoms exchanged per molecule in the products are much smaller than 0.5, which is expected if the reaction involves an intermolecular hydrogen transfer, the reaction proceeds exclusively with an intramolecular hydrogen rearrangement. There were sizable differences in reactivities between nondeuterio and perdeuterio cis-2-butene. The ratios of light material to heavy material in the unisomerized cis-2-butene were smaller than that in the starting material. This indicates that C-H bond cleavage is probably involved in the rate-determining step. These two facts coming from deuterium tracer study are supplemental evidences supporting the existence of basic sites over high-temperature evacuated hydroxyapatite.

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