CHEMISTRY LETTERS, pp. 1465-1466, 1977. Published by the Chemical Society of Japan

CATALYTIC ACTIVITY OF ALKALINE EARTH METAL OXIDES FOR ISOMERIZATION OF 1-N-PYRROLIDINO-PROP-2-ENE TO 1-N-PYRROLIDINO-PROP-1-ENE

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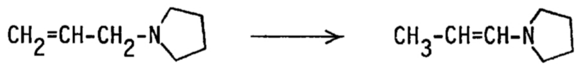
Isomerization of 1-N-pyrrolidino-prop-2-ene to 1-N-pyrrolidino-prop-1-ene was carried out at 40°C over alkaline earth metal oxides. MgO and CaO exhibited high activity and selectivity, while SrO and BaO degradated their activities during the reaction.

Base-catalyzed isomerization of allylamines is known as one of the preparation methods of propenylamines (a group of enamines).[1] Most of the catalysts used for the isomerization are homogeneous ones such as potassium t-butoxide in dimethyl sulfoxide[2] and sodium in liquid ammonia.[3] Only potassium amide on Al_2O_3[4] and potassium hydroxide on Al_2O_3[5] were used as heterogeneous catalysts which have several advantages compared with homogeneous catalysts. However, potassium amide on Al_2O_3 loses its activity during the reaction and potassium hydroxide on Al_2O_3 requires high reaction temperatures (260-270°C). Since alkaline earth metal oxides show basic property on the surface and are known to catalyze double bond isomerization of olefins,[6-8] we used them together with the other heterogeneous isomerization catalysts such as SiO_2-Al_2O_3, Al_2O_3 and ZnO for the preparation of 1-N-pyrrolidino-prop-1-ene by double bond isomerization of 1-N-pyrrolidino-prop-2-ene,



A microcatalytic pulse reactor was employed. One micro liter of 1-N-pyrrolidino-prop-2-ene was introduced into the helium stream ahead of the catalyst which had been pretreated under a helium stream at each temperature (300-1000°C). The reaction was carried out at 40°C. Products were analyzed by gas chromatography and mass spectrography. NMR was also used to identify 1-N-pyrrolidino-prop-1-ene.

The compositions of the products over MgO, CaO, SrO and BaO that were pretreated under their optimal conditions are given in Table 1. The main product was 1-N-pyrrolidino-prop-1-ene. The other products were pyrrolidine, propionaldehyde and a few kinds of the condensates of 1-N-pyrrolidino-prop-1-ene with pyrrolidine. Relatively large amounts of propionaldehyde was formed at the first pulse. Magnesium oxide and CaO showed high activities when they were pretreated at proper temperatures. The activities were so high that the percentage of 1-N-pyrrolidino-prop-1-ene was almost independent of the change in flow rate. Barium oxide rapidly lost its activity with successive pulses and SrO gradually lost. Any catalysts other than alkaline earth metal oxides, SiO_2-Al_2O_3, Al_2O_3 and ZnO, showed no activity. The acidic sites on these catalysts may strongly adsorb the reactant at a lone pair of nitrogen atom and become inactive.

Table I Isomerization of 1-N-pyrrolidino-prop-2-ene at 40°C

Catalyst	Pretreat. temp., °C	Weight mg	Pulse No.	Flow rate ml/min	% each product a)			
					reactant b)	enamine c)	pyrrolidine	propionaldehyde
MgO	600	30	1	30	0	79.8	9.9	10.3
			2	30	0.2	81.3	14.0	4.4
			4	61	0.2	83.3	13.0	3.5
			5	88	1.0	83.9	12.3	2.7
CaO	700	34	1	30	0.5	61.5	26.2	11.8
			2	30	0.2	84.7	12.7	2.4
			4	59	0.2	79.6	17.5	2.6
			5	113	0.4	76.7	19.8	3.3
CaO	300	31	1	31	0.5	73.5	14.4	11.6
			2	32	17.5	66.1	11.0	5.4
			4	33	74.5	20.1	4.4	1.0
SrO	1000	302	1	29	0.2	77.7	11.8	10.3
			2	31	19.8	65.8	12.1	2.3
			4	31	80.0	19.5	0.4	0.1
			6	30	87.9	11.2	0.8	0.1
BaO	800	313	1	29	0.4	71.9	19.1	8.7
			2	29	96.5	2.9	0.4	0.2

a) Small quantities of unidentified compounds and condensates of the enamine with pyrrolidine were neglected in the calculation.
b) 1-N-pyrrolidino-prop-2-ene.
c) 1-N-pyrrolidino-prop-1-ene.

The reaction mechanism for the formation of 1-N-pyrrolidino-prop-1-ene over alkaline earth metal oxides is considered to be similar to that of isomerization of butenes.7) The basic sites abstract a proton from 1-N-pyrrolidino-prop-2-ene at carbon atom 1 to form a π-allylic anion. The proton transfers to the carbon atom 3 to form 1-N-pyrrolidino-prop-1-ene. Calcium oxide that was pretreated at 300°C showed little activity for the isomerization of 1-butene,7) but showed activity for the formation of 1-N-pyrrolidino-prop-1-ene. The abstraction of a proton from allyl amines seems to be much easier than that from olefins.

Since enamines are highly reactive reagent, the produced enamine reacted even with an oxygen on the surface, which was evidenced by the formation of propionaldehyde. Rapid degradation of the activity of BaO may be due to the reaction of the enamine with the strong basic sites. Therefore, MgO and CaO, whose basic sites are not too strong, are highly active and selective for the isomerization of 1-N-pyrrolidino-prop-2-ene to 1-N-pyrrolidino-prop-1-ene.

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(Received September 16, 1977)