Acidic Property and Catalytic Activity of Tungsten Oxide

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(Received January 5, 1978)

A maximum activity of tungsten oxide for the isomerization of 1-butene was observed when the catalyst was evacuated at 600 °C, the ratio of *cis*-2-butene to *trans*-2-butene being 1.4. The activity was lost by the addition of NH_3, but not affected by the addition of CO_2 or H_2O. The oxidation states of tungsten oxide treated with hydrogen at 550 and 650 °C were $WO_{2.89}$ and WO_2, respectively. The activity of $WO_{2.89}$ for the double bond isomerization of 1-butene was almost the same as that of WO_3, but the activity of WO_2 for the double bond and skeletal isomerization of 1-butene and the dehydration of isopropanol was higher than that of WO_3 or $WO_{2.89}$. The coisomerization of *cis*-2-butene-d_0/d_8 revealed that the double bond isomerization of butenes proceeds by an intermolecular hydrogen transfer mechanism. When *cis*-2-butene-d_8 was introduced to the catalyst on which *cis*-2-butene-d_0 had been preadsorbed, the reactant and the product containing much of H were obtained, no d_0-species being observed. It was concluded that the active sites for the isomerization of butenes are protons of polymerized butene formed by the adsorption on Lewis acid sites of tungsten oxide surface and the isomerization takes place *via* carbenium ion intermediates.

Tungsten oxide mixed with SiO_2 or Al_2O_3 is a well-known catalyst for the hydration$^{1)}$ and disproportionation$^{2)}$ of olefins. Combined with MoO_3, NiO, V_2O_5, or CeO_2, tungsten oxide becomes catalytically active for the hydrocracking,$^{3)}$ hydrotreating$^{4)}$ and reforming$^{5)}$ of hydrocarbons, the isomerization of paraffins,$^{6)}$ and the oxidative dehydrogenation of butene.$^{7)}$ Thus, tungsten oxide is one component of industrially important catalysts. Tungsten oxide itself is known to catalyze the oxidation of 1-butene to carbon dioxide$^{8)}$ and tungsten oxide reduced with hydrogen was reported recently to catalyze the isomerization and hydrocracking of heptane, the dealkylation of isopropyl benzene and the dehydration of isopropyl alcohol, where the change in catalytic action with the change of oxidation state and acidic property of tungsten oxide was studied.$^{9)}$ The present work was initiated to learn more about the role of acid-base property of tungsten oxide for the isomerization of butenes and to elucidate the nature of active sites and the reaction mechanism.

Experimental Methods

Tungsten trioxide was prepared by calcination of ammonium paratungstate $[(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O]$ at 550 °C for 10 h in air. This was used for the reaction after evacuation at different temperatures for 3 h. X-Ray diffraction patterns were recorded on a Toshiba ADG-301 with a powdered sample over the range of $2\theta=10$—60°. Cu K_α was used as the radiation source.

1-Butene was purified by passage through 4A molecular sieves kept at −78 °C. Perdeuterated *cis*-2-butene was prepared by exchange of butenes with D_2 over MgO.$^{10)}$ Isopropanol was purified by passage through 4A molecular sieves at 0 °C.

Two different types of reactors were employed. A recirculation reactor which had a volume of 270 cm^3 was used for kinetic measurements of the double bond and skeletal isomerization of 1-butene and the dehydration of isopropanol. Reaction products were periodically withdrawn from the system and analyzed by gas chromatography. For the isomerizations, a 4-m gas chromatographic column containing propylene carbonate on Celite 545 was operated at 0 °C. For the dehydration, a 1-m column packed with TPC on Celite 545 was operated at 100 °C.

In poisoning experiments, NH_3, H_2O, CO_2, and a mixture of H_2O and CO_2 were used as poisons. The catalyst that had been evacuated at 500 °C was exposed to a poison at 100 °C for 30 min (NH_3, H_2O+CO_2) or 60 min (H_2O, CO_2) and then evacuated at 100 °C for 1 or 3 h.

Oxygen and H_2 treatments were carried out as follows. To the catalyst that had been evacuated at 500 °C, 15 Torr of O_2 was admitted at 500 °C and recirculated at this temperature for 1 h, the trap attached to the recirculating loop being cooled by liquid N_2. After the treatment, the catalyst was evacuated at 500 for 30 min. Hydrogen treatment was performed at 500 and 650 °C. In the treatment at 500 °C, 50 Torr of H_2 was admitted to the catalyst that had been evacuated at 500 °C and recirculated for 1 h with a liquid N_2 trap. The catalyst was evacuated at 500 °C for 1 h. In the treatment at 650 °C, the catalyst that had been evacuated at 650 °C was exposed to 400 Torr of H_2. After H_2 was recirculated for 5 h with a liquid N_2 trap, the catalyst was evacuated with a gradual rise of temperature and finally evacuated at 700 °C for 1 h.

For the deuterium tracer experiments, a microcatalytic pulse reactor was employed. About 29 μmol of *cis*-2-butene was introduced into the He stream (flow rate, 35 ml/min) ahead of the catalyst. The produced butenes were gas chromatographically separated. The separated isomers were trapped at −196 °C and subjected to a mass spectrographic analysis. Mass spectra were recorded on Hitachi mass spectrometer RMU-2 at low ionization voltage. A deuterated catalyst was prepared by exposure of D_2O vapor at 400 °C to the catalyst that had been evacuated at 500 °C and then evacuated at 500 °C for 3 h. Another deuterated catalyst was obtained by exposure of D_2O vapor at 100 °C to the 500 °C evacuated catalyst, followed by evacuation at this temperature for several hours.

Results

Activity was expressed by percent conversion of 1-butene per unit time, min, per unit weight of catalyst, g, at the initial stage of the reaction. The variations of the activity for the isomerization of 1-butene at 100 °C and the ratio of *cis*-2-butene to *trans*-2-butene are shown in Fig. 1 as a function of evacuation temperature of the catalyst. The activity reaches a maximum value on evacuation at 600 °C. The ratio of *cis*-2-butene to *trans*-2-butene gradually decreases from 1.7 to 1.2 with

TABLE 1. EFFECT OF POISONING ON ACTIVITY AND *cis-/trans*-2-BUTENE

Evac. temp, °C	Poison	Poisoning temp, °C	Evac. after temp, °C	Poisoning time, min	Activity $\%\mathrm{min}^{-1}\,\mathrm{g}^{-1}$	Relative activity	*cis-/trans*-2-Butene
500	—	—	—	—	5.87	1.00	1.41
500	NH_3	100	100	30	0.00	0.00	
500	CO_2	100	100	60	4.73	0.81	1.66
500	H_2O	100	100	60	5.05	0.86	1.75
500	H_2O	100	100	1	5.02	0.85	2.70
500	H_2O+CO_2	100	100	30	7.35	1.25	2.15

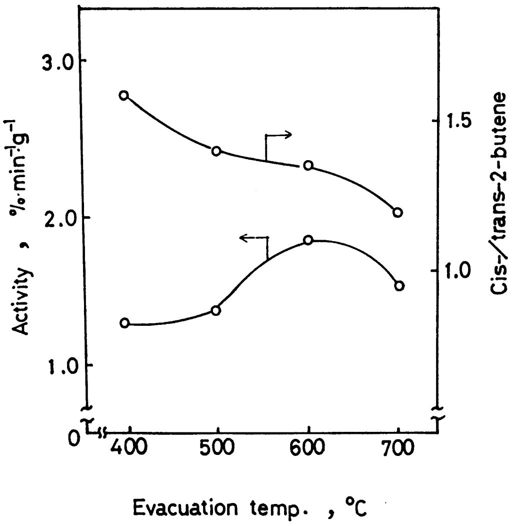

Fig. 1. Effect of evacuation temperature of WO_3 on activity and selectivity for isomerization of 1-butene.

a rise of evacuation temperature.

Poisoning effects of NH_3, CO_2, H_2O, and a mixture of CO_2 and H_2O on the activity and the ratio of *cis*-2-butene to *trans*-2-butene are included in Table 1. Ammonia completely poisoned the active sites, while CO_2, H_2O, and a mixture of CO_2 and H_2O scarcely showed poisoning effect. A mixture of CO_2 and H_2O even increased a little the activity.

The catalysts evacuated at various temperatures showed yellow color and the X-ray diffraction pattern of WO_3. During the treatment with H_2 at 500 °C, 0.00048 mol/g of H_2 was consumed, which corresponds to the number of H_2 required for the change of WO_3 to $WO_{2.89}$. The catalyst became dark blue on the treatment and showed the X-ray diffraction pattern of mixture of WO_3 and $WO_{2.87}$. The treatment with H_2 at 650 °C resulted in a consumption of 0.0046 mol/g of H_2, which corresponds to the number of H_2 required for the change of WO_3 to WO_2. The resulting catalyst was brown and showed the X-ray diffraction pattern of WO_2. The effects of the treatments are given in Table 2. The treatment with H_2 or O_2 at 500 °C did not result in an appreciable effect on the activity for the double bond isomerization of 1-butene. However, the treatment with H_2 at 650 °C greatly increased the activities for the double bond and skeletal isomerizations and the dehydration of isopropanol.

Results of microcatalytic tracer experiments are given in Table 3. In the coisomerization of *cis*-2-butene-d_0/d_8 over WO_3 that had been evacuated at 500 °C, a large number of exchanged isotopic species were produced in 1-butene and *trans*-2-butene. The number of H(or D) atoms exchanged per molecule (AEM value) was calculated from the equation,[11]

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

where N_i is the fraction of isotopic species containing i D atoms. The AEM values of the products were close to 0.5 (see Table 3). This indicates that the double bond isomerization involves intermolecular hydrogen transfer.[11]

In the isomerization of *cis*-2-butene over the deuterated catalyst that was evacuated at 500 °C after exposed to D_2O, negligible amounts of D atoms were incorpo-

TABLE 2. EFFECT OF PRETREATMENTS OF TUNGSTEN OXIDE ON DOUBLE BOND ISOMERIZATION OF 1-BUTENE, DEHYDRATION OF 2-PROPANOL, AND SKELETAL ISOMERIZATION OF 1-BUTENE

Evac. temp, °C	Treatment reagent	Treated temp, °C	Evac. after treatment		Activity $\%\mathrm{min}^{-1}\,\mathrm{g}^{-1}$	Relative activity	*cis-/trans*-2-Butene
			temp, °C	time, min			
500	—	—	—	—	1.17$^{a)}$	1.00	1.41
500	H_2	500	500	60	1.04$^{a)}$	0.89	1.40
500	O_2	500	500	60	1.34$^{a)}$	1.14	1.76
700	—	—	—	—	0.92$^{a)}$	1.00	1.20
650	H_2	650	700	180	2.09$^{a)}$	2.21	1.40
700	—	—	—	—	109.4$^{b)}$	1.00	—
650	H_2	650	700	180	316.6$^{b)}$	2.89	—
700	—	—	—	—	0.10$^{c)}$	1.00	—
650	H_2	650	700	180	0.92$^{c)}$	8.88	—

a) Double bond isomerization at 100 °C over 0.5 g of WO_x. b) Dehydration of 2-propanol at 100 °C over 50 mg of WO_x. c) Skeletal isomerization at 400 °C over 0.5 g of WO_x.

TABLE 3. RESULTS OF MICROCATALYTIC TRACER EXPERIMENTS AT 100 °C

Reactions and Catalysts	Pulse number	Products		Isotopic distributions, %									AEM[e]	ϕ[f]
		kinds	%	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
a	1	1	6.02	46.36	18.9	3.1	0.7	0.5	0.9	5.5	18.2	5.9	0.609	
		t	19.65	35.8	13.7	2.6	0.7	0.9	2.3	7.5	20.3	16.3	0.667	
		c	74.33	41.5	6.0	0.8	0.3	0.3	0.6	2.7	12.5	35.2	0.297	
b	1	1	7.07	97.90	2.0	0.10	0	0	0	0	0	0		2.20
		t	29.72	98.14	1.74	0.12	0	0	0	0	0	0		1.98
		c	63.21	98.92	1.08	0	0	0	0	0	0	0		1.08
c	1	1	5.04	0.34	0.26	0.20	0.20	0.54	1.56	6.12	28.04	62.74		7.46
		t	16.09	0.46	0.27	0.10	0.11	0.50	1.69	7.36	27.22	62.28		7.44
		c	78.87	0.57	0.38	0	0	0.24	0.48	21.8	13.03	83.11		7.73
c	2	1	4.76	1.23	1.10	0.17	0.14	0.28	0.56	2.86	17.55	76.10		7.546
		t	13.71	0.29	0.06	0	0	0.36	0.77	3.12	17.73	77.66		7.695
		c	81.53	0.16	0	0	0	0.16	0.15	1.33	8.97	89.24		7.860
d	1	1	7.01	78.23	18.05	2.90	0.82	0	0	0	0	0		0.263
		t	29.13	79.58	17.29	2.50	0.63	0	0	0	0	0		0.241
		c	63.86	92.00	7.03	0.84	0.13	0	0	0	0	0		0.091
d	2	1	7.46	95.88	3.86	0.27	0	0	0	0	0	0		0.0440
		t	23.28	95.29	4.16	0.55	0	0	0	0	0	0		0.0526
		c	69.26	98.07	1.74	0.19	0	0	0	0	0	0		0.0212

a) Coisomerization of *cis*-2-butene-d_0/d_8 over WO_3. b) Isomerization of *cis*-2-butene-d_0 over WO_3 treated with D_2O at 400 °C. c) Isomerization of *cis*-2-butene-d_8 over WO_3 treated with *cis*-2-butene-d_0 at 100 °C. d) Isomerization of *cis*-2-butene-d_0 over WO_3 treated with D_2O at 100 °C. e) $\mathrm{AEM}=\sum_{i=0}^{4} iN_i+\sum_{i=5}^{8} iN_i$. f) $\phi=\sum_{i=0}^{8} iN_i$.

rated into butenes. However, over the deuterated catalyst that was evacuated at 100 °C after being deuterated, a considerable number of D atoms were incorporated into the products. The cumulative number of D atoms picked up by butenes till the 3rd slug was 29.2×10^{17} atoms/g.

Over the catalyst that had been evacuated at 500 °C, a slug of *cis*-2-butene-d_8 was introduced after 4 slugs of *cis*-2-butene-d_0. The products as well as the reactant contain a large number of H exchanged isotopic species. The average number of D atoms per molecule, ϕ value, was calculated from the equation,

$$\phi = \sum_{i=0}^{8} i\cdot N_i.$$

The ϕ values of 1-butene, *trans*-2-butene, and *cis*-2-butene were 0.54, 0.56 and 0.27, respectively (Table 3). There was a very small amount of d_0 species which would be detected if adsorbed butene-d_0 were replaced by butene-d_8.

Discussion

All results obtained can be explained in terms of acidic property of the catalyst.

Strong poisoning effect with NH_3 suggests that the acid sites are acting as active sites for the double bond isomerization of butene. In the acid-catalyzed isomerization of 1-butene, the ratio of *cis*-2-butene to *trans*-2-butene is usually close to unity.[12] The ratios obtained over tungsten oxide treated under different conditions were close to unity, which also supports that the acid sites are active. No poisoning effect with CO_2 indicates that the basic sites, even if present, do not participate in the reaction.

Since the reaction involves intermolecular hydrogen transfers and the active sites are acidic, it is quite plausible that the reaction intermediate is a carbenium ion. In the reaction over the deuterated catalyst that was evacuated at 500 °C after D_2O treatment, the numbers of D atoms incorporated into the products were small. On the other hand, considerable numbers of D atoms were incorporated into the products when *cis*-2-butene was reacted over the deuterated catalyst evacuated at 100 °C after D_2O treatment. Therefore, the surface OH groups on the catalyst evacuated at 100 °C participate in the reaction as a source of H^+, but the OH groups on the catalyst evacuated at 500 °C, even if they present, do not participate. Instead of surface OH groups, H^+ is provided by preadsorbed butene over the catalyst evacuated at 500 °C, since much of H^+ was contained in the reaction products of *cis*-2-butene-d_8 over the catalyst on which *cis*-2-butene-d_0 had been preadsorbed. The butene which serves as the source of H^+ may not retain the form of C_4H_8 and may be polymerized on the acid sites of Lewis type, because the preadsorbed butene-d_0 was not replaced by the introduction of butene-d_8. This type of active sites were proposed by Kimura and Ozaki for the isomerization of butenes over SiO_2–Al_2O_3.[13]

The addition of water retarded the reaction of heptane,[9] but it did not appreciably retard the isomerization of 1-butene. This is considered due to that the protons formed by the adsorption of water on Lewis acid sites act as active sites for the isomerization of 1-butene, but not for the reaction of heptane.

The treatment with H_2 at 500 °C did not result in the reduction of WO_3 to WO_2, but only to $WO_{2.87}$, while the treatment with H_2 at 650 °C resulted in the formation of WO_2. The increase in the activity for the isomerization of butene by the treatment with H_2 at 650 °C indicates that the acidity and acid strength of WO_2 are higher than those of WO_3 or $WO_{2.87}$. The enhancement of acidic property by the treatment at 650 °C also interprets the increases of the activities for the dehydration of isopropanol and the skeletal isomerization of 1-butene, which are known as acid-catalyzed reaction.

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