The Nature of Active Sites on TiO_2 and TiO_2–SiO_2 for the Isomerization of Butenes

II. Tracer Study on the Variation of Active Sites with Pretreatments

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The coisomerization of light and perdeuterated *cis*-2-butene was carried out over TiO_2 and TiO_2–SiO_2 catalysts pretreated under different conditions. The reaction involved an intermolecular hydrogen transfer over the catalysts evacuated at 250°C, while an intramolecular hydrogen transfer became involved over the catalysts evacuated at 600°C. Oxygen treatment on the catalysts previously evacuated at 600°C resulted in the intermolecular hydrogen transfer on TiO_2–SiO_2, but did not change the intramolecular hydrogen transfer on TiO_2. These results confirm the variations of the nature of active sites with pretreatment conditions that were suggested in the previous paper.

INTRODUCTION

In the previous paper, the nature of active sites on TiO_2 and TiO_2–SiO_2 for the isomerization of butenes was studied (*1*). The remarkable variations of the activity, the selectivity, and the electron donating property of these catalysts with the evacuation temperature led us to estimate the nature of active sites as follows. On both catalysts evacuated at low temperature (<400°C), acidic sites were operative and the reaction proceeded via carbenium ion intermediates. When evacuated at high temperature, acidic sites were eliminated, electron donating sites were generated, and the reaction proceeded via carbanion intermediates. It was suggested that the oxygen treatment results in the regeneration of acid sites on TiO_2–SiO_2 that had been evacuated at high temperature, but on TiO_2 it appeared that oxygen treatment results only in elimination of electron donating sites without regeneration of acid sites.

In the present work, we have tried to confirm the above estimations by the tracer study of butene isomerization; mainly by the coisomerization of light and perdeuterated butene which was developed by Hightower and Hall (*2*). If the reaction proceeds via a carbenium ion mechanism on acid sites, it should involve intermolecular hydrogen transfer and if the reaction takes place via a carbanion mechanism on electron donating sites, intramolecular hydrogen transfer should be involved.

EXPERIMENTAL

A microcatalytic pulse reactor was employed for carrying out the reaction. About 20 μmol of butene was passed over 0.25 g of the catalyst in a helium carrier, and products were trapped by liquid N_2 before flash evaporated into a gas chromatographic column (10 m of propylene carbonate on Uniport C in 8-mm-o.d. Cu tubing) operated at 0°C. The separated

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products were collected at liquid N_2 and subjected to mass spectral analysis. Appropriate conversion levels could be achieved by varying the reaction temperature and the flow rate of the carrier gas. In some experiments, 1.0 g of the catalyst was employed.

TiO_2 was prepared by the hydrolysis of titanium tetrachloride, which was named TiO_2 (I) in the previous paper (1). TiO_2–SiO_2 was prepared by the coprecipitation of a mixed solution of ethyl orthosilicate and titanium tetrachloride. The atomic ratio of Ti and Si was 9. Details of the preparation were described in the previous paper (1). Specific surface areas of TiO_2 were 222 and 52 m^2/g, and those of TiO_2–SiO_2 were 272 and 135 m^2/g after the evacuation at 250 and 600°C, respectively.

The catalyst was pretreated by evacuating at 250° or 600°C for 2 hr. A subsequent oxygen treatment was done on the catalyst previously evacuated at 600°C for 2 hr. Five Torr (1 Torr = 133.3 N/m^2) of oxygen was introduced into the reactor at 450°C and recirculated in the loop with a liquid N_2 trap for 1 hr. The catalyst was then cooled to 200°C under the oxygen gas followed by evacuation at this temperature for 30 min. For the reaction over deuterated catalyst, surface H was exchanged with D by exposing the catalyst previously evacuated at 250°C to a D_2O stream of about 10 Torr and finally evacuating at 250°C for 2 hr.

A mixture containing about equal amounts of cis-2-butene and perdeuterated cis-2-butene was used for the coisomerization reaction, and cis-2-butene was used for the reaction over deuterium exchanged catalyst. Isotopic purity of the perdeuterated cis-2-butene was more than 99.6%.

RESULTS AND DISCUSSION

The isotopic distributions of butenes are listed in Table 1. Over TiO_2 and TiO_2–SiO_2 pretreated at 250°C, the products contained considerable fraction of mono-exchanged d_1 and d_7 isotopic species. The numbers of H (or D) atoms exchanged per molecule (AEM) were more than 0.34. If there were no isotope effect, AEM would be 0.5 for the intermolecular H transfer and would decrease as the isotope effect becomes larger. Therefore, the isomerization mostly involves intermoleculare hydrogen transfer.

Over deuterium exchanged catalysts, considerable amounts of d_1 were produced. This, combined with the conclusion of the intermolecular H (or D) transfer, strongly suggests that the reaction proceeds via carbenium ion intermediates mainly on Brönsted acid sites of the catalysts evacuated at 250°C.

The number of H (or D) atoms exchanged per molecule was always lower in trans-2-butene than in 1-butene. If butylcarbenium ions can rotate around the C_{II}–C_{III} bond in the adsorbed state, trans-2-butene may be formed from the carbenium ion by releasing either the H that came from the surface or the H that was originally the vinyllic hydrogen of cis-2-butene. This might result in the smaller number of exchanged H (or D) in trans-2-butene.

Over TiO_2 and TiO_2–SiO_2 pretreated at 600°C, only negligible amounts of butenes other than d_0 and d_8 were produced. This indicates that the reaction involves intramolecular H (or D) transfer which is expected when reactions proceed via carbanion intermediates. A large ratio of "light molecule" to "heavy molecule" (IE) in the 1-butene suggests that the slow step is the cleavage of a C–H bond. On the other hand, cis–trans rotation within the carbanion or allyl carbanion is probably the slow step as seen by the small isotope effect for the formation of trans-2-butene.

The oxygen treatment produced a different effect on the TiO_2–SiO_2 than it did on TiO_2. Considerable amounts of d_1–d_7 species were formed over the oxygen treated TiO_2–SiO_2, and the AEM were

TABLE 1

Isotopic Distributions of Butenes

Catalyst	Treatment	Reaction temperature (°C)	Flow rate (ml/min)	Product	Each product (%)	Isotopic distributions (%)									AEM[a]	IE[b]
						d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
TiO$_2$	250°C evacuation	68	70.5	1	2.1	55.4	11.5	0.4	0	0	0.3	3.1	23.3	6.1	0.43	2.1
				t	7.2	43.0	9.9	0.2	0	0	0	2.8	18.3	25.9	0.34	1.1
				c	90.7	46.7	1.3	0	0	0	0	0.5	5.8	45.7	0.10	0.9
TiO$_2$	D$_2$O treatment	68	70.5	1	5.5	46.5	46.3	6.8	0.5	0	0	0	0	0	0.61	—
				t	17.1	63.4	32.9	3.7	0	0	0	0	0	0	0.40	—
				c	77.4	88.8	10.6	0.6	0	0	0	0	0	0	0.12	—
TiO$_2$	600°C evacuation	85	70.5	1	0.45	78.0	1.4	0	0	0	0	0	3.5	17.1	0.049	3.9
				t	0.48	51.8	0.6	0	0	0	0	0	3.0	44.5	0.036	1.1
				c	99.1	49.2	0	0	0	0	0	0	2.9	47.9	0.029	1.0
TiO$_2$[c]	600°C evacuation	150	39.0	1	5.6	72.9	0.6	0	0	0	0	0.1	2.4	24.1	0.032	2.8
				t	2.6	62.7	0.5	0	0	0	0	0	2.6	34.2	0.031	1.7
				c	91.8	49.2	0	0	0	0	0	0.1	3.0	47.7	0.032	1.0
TiO$_2$[c]	O$_2$ treatment	100	18.0	1	8.8	76.3	1.9	0	0	0	0	0.2	3.3	19.7	0.055	3.6
				t	3.8	68.1	3.7	0	0	0	0	0	5.1	23.0	0.088	2.6
				c	87.4	44.8	0.4	0	0	0	0	0.3	3.8	50.7	0.048	0.8
TiO$_2$	O$_2$ treatment	150	34.5	1	1.70	75.7	0.6	0	0	0	0	0.3	2.6	20.8	0.038	3.2
				t	0.38	53.8	1.4	1.1	1.3	1.7	1.3	1.3	3.5	34.6	0.24	1.6[a]
				c	97.9	47.8	0	0	0	0	0	0.3	2.9	49.0	0.035	0.9

Catalyst	Treatment					d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
TiO₂[c]	O₂ treatment	200	100	l	14.3	64.4	2.4	0	0	0	0	0	0.3	5.4	27.4	0.084	2.0
				t	5.5	67.9	3.5	0	0	0	0	0	0.3	7.1	21.2	0.112	2.5
				c	80.2	43.2	0.6	0	0	0	0	0	0.2	4.2	51.8	0.052	0.8
TiO₂-SiO₂	250°C evacuation	68	75.0	l	5.0	47.4	17.8	1.5	0	0	0.5	4.6	21.6	6.6	0.53	2.0
				t	19.5	40.1	13.6	0.7	0	0	0.2	4.0	21.7	19.7	0.45	1.2
				c	75.5	43.9	4.7	0.1	0	0	0	1.3	9.7	40.3	0.17	1.0
TiO₂	D₂O treatment	68	75.0	l	7.3	56.1	36.1	7.2	0.6	0	0	0	0	0	0.52	—
				t	39.6	66.2	29.9	3.8	0.1	0	0	0	0	0	0.38	—
				c	53.2	80.9	17.3	1.8	0	0	0	0	0	0	0.21	—
TiO₂	600°C evacuation	85	70.5	l	1.03	80.7	0.6	0	0	0	0	0	1.7	17.0	0.023	4.4
				t	0.59	54.1	1.2	0	0	0	0	0	3.3	41.5	0.045	1.2
				c	98.4	48.7	0	0	0	0	0	0	3.1	48.0	0.031	1.0
TiO₂	O₂ treatment	85	70.5	l	0.50	60.5	11.0	1.9	0.3	0	0.5	2.0	9.1	14.7	0.30	2.8
				t	1.18	37.4	10.4	3.0	0.9	0.9	1.3	3.6	11.7	30.8	0.46	1.1
				c	98.3	48.1	0.1	0	0	0	0	0.4	3.0	48.4	0.039	0.9
TiO₂	O₂ treatment	150	35.3	l	3.9	52.9	14.0	1.0	0.1	0	0.3	1.8	13.3	16.6	0.34	2.1
				t	4.3	39.1	14.4	1.7	0.3	0.2	0.0	3.2	16.4	24.1	0.44	1.3
				c	91.7	46.7	1.2	0	0	0	0	0.7	4.4	47.0	0.070	0.9

[a] Obtained by the equation $\sum_{i=0}^{4} i \cdot d_i + \sum_{i=5}^{8} (8-i) \cdot d_i$.

[b] $\sum_{i=0}^{3} d_i + \tfrac{1}{2}d_4 \Big/ \sum_{i=5}^{8} d_i + \tfrac{1}{2}d_4$.

[c] 1.0 g of catalyst was employed.

[d] Ratio of d_0 to d_8.

above 0.3 for both 1-butene and *trans*-2-butene. Therefore, intermolecular hydrogen transfer became the predominant isomerization after the oxygen treatment. This result is in agreement with the previous suggestion that acid sites could be regenerated by oxygen treatment on TiO_2–SiO_2. Since no hydrogen atoms were involved, the regenerated acid sites should be of the Lewis type.

For TiO_2, the oxygen treatment resulted in a decrease in activity. Although H–D scrambling was observed in the *trans*-2-butene to some extent, the isomerization still involved intramolecular hydrogen transfer, since d_0 and d_8 were the main products with only small fractions of d_1 and d_7 being produced.

These results provide strong support for the conclusions suggested in our previous paper. The active sites on TiO_2 and TiO_2–SiO_2 evacuated at low temperature are acidic. By evacuation at high temperature, electron donating sites are generated with the consumption of acid sites. The electron donating sites on TiO_2–SiO_2 are able to reconvert into acid sites on treatment with oxygen, but those on TiO_2 are simply eliminated by oxygen treatment without the acid sites being regenerated.

REFERENCES

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