February, 1988] NOTES Bull. Chem. Soc. Jpn., 61, 565—566 (1988)

The Isomerization of 1-Butene to *cis*-2-Butene over CaO by Means of the Pulse-Reaction Method

Kazushi ARATA,* Makoto HINO,† and Sakari KOBAYASHI†
Hokkaido University of Education, Hachiman-cho, Hakodate 040
†Hakodate Technical College, Tokura-cho, Hakodate 042
(Received July 10, 1987)

Synopsis. The title reaction was studied over CaO catalysts which had been prepared by the calcination of $Ca(OH)_2$ in air, followed by heating in a He stream or by thermal decomposition in a He flow. The former catalysts gave high cis/trans ratios (up to 21.6), while the latter ones were higher in activity but showed much lower ratios (ca. 1).

It is well-known that alkaline earth metal oxides, like MgO and CaO, are solid bases which catalyze various kinds of reactions.[1–4] Among a number of reactions over the solid bases, double bond and cis-trans isomerizations of butenes have been studied by many workers to clarify the surface properties. It has been recognized that basic sites convert 1-butene into *cis*-2-butene via π-allyl anion intermediates formed by the abstraction of H^+ from 1-butene;[5,6] the ratio of *cis*-2-butene to *trans*-2-butene is large (8 for CaO and 16 for MgO), compared with 1—2 in the case of the acid catalysts.[7,8]

For the above experiments, the reactions have mostly been carried out in a closed circulating reactor with a fixed-bed catalyst pretreated in vacuo. In this study, the isomerization of 1-butene was performed over CaO under pulse conditions; the results were exceedingly far from those obtained with a recirculation reaction.

Experimental

The calcium oxide was prepared by calcining $Ca(OH)_2$ (Wako Pure Chemical, Ltd.) in air for 3 h. The reactions were carried out in a microcatalytic reactor (3 mm in diameter) of stainless steel with a fixed-bed catalyst [flow rate of He carrier gas: 20 ml/min; pulse size: 0.05 ml (in gas); catalyst: 30 mg (32-60 mesh); height of the catalyst bed: ca. 3 mm]. The reactants were injected into the reactor with a syringe. For analysis, the effluent products were directly introduced into a gas chromatographic column connected to the reactor (VZ-7, 4 m, 25 °C). Since the yields were almost constant with the pulse number, conversions were taken as an average of pulse values from the first to the fifth.

Results and Discussion

The catalytic activity of CaO for the isomerization of 1-butene to 2-butenes and the selectivity to *cis*-2-butene largely depend on the temperatures of calcination in air and of treatment in a He flow in the reactor. $Ca(OH)_2$ was calcined at 300—1000 °C in air, heated in He at various temperatures, and then employed for the reaction of 1-butene. The results are shown in Table 1. The CaO catalysts were also obtained by the thermal decomposition of $Ca(OH)_2$ in a He flow, without calcination in air. High activities were observed with the catalysts heated at 600 or 700 °C in air and then in He; high ratios of *cis*-2-butene to *trans*-2-butene (c/t) were obtained when it was treated at 500 °C in He after 600 or 700 °C in air, the value of 21.4 being exceedingly high. It may be seen that the ratios were lowered with treatment in He at high temperatures, in particular >700 °C. Conversions were high for the catalysts pretreated at higher temperatures, but they lowered with calcination in air at higher temperatures; for instance, the catalysts calcined at 600, 700, 800, 900, and 1000 °C in air, followed by treatment at 600 °C in He, gave conversions of 86, 83, 37, 24, and 0% respectively. The reaction of *cis*-2-butene was performed over the CaO calcined in air at 700 °C; the isomerization of cis- to trans-form was negligible under the conditions shown

Table 1. Isomerizations of 1-Butene and 1-Pentene at 30 °C

Calcination temperature in air/°C	Pretreatment temperature[a] / °C	Conversion[c] / %	c-2/t-2[c]
300	300	0	
	300[b]	3	
350	350	0	
	400[b]	44	9.4
450	450	19	9.8
500	500	26	13.0
	500[b]	82	6.9
	500[b,d]	60(40)	10.1(5.3)
600	500	18	17.2
600	550	35	14.1
600	600	86	4.5
	600[b]	93	1.0
	600[b,d]	73(73)	7.0(1.6)
700	500	17(8)	21.4(18.8)
700	525	54(36)	15.4(6.2)
700	550	68(50)	11.4(5.5)
700	600	83(85)	5.7(2.3)
700	700	85	1.1
	700[b]	94	0.8
	700[b,d]	85	1.4
800	550	20	17.8
800	600	37	15.8
800	700	75	3.2
800	800	82	1.6
	800[b]	97	0.6
	800[b,d]	83	1.1
900	600	24	15.1
900	700	52	3.0
900	800	55	2.8
900	900	Trace	
	900[b]	88	0.8
	900[b,d]	60	2.7
1000	600	0	

a) In He stream for 1 h. b) $Ca(OH)_2$ was thermally decomposed in He for 1 h. c) Numerals in parentheses show values for the reaction of 1-pentene. d) Catalyst amount: 10 mg.

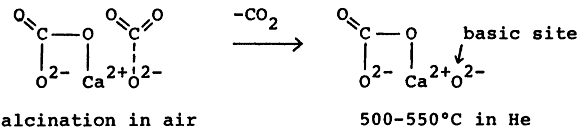
in Table 1 when the CaO was pretreated at 500—550 °C. The conversion and the c/t ratio were almost steady after a 30-min treatment. The CaO catalysts obtained by calcination in a He stream for 1 h were higher in activity, but much lower in the c/t ratio than those prepared by calcination in air.

The surface areas measured by the BET method using nitrogen gas were 46 and 34 m^2/g for the catalysts calcined at 700 and 900 °C in air respectively. The base strength of the present catalysts was examined by a color-change method using acid indicators; the highest strength was $27.0 \leqq H_- < 33.0$. The CaO prepared by calcination in air and then in He at 600 °C was completely poisoned with butylamine, NH_3, H_2O, and CO_2.

The catalysts heated at 600 and 700 °C, which showed high activities and c/t ratios, were also examined in the isomerization of 1-pentene (Table 1). The reactivity and c/t ratio were lower than those in the case of 1-butene, the highest ratio being 18.8.

High c/t ratios were observed compared with the literature values,[7] and higher values still were obtained from the reaction of 1-butene at 0 °C. That is, the catalyst calcined at 600 °C in air, followed by treatment at 550 °C in He, gave the ratio of 32.6 with a 52% conversion (catalyst amount: 100 mg) and that of 41.6 with a 32% conversion in the case of the catalyst treated at 700 °C in air and 500 °C in He. As for the high ratio given by solid base catalysts, it has been reported that the ratio of 55 was obtained over Na/Na_2CO_3 with only a 5% conversion from 1-butene.[9] O'Grady et al. achieved a reaction at −60 °C over Na/Al_2O_3 in a flow system, where the c/t ratio was observed to be 21.5 with a 54% conversion.[10]

The basic properties of CaO have been studied in detail by Tanabe et al.[1,11,12] The active sites for the isomerization of 1-butene to *cis*-2-butene are strongly basic O^{2-} ions, which occupy a large fraction of the basic sites. The strong basic site, O^{2-}, is easily poisoned with the acidic molecule, CO_2; CO_2 is adsorbed on CaO as a unidentate complex when the pressure of CO_2 is high and as a bidentate complex at low pressure. When CaO is prepared by calcining $Ca(OH)_2$ in air, the basic sites are poisoned with CO_2, and it does not work as a basic catalyst. The CO_2 is removed by evacuation at 300—500 °C, resulting in a high selectivity to *cis*-2-butene; Ca^{2+} ions exposed by evacuation at high temperatures are active as acidic sites for the formation of *trans*-2-butene from 1-butene, the c/t ratio being low. The cis-trans interconversion also occurs on unusually strong basic sites, which appear on evacuation at 700—900 °C.[13]



In view of the above explanation, the high c/t ratios under the pulse conditions may be interpreted by the following scheme. The unidentate CO_2 is removed by heating at 500—550 °C in a He flow, while the bidentate CO_2 remains at the surface; the exposed basic site, O^{2-}, is effective as the base catalysis for olefines. The following experimental phenomena seem to support this explanation: (1) When the catalyst was pretreated in He over 700 °C, the gas chromatographic peaks, as analyzed by a column connected to the reactor, were broadened; it is considered that the electrons of butenes were adsorbed on the Ca^{2+} created by the elimination of the bidentate CO_2. In this case, the conversion is high, and the c/t ratio is small, because of the acidic effect of Ca^{2+} (Table 1). (2) When CaO was prepared by the thermal decomposition of $Ca(OH)_2$ in a He stream, it is likely that the removal of CO_2 was easier; both acidic, Ca^{2+}, and basic, O^{2-} sites caused high conversions with low c/t ratios (Table 1). (3) The CaO catalyst obtained by calcination in air, followed by pretreatment in He at 450 °C, showed a 69% conversion for the reaction of 1-butene, but it was completely inactive when pretreated in air at 450 °C. (4) The cis to trans interconversion is more suppressed by the short contact time under the present pulse conditions than a closed circulating reaction.

References

1) T. Iizuka, H. Hattori, Y. Ohno, J. Sohma, and K. Tanabe, *J. Catal.*, **22**, 130 (1971).
2) H. Hattori, K. Shimazu, N. Yoshii, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **49**, 969 (1976).
3) M. Mohri, K. Tanabe, and H. Hattori, *J. Catal.*, **32**, 144 (1974).
4) H. Hattori, K. Maruyama, and K. Tanabe, *J. Catal.*, **44**, 50 (1976).
5) H. Pines and L. A. Schaap, *Adv. Catal.*, **12**, 117 (1960).
6) M. J. Baird and J. H. Lunsford, *J. Catal.*, **26**, 440 (1972).
7) K. Tanabe, N. Yoshii, and H. Hattori, *J. Chem. Soc., Chem. Commun.*, **1971**, 464.
8) H. Hattori, N. Yoshii, and K. Tanabe, Proc. 5th Intern. Congr. Catal., Palm Beach, 10-233 (1973).
9) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960).
10) H. Pines and W. M. Stalick, "Base-Catalyzed Reactions of Hydrocarbons and Related Compounds," Academic Press, New York, San Francisco, London (1977), p.32.
11) Y. Fukuda and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **46**, 1616 (1973).
12) K. Tanabe and R. Noyori, "Superacid-Superbase," Kodansha Scientific, Tokyo (1980), p.121.
13) T. Iizuka, Y. Endo, H. Hattori, and K. Tanabe, *Chem. Lett.*, **1976**, 803.