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ISOMERIZATION OF BUTYNES TO 1,3-BUTADIENE OVER SOLID BASE CATALYSTS

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1-Butyne and 2-butyne underwent isomerization to 1,3-butadiene over CaO, SrO, MgO, La_2O_3, ThO_2 and ZrO_2 catalysts below 100°C. Among these catalysts, the CaO catalyst exhibited the highest activity, and was active even at 30°C.

Although alkynes easily undergo isomerization to yield isomeric alkynes and allenes with basic catalysts, isomerization of alkynes to the most stable isomers, conjugated dienes, takes place only under a severe condition.[1)] For instance, 1-hexyne isomerized to give only 2.3% 1,3-hexadiene with t-BuOK in dimethylsulfoxide at 72°C in 92h.[2)] Isomerization of 1-butyne over $NaOH/Al_2O_3$ at 400°C yielded only 9% 1,3-butadiene.[3)] We wish to report that certain types of solid base catalysts are active for isomerization of 1-butyne or 2-butyne to 1,3-butadiene below 100°C.

The catalysts which showed activities were MgO, CaO, SrO, La_2O_3, ThO_2, and ZrO_2. The MgO, CaO, and SrO catalysts were prepared by decomposition of $Ca(OH)_2$ (Kanto Chemicals Co.), $Mg(OH)_2$ (Kanto Chemicals Co.), and $SrCO_3$ (E. Merck Co.), respectively, under a vacuum at elevated temperatures. The La_2O_3 catalyst was prepared from aqueous $La(NO_3)_3$ by precipitation with aqueous ammonia followed by washing, drying, and outgassing at elevated temperatures. The ThO_2 and ZrO_2 catalysts were prepared from aqueous solutions of $Th(NO_3)_4$ and $ZrOCl_2$ by precipitation with aqueous ammonia followed by washing, drying, calcining in air, and outgassing at elevated temperatures.

1-Butyne and 2-butyne were obtained from Tokyo Chemical Industry Co., Ltd. and purified by passage through 3A molecular sieves at dry ice-acetone temperature.

A closed recirculation reactor of a volume 300ml was

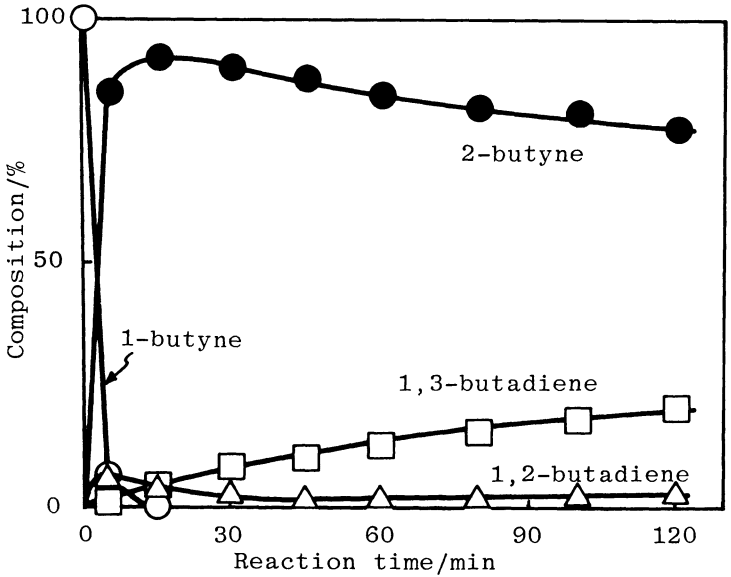

Fig.1 Time dependence of composition in isomerization of 1-butyne at 30°C on CaO(0.10 g) outgassed at 600°C

Table 1 Activities of Catalysts for Isomerization of 1-Butyne and 2-Butyne

Reactant	Catalyst	Pretreat. temp./°C	Reaction temp./°C	Activity[a)]
1-Butyne	CaO	600[b)]	0	123
	SrO	1000	0	4
	La_2O_3	800	0	3
	MgO	800	30	12
	ThO_2	500	30	2
	ZrO_2	700	30	1
2-Butyne	CaO	800	30	20
	SrO	1000	30	1
	La_2O_3	700	100	15
	MgO	600	100	5
	ThO_2	500	100	1
	ZrO_2	700	100	1

a) unit: 10^{18} molecules·min^{-1}·g^{-1} b) CaO pretreated at 800 °C showed the maxinum activity which was too high to measure.

employed for carrying out the reactions. About 20 Torr of 1-butyne or 2-butyne was allowed to react. In some experiments, the reaction was carried out with 40 Torr H_2. The presence of H_2 did not affect at all.

Time depencence of the composition in the reaction of 1-butyne over the CaO catalyst which had been outgassed at 600 °C is shown in Fig. 1. 1-Butyne rapidly underwent isomerization to 2-butyne and 1,2-butadiene followed by rather slow isomerization to yield 1,3-butadiene. Over the catalyst outgassed at 800 °C, the reaction proceeded much faster than that observed for the CaO catalyst outgassed at 600 °C, and 1-butyne converted to 100% 2-butyne in 5 min followed by isomerization to 1,3-butadiene.

The activities of the catalysts examined for the reactions of 1-butyne and of 2-butyne are summarized in Table 1. Since the isomerization of 1-butyne to 2-butyne and 1,2-butadiene was much faster than that of 1-butyne to 1,3-butadiene, the activity for the reaction of 1-butyne represents the rate of conversion of 1-butyne to 2-butyne and 1,2-butadiene. The data given in Table 1 are those obtained for the catalysts pretreated under optimum conditions.

For both 1-butyne isomerization and 2-butyne isomerization, the activities of the catalysts per on the unit weight basis were in the following order;

$$CaO > SrO > La_2O_3 > MgO > ThO_2 > ZrO_2.$$

Of these catalysts, the CaO and SrO catalysts catalyzed the isomerization to produce 1,3-butadiene at 30 °C, which are much more active than known catalyst $NaOH/Al_2O_3$ which needs 400 °C to produce 1,3-butadiene.

References

1. H. Pines and Y. M. Stalick, "Base-Catalyzed Reactions of Hydrocarbons and Related compounds" Academic Press Inc., New York (1977), p.124.
2. M. L. Farmer, W. E. Billups, R. B. Greenlee, and A. N. Kurtz, J. Org. Chem., 31, 2885 (1966).
3. L. E. Calihan, E. L. Kay, D. T. Roberts, Jr., and L. B. Wakeflied, Ind. Eng. Chem., Prod. Res. Dev., 14, 287 (1975).

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