Isomerization of Butene over ZnO-SiO₂*

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Summary: Isomerization of *n*-butenes was investigated over binary oxides ZnO-SiO₂ having different mole ratios and the nature of active sites and the mechanism of the reaction were examined.

On mixing of ZnO and SiO₂, there appeared acidic sites and basic sites on the surface. The type of the acid sites was of Lewis acid which was determined by IR study of adsorbed pyridine.

The isomerization was not retarded by acidic molecule of CO₂ but by basic molecules such as pyridine and ammonia. The products formed over the deuterated catalyst contained a small amount of D atoms. The results of co-isomerization indicate that the reaction involves intramolecular hydrogen transfer and that the slow step is C-H bond cleavage. Therefore, it is concluded that the isomerization of butenes takes place on Lewis acid sites and is initiated by the abstraction of hydride ion which is the rate determining step.

1 Introduction

The mixed oxides of TiO₂-ZnO¹⁾ and TiO₂-SiO₂²⁾ were reported to show high acidity as well as high catalytic activity and selectivity which were not found in each component oxide. Recently, we found that ZnO-SiO₂ also exhibited high activity for the isomerization of 1-butene, though ZnO or SiO₂ showed little or no activity³⁾.

In the present work, we have studied the relation of the acidic and basic property of ZnO-SiO₂ with the catalytic action for the isomerization of butenes in order to elucidate the active sites and the reaction mechanism.

2 Experimental

2.1 Catalyst Preparation

ZnO-SiO₂ having different ratios of ZnO to SiO₂ was prepared from aqueous solution of zinc nitrate and ethyl silicate by co-precipitation with 28% aqueous ammonia. The final pH of the supernatant layer was 7~8. The precipitate was thoroughly washed with deionized water and dried at 110°C for 20 hr and then calcined in air at elevated temperatures (mostly 500°C) for 3 hr.

ZnO and SiO₂ were prepared from the aqueous solutions of zinc nitrate and ethyl silicate, respectively, by adding 28% aqueous ammonia

and washed, dried and calcined as above.

Deuteration of the catalyst was carried out as follows. Catalyst evacuated at 500°C was exposed to 10 torr of D₂O at 500°C for 5 min and evacuated for 15 min. This procedure was repeated three times and finally evacuated at 500°C for 1 hr.

2.2 X-Ray Diffraction and Surface Area

X-ray diffraction pattern was measured in powdered method by using Cu-K α ray as a source. Specific surface area was determined by BET method of nitrogen adsorption at liquid nitrogen temperature.

2.3 Acidity and Basicity

Acidity was measured by Johnson's method⁴⁾, using a series of Hammett indicators⁵⁾. 0.5 g of catalyst pretreated at various temperatures was put into benzene and titrated with 0.1 N *n*-butylamine benzene solution. Indicators used here were dicinnamalacetone (pK_a=-3.0), benzeneazodiphenylamine (pK_a=1.5), and dimethyl yellow (pK_a=3.3). Basicity was measured by the titration with 0.1 N benzoic acid in benzene, using phenolphthalein (pK_a=9.3) as an indicator.

2.4 Infrared Spectrum of Pyridine Adsorbed

Powdered sample was formed into disk by pressing at 1,800 kg/cm². The disk was evacuated at 500°C for 1 hr in *in situ* cell made of quartz with NaCl windows. After cooling to 150°C, the sample was exposed to pyridine vapor at 10 torr for 15 min followed by evacuation at 100°C for 30 min. All spectra were measured at room temperature on a Hitachi 215 IR spectrometer.

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2.5 Reaction Procedure

Reaction was carried out in a micro catalytic pulse reactor. A 0.25 g of catalyst calcined in air was placed in the reactor and pretreated at 500°C under the stream of helium for 3 hr. After cooling to the reaction temperature, 2.0 ml (NTP) of the reactant was introduced into helium stream of 1.1 ml/sec. The products were directly introduced to 5 m×6 mm chromatographic column which contained 30% DMF on alumina and operated at 0°C. The reaction temperature was in the range of 230~320°C. In poisoning experiments, O₂, CO₂, NH₃ and pyridine were injected between or mixed with butene pulses.

Two kinds of tracer experiments were carried out in which deuterium was used as a tracer. One was the reaction over deuterated catalyst and the other was co-isomerization reaction where nearly equimolar mixture of *cis*-2-butene (*d*₀) and perdeuterated *cis*-2-butene (*d*₈) was used as a reactant. In the tracer experiment, 1.0 ml (NTP) of the reactant was used and the products were trapped at liquid nitrogen temperature and introduced into 10 m×8 mm chromatographic column in which 30% propylene carbonate on Unipor C was packed and operated at 0°C. Each product was trapped separately and subjected to Mass spectral analysis. The mass spectral analyses were made on Hitachi RMU-6 spectrometer. The ionization voltages were kept sufficiently low so as to minimize fragmentation.

2.6 Preparation of Perdeuterated Butenes

Perdeuterated butenes were prepared by the exchange reaction of butene with D₂. The mixture of butene and D₂ (1 : 4) was recirculated for several hours at room temperature over MgO which had been evacuated at 550°C. Partly exchanged butenes were trapped at liq. N₂ and gas phase was replaced by fresh D₂. This procedure was repeated more than seven times. Finally butenes was isomerized at 400°C so as to enrich the 1-butene and *cis*-2-butene in the mixture. Then, three butenes were separated chromatographically and each butene was trapped. The isotopic purity was more than 99.6%, that is 97% of *d*₄ and 3% of *d*₇.

3 Results

3.1 Surface Properties

X-ray diffraction analyses showed that the

Table 1 X-Ray Analysis and Specific Surface Area of ZnO-SiO₂, ZnO, and SiO₂ after Calcined at 500°C in Air for 3 hr.

Catalyst	X-Ray Analysis	Specific Surface Area (m ² /g)
ZnO	ZnO	12
ZnO-SiO ₂ (9 : 1)	ZnO, Zn ₂ SiO ₄	25
ZnO-SiO ₂ (7 : 3)	ZnO	115
ZnO-SiO ₂ (1 : 1)	ZnO	140
ZnO-SiO ₂ (3 : 7)	amorphous	290
ZnO-SiO ₂ (1 : 9)	amorphous	103
SiO ₂	amorphous	291

●: $H_0 \leq -3.0$, ○: $H_0 \leq 1.5$, ●: $H_0 \leq 3.3$

Fig. 1 Acid Amount vs. % of ZnO

mixed oxides whose ZnO content was less than 30% were amorphous after calcination in air at 500°C. The pattern due to ZnO appeared in the samples whose ZnO content was over 50%. Specific surface areas of samples calcined at 500°C are listed in Table 1.

In Fig. 1, acidities at various acid strengths are plotted against catalyst composition. Although the single component oxides, SiO₂ and ZnO showed no and little acidity, respectively, remarkable increase in acidity was observed by mixing two oxides. The maximum acidity at $H_0 \leq 3.3$ was at the composition of ZnO : SiO₂ = 3 : 7. Basicity as well as acidity increased by mixing two oxides as shown in Fig. 2, where the maximum basicity was observed at the composition of ZnO : SiO₂ = 7 : 3.

The infrared spectra of pyridine adsorbed on the mixed oxides are shown in Fig. 3. On all the mixed oxides, bands at 1,450, 1,490, and 1,610 cm⁻¹ were observed. These bands are characteristic bands of coordinated pyridine⁶). On all samples, no bands were detected at 1,540 cm⁻¹ which was due to pyridinium ion⁶).

Fig. 2 Base Amount vs. % of ZnO

1: SiO₂, 2: ZnO-SiO₂ (1 : 9), 3: ZnO-SiO₂ (3 : 7),
4: ZnO-SiO₂ (1 : 1), 5: ZnO-SiO₂ (9 : 1), Broken
lines indicate backgrounds

Fig. 3 Infrared Spectra of Pyridine Adsorbed on ZnO-SiO₂

Therefore, the kind of acid sites on mixed oxides is Lewis type.

3.2 Isomerization of Butenes

In the reaction condition employed, only three *n*-butenes were produced. The first pulse was always converted higher than the following pulses. But the conversion became constant after the third pulse, which was about 20% less than that of the first pulse in all cases except over ZnO-SiO₂ (3 : 7) at 250°C. In this case, the

Conversions at indicated temperatures vs. ZnO content

Fig. 4 Isomerization of *cis*-2-Butene over ZnO-SiO₂

Conversions at indicated temperatures vs. ZnO content

Fig. 5 Isomerization of 1-Butene over ZnO-SiO₂

conversion decreased to a half of the first pulse. The conversions of *cis*-2-butene and of 1-butene over ZnO-SiO₂ having different ZnO/SiO₂ ratios are shown in **Figs. 4** and **5**.

For the isomerization of *cis*-2-butene, ZnO-SiO₂ (9 : 1) showed the maximum activity at all temperatures. For the isomerization of 1-butene, ZnO-SiO₂ (3 : 7) was most active at 250°C and 230°C but, at 270°C, ZnO-SiO₂ (9 : 1) was. In these figures, it is shown that the activity increased or appeared by mixing two oxides which were almost inactive by themselves.

The ratios of two butenes formed over ZnO-SiO₂ (3 : 7) and ZnO-SiO₂ (9 : 1) at 270°C are

listed in **Table 2** together with the equilibrium values at the same temperature. These ratios were obtained by extrapolation to zero conversion. On these catalysts, *cis*-2-butene was preferably formed from 1-butene and from *trans*-2-butene as well.

The effects of O₂, CO₂, pyridine and ammonia on the isomerization of *cis*-2-butene were examined over ZnO-SiO₂ (3 : 7) and ZnO-SiO₂ (9 : 1) at 270°C. Pyridine and ammonia decreased the activity and changed the selectivity. However, O₂ and CO₂ had no effect on both activity and selectivity. The poisoning effect of ammonia on ZnO-SiO₂ (9 : 1) is shown in **Fig. 6(a)**. The activity diminished when the mixture of *cis*-2-butene and ammonia was injected (*t*=0) and gradually recovered until 95% of its original one after 90 min. The ratio of *trans*-2-butene to 1-butene increased with the recovery of the activity and finally showed 3.2 which was higher than 2.5 of unpoisoned value. Substantially the same feature was observed with ZnO-SiO₂ (3 : 7) as shown in **Fig. 6(b)**.

Deuterium distributions in the isomerizations over deuterated catalyst and the co-isomerization are listed in **Table 3**. Catalyst used here was

Table 2 Selectivities in the Isomerization of Butenes over ZnO-SiO₂ at 270°C

Catalyst	Selectivity		
	<i>cis</i> -/ <i>trans</i> - from 1-Butene	1-/ <i>cis</i> - from <i>trans</i> -2- Butene	<i>trans</i> -/1- from <i>cis</i> -2-Butene
ZnO-SiO ₂ (3 : 7)	2.2	0.42	2.2
ZnO-SiO ₂ (9 : 1)	2.0	0.15	3.2
Equilibrium Value at 270°C	0.63	0.53	3.0

Table 3 D Atom Distribution in the Isomerization over Deuterated Catalyst and Co-isomerization of *cis*-2-Butene *d*₀/*d*₈

Catalyst: ZnO-SiO₂ (1 : 1), Reaction temperature: 250°C

Reactant	Product	% Each Product	Isotopic Fraction %							ϕ Value	Light Molecule /Heavy Molecule	Atoms Exch. /Molecule
			d_0	d_1	d_2	d_3	$d_4 \sim d_6$	d_7	d_8			
<i>cis</i> -	1-	2.1	86.5	13.4	0.1	0	0	0	0	0.136		
	<i>trans</i> -	6.4	98.6	1.4	0	0	0	0	0	0.014		
	<i>cis</i> -	91.5	100.0	0	0	0	0	0	0	0.0		
<i>cis</i> -	1-	17.3	93.6	6.3	0.1	0	0	0	0	0.065		
	<i>trans</i> -	30.2	97.3	2.6	0.1	0	0	0	0	0.028		
	<i>cis</i> -	52.7	98.2	1.8	0	0	0	0	0	0.018		
<i>cis</i> -	1-	16.7	82.0	14.5	3.0	0.3	0	0	0	0.206		
	<i>trans</i> -	50.8	88.8	8.7	2.5	0	0	0	0	0.137		
	<i>cis</i> -	32.5	86.6	9.7	3.4	0	0	0	0	0.174		
1-	1-	42.4	97.2	2.5	0	0	0	0	0	0.025		
	<i>trans</i> -	26.6	99.1	0.9	0	0	0	0	0	0.009		
	<i>cis</i> -	31.0	98.9	1.1	0	0	0	0	0	0.011		
<i>cis</i> - (d_0/d_8)	1-	8.2	63.7	2.7	0	0	0	2.3	31.3		1.98	0.06
	<i>trans</i> -	13.7	67.0	0.8	0	0	0	1.2	31.0		2.18	0.02
	<i>cis</i> -	78.1	45.6	0	0	0	0	1.4	53.0		0.82	

ZnO-SiO₂ (1 : 1)

Over deuterated catalyst, only a small amount of D atoms were included in three butenes. The D concentration was the highest in 1-butene even when 1-butene was used as a reactant. The number of D atoms exchanged under the condition that the reaction products reached almost an equilibrium composition by circulating *cis*-2-butene over deuterated catalyst for 15 min was 1.7×10^{19} atoms/g·catalyst (1.2×10^{13} atoms/cm²).

In co-isomerization, the products were mostly *d*₀ and *d*₈ compounds. The number of H(or D) atoms exchanged per molecule (AEM) was calculated by the equation⁷⁾,

$$\text{AEM} = \sum_{i=1}^4 i \cdot d_i + \sum_{i=5}^8 (8-i) \cdot d_i,$$

Fig. 6 The Effect of Ammonia Poisoning on the Isomerization of *cis*-2-Butene over ZnO-SiO₂ (1 : 1) (a) and ZnO-SiO₂ (3 : 7) (b) at 270°C

where d_i represents the fraction containing i atoms of D in a molecule. AEM was calculated to be 0.06 and 0.02 for the formation of 1-butene and *trans*-2-butene, respectively. If the reaction involved intermolecular H (or D) transfer, AEM should be $2IE/(IE+1)^{2,8)}$ where IE represents isotope effect. AEM should be zero for the isomerization which involves intramolecular H (or D) transfer. Small values of AEM (0.06 and 0.02) demonstrate that both of the formations of 1-butene and *trans*-2-butene involve mostly intramolecular H(or D) transfer.

The ratios of "Light molecule" to "heavy molecule" were calculated by the equation⁷⁾,

$$\begin{aligned} & \text{"light molecule"/"heavy molecule"} \\ &= \sum_{i=0}^3 d_i + \frac{1}{2} d_4 \bigg/ \sum_{i=5}^8 d_i + \frac{1}{2} d_4, \end{aligned}$$

where d_4 was assumed to come equally from d_0 and d_8 reactant, "light molecule" and "heavy molecule" represent the molecules which come from light reactant and perdeuterated reactant, respectively. The ratios were calculated to be 1.98 and 2.18 for the formation of 1-butene and *trans*-2-butene, respectively. Since this ratio represents the isotope effect (IE), both of the reactions from *cis*-2-butene showed nearly the same isotope effect.

4 Discussion

Mixing of two oxides which had no or little acidity, basicity, and activity by themselves resulted in remarkable increase in these properties. Since the isomerization of butenes is well known to be catalyzed by acid sites and by basic sites, either acid sites or basic sites or both of them in the mixed oxides are considered to be active sites for the reaction.

Foster and Cvetanovic have studied the stereoselectivity of the isomerization of butenes over basic, acidic and metal catalysts and found a general rule of the stereoselectivity⁹⁾. Over basic catalysts where π -allyl carbanions were considered to be intermediates, high ratio of *cis*-2-butene to *trans*-2-butene from 1-butene and exclusive double bond shift in the isomerization of 2-butenes were observed. Over acidic catalysts where carbonium ions were considered to be intermediates, the *cis/trans* ratios from 1-butene were low and *cis-trans* conversions were much faster than the double bond shift in the isomerization of 2-butenes. In accordance with the rule, many workers have found the same selectivities^{10)~13)}.

Judging from the selectivity observed in this study, the active sites of ZnO-SiO₂ are considered to be acidic sites. In poisoning experiments, only basic molecules such as pyridine and ammonia retarded the reaction and acidic molecule of CO₂ which was assumed to adsorb on basic sites did not decrease the activity. This also suggests that the active sites are acidic sites.

The nature of the acidic sites on the mixed oxides is suggested to be Lewis acid by IR spectra of adsorbed pyridine which showed no absorption of pyridinium ion but of coordinated pyridine. This estimation was also supported by the tracer experiments in which only small amount of D atom was included in the products when reacted over deuterated catalyst.

Furthermore, the result of co-isomerization of *cis*-2-butene indicates that the reaction involves intramolecular H(or D) transfer. The intramolecular H (or D) transfer means inevitably that the abstraction of H (or D) from the reactant occurs first, followed by the addition of H(or D) at a later step. If the active sites are Brønsted acid, the addition of H(or D) to the reactant should occur first to form carbonium ion and the reaction involves intermolecular H(or D) transfer. This is not the case. So, active sites are suggested to be Lewis type.

The ratios of "light molecule" to "heavy molecule" were close to 2 for the formation of both 1-butene and *trans*-2-butene. The ratio can be regarded as isotope effect. According to the normal calculation of the isotope effect, the maximum value is 3.5 at 250°C. Relatively high values of the isotope effect observed indicate that the slow step is the cleavage of C-H bond. The slow step is common for two kinds of isomerizations and the abstraction of H from the reactant. Since the active sites were estimated to be acidic, hydride ion (H⁻) may be abstracted at allylic hydrogen of butenes to form allylic carbonium ion.

The formation of *trans*-2-butene from *cis*-2-butene involves the rotation of C²-C³ bond. If the allylic carbonium ions are adsorbed in such a configuration as the rotation of C²-C³ bond being limited, the ratio of *trans*-2-butene to 1-butene would be low and the isotope effect would not be observed for the formation of *trans*-2-butene. On the other hand, if the C²-C³ bond rotates freely, the ratio of *trans*-2-butene to 1-butene would be close to the equilibrium

value. This is the observed result.

The mechanism of the acidity generation of ZnO-SiO₂ is explained by the hypothesis regarding the surface acidity of various mixed oxides that we proposed previously¹⁴⁾.

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