JOURNAL OF CATALYSIS 32, 144–147 (1974)

Isomerization of 1-Butene Catalyzed by Strontium Oxide

MAMORU MOHRI, KOZO TANABE, AND HIDESHI HATTORI

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

Received August 16, 1973

The nature of the isomerization of 1-butene over SrO has been investigated. The isomerization rate and selectivity (*cis*-2-butene/*trans*-2-butene) depended strongly on the pretreatment temperature of the catalyst. The activity appeared on pretreating *in vacuo* at 650°C or higher temperature and reached a maximum at 1000°C. The selectivity gradually decreased with the rise of pretreatment temperature. The degree of the removal of CO_2 correlated with the change in the activity and the selectivity.

n-Butylamine and ammonia poisoned preferentially the formation of *trans*-2-butene. Hydrogen treatment of the surface at high temperature resulted in the retardation of the formation of *cis*-2-butene, while the *trans*-2-butene formation was retarded by oxygen treatment.

The isomerization, both the formation of *trans*- and *cis*-2-butene, may occur on acid–base pair sites. The acid sites, presumably surface Sr^{2+}, largely contribute to the formation of *trans*-2-butene, whereas basic sites, presumably surface O^{2-}, do to the formation of *cis*-2-butene.

INTRODUCTION

Calcium and magnesium oxides have been reported to have basic property as well as reducing property on their surface (*1–7*). They also catalyze several kinds of reactions such as decomposition of diacetone alcohol (*8*), esterification of benzaldehyde (*9*), polymerization of styrene (*1*) and isomerization of unsaturated hydrocarbons (*10*). Among these reactions was the isomerization of butenes for which CaO and MgO showed very high activity and characteristic selectivity (*2, 3, 11*).

Strontium is the congener of calcium and magnesium, and its oxide form is expected to show similar catalytic action for these reactions. To investigate the catalysis by SrO would clarify more the catalytic properties of alkaline earth oxides and also the base-catalyzed reactions. From these points of view, the isomerization of 1-butene over SrO was investigated in connection with the change in surface state which was caused by evacuation at different temperatures, by treatment with oxygen or hydrogen and by poisoning with basic or acidic molecules.

EXPERIMENTAL METHODS

Strontium oxide was prepared by calcining strontium hydroxide in nickel crucible at 500°C in air for 4 hr and stored in a sealed glass tube. 1-Butene was purified by passing through molecular sieves 13X maintained at dry ice temperature after distilled in a vacuum system.

A closed circulation reactor having a volume of 880 ml was used for kinetic measurement. Strontium oxide of 10–20 mg was transferred into the reaction vessel made of quartz and evacuated at various temperatures for 2 hr. Fresh sample was used for each reaction.

The amount of dehydrated water and decarboxylated carbon dioxide were measured as follows. Strontium oxide was evacuated at room temperature in the system to which the trap and the manometer were attached. Then the oxide was heated at desired temperature for 2 hr, evolving gas being trapped with liquid nitrogen. The amount of gas evolved when liquid nitrogen was replaced by dry ice–acetone or when dry ice was taken off was taken as that of carbon dioxide or water, respectively.

In poisoning experiment, water, ammonia, carbon dioxide and *n*-butylamine were used as poison. Strontium oxide evacuated at 1000 or 1100°C was exposed to these gases at 30 or 60°C at certain pressure followed by evacuation at various temperatures.

The effect of the treatment with hydrogen or oxygen was also tested. Strontium oxide evacuated at 1000°C was treated with these gases at 1000 or 30°C under certain pressure followed by evacuation or, some time, no evacuation.

RESULTS

Surface areas of strontium oxide measured by nitrogen adsorption are 2.80, 1.60, 1.60, 1.65, 1.75 and 1.80 m^2/g when evacuated at 500, 600, 700, 800, 900 and 1000°C, respectively.

The activity is strongly dependent upon the evacuating temperature of strontium oxide. Figure 1 shows the change in activity with various evacuating temperatures. The activity appears when SrO is evacuated at 650°C and increases with the evacuation temperature to reach a maximum at 1000°C. This activity per unit surface area is almost 30 times higher than that of calcium oxide or magnesium oxide (*2*). The ratio of *cis*-2-butene to *trans*-2-butene produced from 1-butene decreases gradually with the increase of evacuating temperature as shown in Fig. 1.

The remarkable evolvement of dehydrated water at 350°C and that of decarboxylated CO_2 at 700°C were observed as shown in Fig. 2. The total amount of CO_2 evolved from SrO is 40 times as much as the amount which makes monolayer on its surface. The agreement of the temperature at which CO_2 starts to evolve with the temperature at which the activity appears demonstrates that the active sites are created by removing CO_2 from the surface.

The results of the poisoning experiments are listed in Table 1. All molecules listed in Table 1 poisoned the activity completely when evacuated at low temperature. On evacuating the catalyst adsorbing H_2O at 500°C, the activity became even higher than that of original surface. The selective poisoning for the formation of *trans*-2-butene was observed over the catalyst pretreated with ammonia followed by evacuation at 400°C.

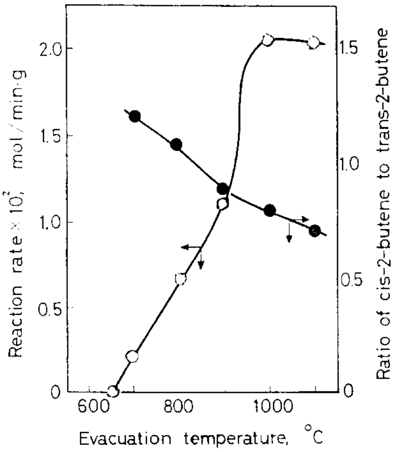

FIG. 1. Changes in activity and selectivity with evacuation temperature. (○-) activity, (●-) selectivity (*cis-/trans-*).

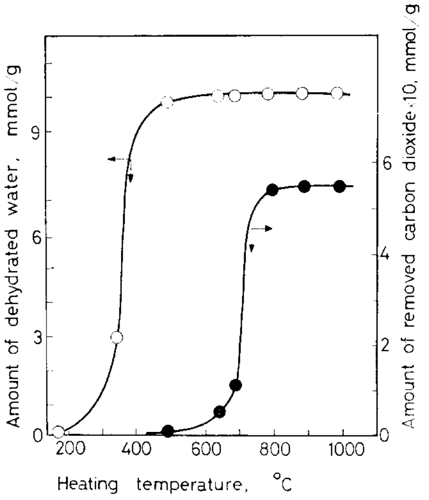

FIG. 2. Evolution of water and carbon dioxide at various temperatures. (○-) water, (●-) carbon dioxide.

TABLE 1
Poisoning Effect with Several Kinds of Molecules

Evacuation temp (°C)	Poisoning molecules	Desorption temp (°C)	Relative activity[a]		
			Total	1- to *cis*-	1- to *trans*-
1100	H_2O	220	0.0	0.0	0.0
	H_2O	500	1.3	1.3	1.2
1000	NH_3	30	0.0	0.0	0.0
	NH_3	400	0.35	0.37	0.06
	CO_2	30	0.0	0.0	0.0
	n-Butylamine	30	0.0	0.0	0.0
	n-Butylamine	400	0.004	0.006	0.001

[a] The ratio of the activity of SrO poisoned to that unpoisoned.

The effects of hydrogen or oxygen treatment are shown in Table 2. Hydrogen treatment at high temperature resulted in the decrease of activity especially for the formation of *cis*-2-butene from 1-butene, while the activity for the formation of *trans*-2-butene from 1-butene retained 80% of its original activity.

When catalyst was pretreated with O_2 at 1000°C and evacuated at the same temperature, the activity did not change so much. However, the pretreatment of catalyst with O_2 at 1000°C and the evacuation after cooling at 30°C resulted in complete deactivation. When the reaction was carried out in the presence of O_2, the remarkable retardation of the formation of *trans*-2-butene was observed.

Discussion

Alkaline earth oxides or hydroxides are easily combined with carbon dioxide by exposing to air to form their carbonate or basic carbonate forms. Magnesium and calcium hydroxides contain carbon dioxide and decarboxylation by evacuating at high temperature results in remarkable change in activity and selectivity for the isomerization of 1-butene (*2*). Strontium oxide prepared by calcining strontium hydroxide at 500°C in air and then evacuating below 650°C also contains large amount of carbon dioxide, which is considered to locate on/near the surface. By evacuating above 650°C, carbon dioxide begins to remove and strontium oxide will appear on the surface. Since the activity appeared on removing carbon dioxide, the surface of strontium oxide is considered to be active for the isomerization of 1-butene.

As calcium and magnesium oxides have been reported to have basic sites on the surface which are active sites for the isomerization of 1-butene (*2*), it is easily conceivable that strontium oxide has also basic sites on the surface and they are

TABLE 2
Effect of Oxygen or Hydrogen Treatment on the Activity[a]

Treating gas	Treating temp (°C)	Evacuation temp (°C)	Relative activity		
			Total	1- to *cis*-	1- to *trans*-
Oxygen	1000	30	0.0	0.0	0.0
	1000	1000	0.97	0.95	1.25
	30	—	0.29	0.50	0.05
Hydrogen	1000	1000	0.49	0.29	0.77

[a] All samples were pretreated at 1000°C.

active for the reaction. The complete poisoning of active sites observed when catalyst was exposed to ammonia or *n*-butylamine followed by evacuation at 30°C shows that not only basic sites but also acidic sites participate in the reaction. Preferential poisoning effect on the formation of *trans*-2-butene from 1-butene when the catalyst was exposed to ammonia or *n*-butylamine followed by evacuation at 400°C suggests that the active sites for the *trans*-2-butene formation are mainly acidic. The same poisoning effect as that observed over calcium and magnesium oxides (*2*) suggests that the nature of the active sites of strontium oxide is similar to that of calcium and magnesium oxides.

Strontium oxide evacuated at 1000°C is considered to have several kinds of sites on the surface such as anion vacancies, cation vacancies, O^{2-} sites or exposed Sr^{2+}. Hydrogen treatment at high temperature is expected to result in the removal of O^{2-} which would increase the number of exposed Sr^{2+}. On the other hand, the exposure of strontium oxide to oxygen at higher temperature results in the formation of peroxide (*12*) on the surface which might not be removed by evacuating at low temperature, but removed to recover its original surface by evacuating at high temperature. At room temperature, oxygen is considered to be adsorbed on Sr^{2+} rather than O^{2-}.

In comparison of these considerations with the results obtained on hydrogen or oxygen treated strontium oxide (Table 2), it could be suggested that Sr^{2+} largely contribute for the formation of *trans*-2-butene and O^{2-} for the formation of *cis*-2-butene. However, the activity for the formation of *trans*-2-butene was reduced by hydrogen treatment, even though it is not so much as that for the *cis*-2-butene formation. Also, the reduction of the activity for *cis*-2-butene formation was observed by adsorbing oxygen at 30°C which is not so drastic as that for *trans*-2-butene formation. These facts suggest that Sr^{2+} or O^{2-} alone is not active site for both reactions. They cooperate and Sr^{2+} plays main role for the formation of *trans*-2-butene and O^{2-} does for the formation of *cis*-2-butene. Since Sr^{2+} and O^{2-} could be considered to be acidic and basic site, respectively, this consideration interprets the results of poisoning experiments.

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