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Active Sites of MoO_3 and MoO_3-SiO_2 Catalysts for Isomerizaiton of Butenes. Characterization by Tracer Study

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Synopsis. Deuterium atom distribution of butenes in the coisomerization of *cis*-2-butene d_0/d_8 over MoO_3 and MoO_3–SiO_2 indicates that the reaction involves intermolecular hydrogen transfer for both catalysts. Butenvs produced over deuterium-exchanged MoO_3–SiO_2 contain deuterium atoms, those produced over deuterium-exchanged MoO_3 none.

Catalytic properties of MoO_3–SiO_2 and MoO_3 were investigated in view of surface acidity and basicity.[1] For the isomerization of butenes, it was suggested from the correlation of activity with acidity or basicity that the active sites on MoO_3–SiO_2 are acidic, while those on MoO_3 are basic. If the isomerization proceeds on the acidic sites, a hydrogen atom of butene is exchanged during the course of reaction. If the active sites are of Brönsted type, surface hydrogen atoms would be incorporated into the products. In the mechanism proposed for basic sites, the isomerization is initiated by the abstraction of a proton from butene to form the carbanion. In this case hydrogen atoms are not exchanged between butenes unless hydrogen atoms rapidly migrate over the surface.

Hightower and Hall investigated the isomerization of butene over Al_2O_3 and SiO_2–Al_2O_3 by means of a "tracer study" using deuterium as a tracer.[2] They developed a coisomerization technique, in which a mixture of nondeuterated and perdeuterated butene was used as a reactant. If the isomerization involves intermolecular hydrogen transfer, the product should contain both non-exchanged isotopic species d_0 and d_8, and mono-exchanged isotopic species d_1 and d_7. In the case of intramolecular hydrogen transfer, only non-exchanged isotopic species should be produced. The relative ratio of product from nondeuterated reactant to that from perdeuterated reactant shows an isotope effect when extraporated to zero conversion.

In the present work the coisomerization of butene over MoO_3–SiO_2 and MoO_3, and the reaction over the deuterium exchanged catalysts were carried out, the reaction mechanism and the nature of active sites being investigated.

Experimental

Molybdenum trioxide (MoO_3) was prepared by the precipitation from an aqueous solution of ammonium molybdate with nitric acid. MoO_3–SiO_2 was prepared by precipitation from a mixture of ammonium molybdate and tetraethyl orthosilicate with nitric acid. Precipitates were dried at 100 °C and finally calcined at 500 °C for 3 h in air. Details were described previously.[1]

A microcatalytic pulse reactor was used for the reaction. A catalyst (0.25 g) was evacuated at 500 °C prior to reaction. For the reaction over deuterium exchanged catalyst, surface hydrogen atoms were exchanged with deuterium atoms by exposing the catalyst evacuated to *ca.* 10 Torr of D_2O at 250 °C, the catalyst being evacuated at 500 °C for 1 h.

ca. 40 μmol of butene was passed over the catalyst in a helium carrier, and products were trapped by liquid nitrogen before being flash evaporated into a gaschromatographic column (Propylene carbonate on Uniport C in 10-m length, 8-mm o.d. Cu-tubing) operated at 0 °C. The separated products were collected in liquid nitrogen traps and subjected to mass spectroscopic analysis.

For the coisomerization, a mixture containing about equal amounts of nondeuterated and perdeuterated *cis*-2-butene was used as a reactant. The isotopic purity of the perdeuterated *cis*-2-butene was higher than 99.6%.

Results and Discussion

The isotopic profiles of butenes in the coisomerization and the reactions over deuterium exchanged catalysts are given in Table 1. The number of H (or D) atoms exchanged per molecule (AEM) was calculated by

$$\sum_{i=0}^{4} i\cdot N_i + \sum_{5}^{8} (8-i)N_i,$$

where N_i is a mole fraction of each isotopic species containing i deuterium atoms. An isotope effect (IE) was obtained by the relative reactivity of nondeuterated species to that of perdeuterated species, which was calculated by

$$\left(\sum_{0}^{3}N_i+\frac{1}{2}N_4\right)\Big/\left(\sum_{5}^{8}N_i+\frac{1}{2}N_4\right),$$

where d_4 species in the product was assumed to be produced equally from d_0 and d_8 reactant.

Over both MoO_3 and MoO_3–SiO_2, the products in the coisomerization contained a considerable fraction of mono-exchanged d_1 and d_7 isotopic species. If there were no isotope effect, the AEM value at zero conversion would be 0.5 for the intermolecular hydrogen transfer, and would decrease when isotope effect becomes larger. AEM values of 1-butene close to 0.5 for both catalysts indicate that the isomerization to 1-butene involves intermolecular hydrogen transfer over both catalysts.

Considerable amounts of d_1 species were produced over deuterium exchanged MoO_3–SiO_2, (Table 2). This in addition to the existence of acidic sites on the surface[1] and the occurrence of intermolecular hydrogen transfer, strongly suggest that the active sites are of a Brönsted type and the isomerization to 1-butene proceeds *via* a carbenium ion intermediate. The number of H (or D) atoms exchanged per molecule in *trans*-2-butene was smaller than that in 1-butene. If the carbenium ions are weakly bonded to the surface, *trans*-2-butene may be produced from the carbenium ion by release of either the hydrogen atom that came from the surface or the hydrogen atom that was originally the vinyllic

Table 1. Isomerization of *cis*-2-butene and coisomerization of *cis*-2-butene d_0/d_8 over MoO_3–SiO_2 and MoO_3 at 250 °C

Catalyst	Pulse number	Reactant	Product	Each product (%)	Isotopic distributions (%)									AEM	IE
					d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
MoO_3–SiO_2	1	d_0	1	5.5											
			t	9.2											
			c	85.3											
	3	d_0	1	4.6											
			t	7.5											
			c	87.9											
	4	d_0, d_8	1	2.9	42.5	17.6	0.4	0	0	0	1.0	23.3	15.2	0.437	1.53
			t	5.7	39.5	10.6	0	0	0	0	0.7	18.3	30.8	0.303	1.00
			c	91.4	50.3	0.4	0	0	0	0	0	2.2	46.7	0.026	1.03
	5	d_0	1	4.2											
			t	6.9											
			c	88.9											
MoO_3	1	d_0	1	10.8											
			t	19.3											
			c	68.9											
	3	d_0	1	3.5											
			t	5.5											
			c	91.0											
	5	d_0	1	2.3											
			t	3.5											
			c	94.2											
	6	d_0, d_8	1	1.4	42.9	20.7	0.1	0	0	0	0.7	19.6	16.0	0.419	1.75
			t	2.9	39.1	11.3	0	0	0	0	0.3	14.0	35.4	0.259	1.01
			c	95.7	50.0	0.8	0	0	0	0	0	2.1	47.1	0.029	1.03
	7	d_0	1	7.1											
			t	10.9											
			c	82.0											

Table 2. Isomerization of *cis*-2-butene over deuterium exchanged MoO_3–SiO_2 and MoO_3 at 250 °C

Catalyst	Product	Each product (%)	Isotopic distributions (%)					ϕ value
			d_0	d_1	d_2	d_3	d_4—d_8	
MoO_3–SiO_2	1	16.9	72.3	24.8	3.0	0.1	0	0.311
	t	36.2	81.1	17.9	1.0	0	0	0.199
	c	46.9	86.3	13.0	0.7	0	0	0.144
MoO_3	1	7.2	100	0	0	0	0	0
	t	11.5	100	0	0	0	0	0
	c	81.3	100	0	0	0	0	0

hydrogen of *cis*-2-butene. This might result in a smaller number of exchanged hydrogen atoms in *trans*-2-butene.

On the other hand, no deuterium was incorporated into the products over deuterium exchanged MoO_3. Surface H (or D) atoms should not participate in the reaction. The active sites on MoO_3 were poisoned not by ammonia but by carbon dioxide, suggesting that MoO_3 is of a basic type of catalyst.[1] The reaction could be initiated by the abstraction of the allylic proton in *cis*-2-butene by basic sites. If the proton migrates over the surface very rapidly, intermolecular hydrogen transfer would occur.

On introducing an oxygen pulse to MoO_3 after the six pulses of butene, the activity was restored to the level of the second butene pulse. The activity was also recovered almost completely by allowing the catalyst to stand in the reactor overnight at room temperature with no carrier gas flowing. The results suggest that surface Mo^{6+} ions rather than Mo^{5+} ions participate in the reaction, though the amplitude of Mo^{5+} signal in the ESR spectrum decreases only slightly by exposure to oxygen at 250 °C. The Mo^{5+} ions may be produced by a loss of oxygen atoms attached to Mo^{6+} ions. By allowing the catalyst to stand overnight, oxygen atoms seem to diffuse from the bulk to the surface and Mo^{6+} ions are reproduced. The abstraction of protons from butene molecules seems to be performed much more easily by oxygen ions than by metal cations. Thus, it is suggested that the active sites on MoO_3 consist of pairs of oxygen ions and Mo^{6+} on the surface, at least in the initial stage of the reaction.

References

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2) J. W. Hightower and K. Hall, *Chem. Eng. Prog. Symp. Ser.*, **63**, 122 (1967).