

Isomerization of *n*-Butene on Reduced Molybdena-Alumina: The Effect of Hydrogen

Reactions of ethene and 2-butenes were studied separately under conditions of propene metathesis (1-3) on a molybdena-alumina catalyst reduced with hydrogen and treated differently after reduction. Isomerization of 2-butenes was found to be accelerated both by hydrogen absorbed previously on the catalyst and by hydrogen present in the gas phase. Acceleration of butene isomerization by hydrogen on non-metal catalysts was described by Fukushima *et al.* (4-6) on cobalt oxide, and by Tanaka *et al.* on sulfurated nickel (7), on molybdenum sulfide (8, 9) and on sulfurized cobalt (10). To shed some light on the role of hydrogen in the isomerization of butenes, experiments were carried out with all three *n*-butene isomers on reduced molybdena-alumina. Since extremely high rates were obtained after the first few minutes, our attention was restricted to the initial stage of the reaction.

The catalyst consisted of 9.1 wt% MoO₃ on Ketjen CK 300 γ -Al₂O₃ (particle size 0.2-0.4 mm). Preparation of it was described previously (1). The experiments were carried out in a closed glass recirculation system (volume: 120 cm³) with U-shaped quartz reactor (volume: 20 cm³). The same charge of catalyst (0.1 g) was used in each experiment; it was regenerated for 1 hr by recirculation of oxygen through the reactor at 550°C and a trap cooled with dry-ice methanol. Three types of activation were applied:

1. *For standard catalyst (SC).* The regenerated catalyst was reduced for 2 hr at 550°C by recirculation of initially atmospheric hydrogen. The water developed in reduction was continuously removed in a trap cooled with dry-ice methanol. After

reduction the hydrogen adsorbed reversibly was removed by pumping off for 1 hr at 550°C; the reactor was cooled to 40°C under pumping.

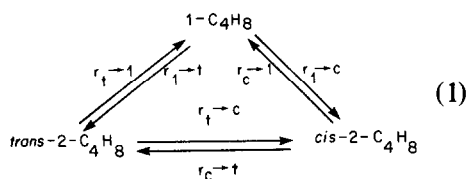
2. *For reduced catalyst with hydrogen adsorbed at 40°C (AC).* The standard catalyst was treated with atmospheric hydrogen by recirculation at 40°C for 10 min. Before admission of butenes the hydrogen was pumped off from the reactor for 2 min.

3. *For reduced catalyst with hydrogen adsorbed at 550°C (DC).* The catalyst was activated as AC, but the treatment with hydrogen for 10 min was carried out at 550°C instead of 40°C. The catalyst was cooled quickly to 40°C in hydrogen; the hydrogen was pumped off for 2 min before admission of butenes.

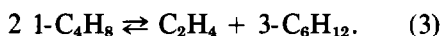
Butenes (5×10^{-3} mole) were recirculated through the reactor at 40°C, atmospheric pressure for 30 s. The reaction was terminated by freezing the reaction mixture into the trap, cooling it with liquid nitrogen, then the reactor was closed, the trap warmed to room temperature, 5 μ l of *n*-pentane as internal standard injected, and the composition of the reaction mixture determined with gas chromatography. After the first run the reactor was pumped at 40°C for 60 min and the experiment was repeated as above with fresh butene.

On catalysts AC and DC experiments were carried out as well with butenes containing 1% H₂ in the first runs (ACH and DCH).

The concentration of products obtained are summarized in Table 1. The values in brackets represent the results in second runs. Isomerization of butenes can phenomenologically be described by the following triangle scheme:



Production of propene and pentene as well as ethene and hexene can be attributed to metathesis reactions:



With 2-butenes as reactant only the products of reaction (2) could be observed besides isomerization. Both (2) and (3) proceeded to the same degree with 1-butene reactant, although the concentration of 1-butene is by far the highest in the reaction mixture. These observations indicate that the cross-metathesis was much faster than the productive metathesis of 1-butene. The conversion of butenes over SC and AC was below 12%, so the approximate initial isomerization rates could be calculated directly

from the conversion data; the calculated values are summarized in Table 2.

The initial rate of *cis-trans* isomerization was extremely high. Over our standard catalyst the specific rate of *cis-trans* transformation was more than four times higher than that estimated by Fukushima *et al.* (6) over cobalt oxide containing prechemisorbed hydrogen. The rate over standard catalyst increased either by preadsorption of hydrogen at low temperature, or hydrogen in the gas phase, but more significantly by hydrogen preadsorbed at high temperatures. Rate values over ACH, DC, and DCH catalysts, could not be calculated from the conversion data of the high conversions obtained.

The rate of *cis-trans* isomerization over SC and AC was about one order of magnitude higher than that of the double bond shift. Similar result was described by Tanaka and Okuhara (9, 11) on *n*-butene isomerization over molybdenum disulfide powder and single-crystal catalysts. According to Tanaka isomerization proceeds

TABLE 1

Concentration of the Products of *n*-Butene Isomerization at 313 K over 0.1 g Molybdena-Alumina Catalyst Reduced for 2 hr at 823 K (mole%)

Reactant	Products	ACH	AC	SC	DC	DCH
<i>cis</i> -2-C ₄ H ₈	<i>trans</i> -2-C ₄ H ₈	19.5 (2.7)	12.6 (1.5)	8.4 (1.3)	39.2 (12.7)	44.9 (17.9)
	1-C ₄ H ₈	0.9 (0.1)	0.6 (t)	0.3 (t)	2.2 (0.7)	2.6 (1.0)
	C ₃ H ₆	0.1 (t)	0.1 (t)	t (t)	t (t)	(t) (t)
	2-C ₅ H ₁₀	0.1 (t)	t (t)	t (—)	— (—)	— (—)
	<i>n</i> -C ₄ H ₁₀	0.3 (t)	t (—)	t (—)	t (—)	0.4 (—)
<i>trans</i> -2-C ₄ H ₈	<i>cis</i> -2-C ₄ H ₈	8.4 (1.9)	6.8 (1.2)	5.2 (0.4)	13.5 (6.4)	15.0 (8.7)
	1-C ₄ H ₈	0.7 (0.1)	0.6 (t)	0.3 (t)	1.7 (0.7)	1.9 (1.0)
	C ₃ H ₆	0.1 (t)	0.1 (t)	t (t)	t (t)	t (t)
	2-C ₅ H ₁₀	0.1 (t)	0.1 (t)	t (t)	t (t)	t (t)
	<i>n</i> -C ₄ H ₁₀	0.4 (—)	t (—)	t (—)	t (—)	0.4 (—)
1-C ₄ H ₈	<i>trans</i> -2-C ₄ H ₈	1.2 (0.3)	1.9 (0.2)	0.5 (0.1)	13.3 (1.3)	14.1 (2.7)
	<i>cis</i> -2-C ₄ H ₈	0.8 (0.2)	1.3 (0.2)	0.4 (0.1)	6.0 (0.8)	6.4 (1.5)
	C ₃ H ₆	0.2 (0.1)	0.3 (0.1)	t (0.1)	t (t)	(t) (t)
	2-C ₅ H ₁₀	0.1 (0.1)	0.1 (t)	t (0.1)	— (—)	— (—)
	C ₂ H ₄	0.2 (0.2)	0.2 (0.2)	0.1 (0.2)	t (—)	t (t)
	3-C ₆ H ₁₂	0.1 (0.2)	0.1 (0.2)	0.1 (0.2)	— (—)	— (—)
	<i>n</i> -C ₄ H ₁₀	0.2 (t)	t (—)	— (—)	— (—)	0.4 (t)

^a t: less than 0.05 mole%.

TABLE 2
Isomerization Rates over SC and AC
Catalysts in the First Run of Experiments,
 $r \times 10^{12}$ [mole \cdot cm $^{-2}$ \cdot s $^{-1}$]^a

	SC	AC
<i>cis</i> \rightarrow <i>trans</i>	68.4	102.1
<i>cis</i> \rightarrow 1	2.7	4.8
<i>trans</i> \rightarrow <i>cis</i>	42.4	55.3
<i>trans</i> \rightarrow 1	2.3	4.7
1 \rightarrow <i>cis</i>	3.4	10.2
1 \rightarrow <i>trans</i>	3.7	15.4

^a Calculated on the basis of total surface area of the catalyst (205 m 2 /g).

on dicoordinatively unsaturated (BH) sites (12) via *sec.*-butyl intermediate. The *cis*-*trans* transformation is resulted by the internal rotation of an ethyl group of the *sec.*-butyl, while the double bond shift requires the rotation of the whole *sec.*-butyl around the Mo-C bond. The much lower rate of double bond shift was explained by the high rotational barrier for the rotation of bulky groups. The same explanation can be applied for the much lower rate of double bond shift compared to *cis*-*trans* isomerization over reduced molybdena-alumina observed by us.

Both *cis*-*trans* isomerization and double bond shift were accelerated by hydrogen preadsorbed at low temperature (AC), and the same acceleration was observed for the cross-metathesis of 1-butene and 2-butenes. These results are in good agreement with the hypothesis that the primary active sites for the isomerization and metathesis of olefins are hydrogens bound to molybdenum ions, and the common intermediates are σ -bound molybdenum alkyls (13, 14).

The reactions, however, were affected differently by hydrogen adsorbed at high temperature. Acceleration of the reactions increased in the sequence: *cis*-*trans* isomerization < double bond shift (2-butenes as reactant) \ll double bond shift (1-butene as reactant). While the isomerization was accelerated, both metathesis of 1-butene and

cross-metathesis of 1- and 2-butenes were suppressed by the hydrogen adsorbed at high temperature. These results suggest that different surface sites are involved in isomerization as in metathesis.

Besides the suppressed metathesis the highly accelerated double bond shift of 1-butene was the most significant difference between the results obtained over DC and those obtained over SC and AC. While over SC and AC the double bond shift of 1-butene was considerably slower than the *cis*-*trans* transformation, the rate of the two reactions was comparable over DC. This result again indicates that the nature of active sites over reduced molybdena-alumina changes considerably to the effect of hydrogen adsorbed at high temperature.

Decrease of initial rapid isomerization within short interval was described by Fukushima *et al.* (6) on cobalt oxide catalyst. This decrease was explained by consumption of chemisorbed "active" hydrogen to form butane. The *n*-butane in the products of our experiments indicates that hydrogen was removed not only from AC and DC but from SC as well. Reactivation of the catalyst however, was not achieved by treating the catalyst with hydrogen at 40°C between the two runs, so the drop of activity cannot be attributed to the removal of adsorbed hydrogen alone.

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