

Double Bond and Skeletal Isomerization of 1-Butene over Lanthanum-Modified Silicated Alumina

Michael Stöcker*, Trygve Riis and Harald Hagen

Department of Petrochemistry, Center for Industrial Research, P.O. Box 350 Blindern, N-0314 Oslo 3, Norway

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The double bond and skeletal isomerization of 1-butene were studied over La-modified silicated alumina with different amounts of lanthanum and silicon. The yield of isobutene decreases with increasing amount of La and increases with increasing Si content. The double bond migration occurred much faster than the skeletal isomerization and the rates of formation decrease with increasing amounts of lanthanum, both for the skeletal and double bond isomerization.

Although considerable work has been carried out on the double bond migration of butenes,^{1–10} much less effort has been devoted to the study of both the skeletal and geometrical isomerization of butenes during the same test run. In recent years, an important trend of research in this field has been the application of, among other things, La-modified catalysts and the search for more effective support materials. Lanthanum sesquioxide, La₂O₃, when properly activated, is an active catalyst for double bond migration in the butenes.^{5–10} Silicated alumina, applied in the butene isomerization, showed much higher conversions and yields of isobutene than pure alumina, which is known to be an effective skeletal isomerization catalyst.^{11,12} Our intention was, therefore, to study the catalytic behaviour of La₂O₃ supported on silicated alumina with regard to the different amounts of lanthanum and silicon.

Results

Isomerization tests. In a screening phase, nine catalysts (1–9) with different amounts of silicon and lanthanum on alumina were synthesized and tested for skeletal and double bond isomerization of 1-butene. The results are summarized in Table 1.

It is obvious that the silicated aluminas without La-content (4 and 7) are good skeletal isomerization catalysts, since they have normal yield (20 %) and selectivity values (about 75 %).¹² As shown in Table 1, the other catalysts have low or no skeletal isomerization activity. Furthermore, the yield of isobutene decreases with increasing amount of La and increases with increasing Si content.

By looking at the isomer distribution (see Table 1), one can see that all the catalysts except 3 give about the same distribution of linear butenes, showing that these catalysts under these conditions isomerize 1-butene almost to the thermodynamic equilibrium with 2-butenes. In catalyst 3 (which has the highest La and lowest Si content), the amount of 1-butene is slightly higher than in the other tests, showing that equilibrium conditions are not reached.

Further investigations were made in order to study both skeletal and double bond isomerization of 1-butene more closely by carrying out the reactions under differential conditions. The catalysts prepared for this series (10–15) contained 1.1 % Si and different amounts of La (0–6 %). The activity and differential test results of 10–15 are summarized in Table 2 and presented in Figs. 1 and 2.

*To whom correspondence should be addressed.

Table 1. Isomerization of 1-butene over La-modified silicated alumina at 475 °C.^a

Catalyst	Amount of		Yield of isobutene/%	Selectivity to isobutene/%	Isomer distribution of linear butenes/%		
	Si/%	La/%			1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene
1	0	0	2.5	55	26	42	32
2	0	3.1	0.5	70	27	42	31
3	0	4.5	0.3	55	33	39	28
4	1.1	0	20	77	28	42	30
5	1.1	2.5	1.5	85	28	42	30
6	1.1	4.9	0.5	70	29	41	30
7	2.4	0	19	75	28	41	31
8	2.4	2.5	5.5	65	27	42	31
9	2.4	5.2	2.0	70	28	41	31

^aMeasured after 6 h on stream, weight hourly space velocity (WHSV): 2, 1 g of catalyst.

Before the differential testing, the catalysts were aged and the deactivation during the course of the experiments was negligible. We used higher temperature (500 °C) than earlier during the introduction period in order to increase the deactivation and obtain a more stable catalyst for the differential tests. We found it necessary to go down to 172 °C to be able to find reaction rates for the double bond migration, whereas the differential tests for the skeletal isomerization were carried out at 425 °C.

As shown in Table 2 and Figs. 1 and 2, the rates of formation of 2-butenes are higher than the rates for skeletal isomerization, even though the temperature is much lower in the case of double bond migration.

Characterization of the catalysts. Some effort was devoted to the characterization of the acidic properties of the catalysts in order to find a possible relationship between the surface structure of the catalysts and their activities for the skeletal and double bond isomerizations.

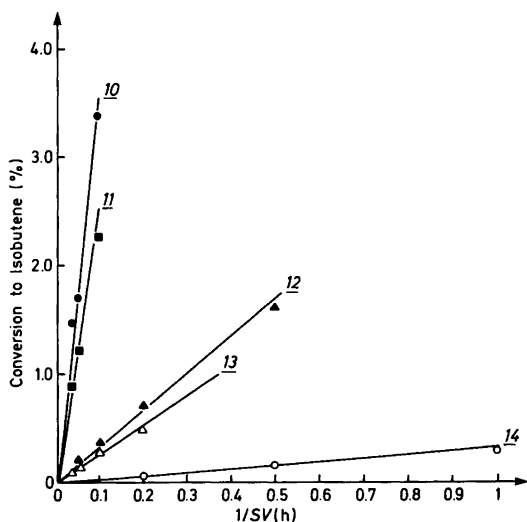


Fig. 1. Conversion of 1-Butene to Isobutene: Dependence on inverse space velocity. Temperature: 425 °C, He/1-Butene ratio = 2:1.

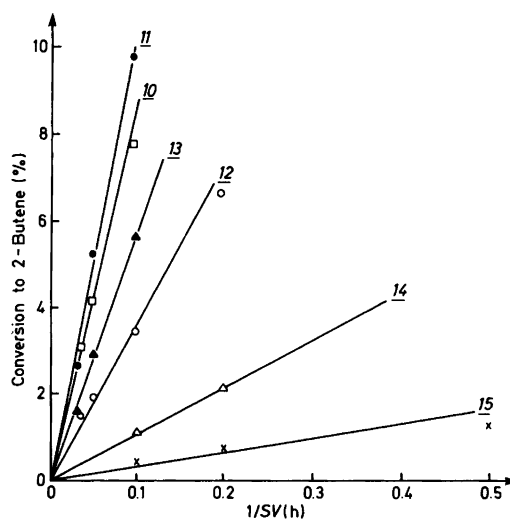


Fig. 2. Conversion of 1-Butene to 2-Butenes: Dependence on inverse space velocity. Temperature: 172 °C, He/1-Butene ratio = 2:1.

Table 2. Isomerization of 1-butene over La-modified silicated alumina with 1.1 % silicon.

Catalyst	Amount of La/%	Introduction period ^a			Differential tests ^b		
		Butene distribution/%		Selectivity/% to	Rates of formation of		
		1-Butene	2-Butenes	Isobutene	Isobutene	2-Butenes	Isobutene 2-Butenes
							/10 ⁴ · mol · g ⁻¹ · h ⁻¹
10	0	18.9	45.4	25.2	70		60 150
11	0.5	21.3	50.4	21.3	75		45 180
12	1.0	23.9	56.5	12.4	65		6 65
13	1.8	26.1	62.9	7.1	65		5 100
14	3.3	28.5	68.3	1.3		96	0.6 20
15	6.0	28.3	69.2	0.4		96.5	~0 6

^aMeasured after 4 h on stream, weight hourly space velocity (WHSV): 2, 1 g of catalyst, temperature: 500 °C, conversion of 1-butene was more than 70 % for all catalysts.

^bMolar ratio He: 1-butene = 2:1, WHSV: 1–30, 1 g of catalyst, temperature: 425 °C (isobutene) and 172 °C (2-butenes).

The strength of acid sites for the catalysts 7 (2.4 % Si, 0 % La) and 9 (2.4 % Si, 5.2 % La) were measured by microcalorimetry (addition of NH₃ to the catalyst). Both catalysts were observed to have about the same adsorption enthalpy for the strongest acid sites (150 kJ/mol), whereas a clear difference was detected for the medium strong sites between 0.4 and 1.0 mmol NH₃/g catalyst, as for example 60 kJ/mol for 7 and 40 kJ/mol for 9.

IR spectroscopy was used to identify the type of acidic sites by adsorption of pyridine to the catalyst. The spectrum of catalyst 7 can be interpreted as follows: The pyridine is primarily adsorbed on H-bonding sites (1445 cm⁻¹), with small amounts of Lewis sites, but no Brønsted sites (no 1540 cm⁻¹ band). Catalyst 9 has, as expected, the same general spectrum.

Discussion

From a mechanistic point of view, the skeletal isomerization of 1-butene requires more activation energy than the double bond migration. Since the catalytic activity for the conversion to isobutene became smaller when the catalyst had been treated with lanthanum, it may be concluded that the lanthanum blocks the active sites for skeletal isomerization. Additionally, the interpretation of our calorimetric and IR spectroscopic results leads to the assumption that the La only blocks up the medium strong acid sites, but

not the strongest ones, indicating an important role for the medium strong sites in relation to the skeletal and double bond isomerization of 1-butene. Furthermore, by increasing the amount of silicon, greater amounts of lanthanum are required to prevent the skeletal isomerization. It is evident that silicon activates the catalytic sites for the skeletal isomerization, whereas lanthanum suppresses them. Finally, it should be underlined that the system 3 (containing a high La-amount) did not show the same tendency to reach thermodynamic equilibrium as the other catalysts. The ability to suppress the skeletal isomerization does not, therefore, imply an acceleration in the double bond migration.

The plots of conversions to isobutene or 2-butene vs. inverse space velocity (Figs. 1 and 2) are straight lines passing through the origin, showing that differential conditions were obtained for both isomerization reactions. On the basis of our results presented in Fig. 1, we can divide the six catalysts into three groups. The catalysts with the highest La-content (14 and 15) showed the smallest rates of isobutene formation. The catalysts belonging to the second group containing 1–2 % La (12 and 13) increase in the isomerization rate, whereas the last systems with small amounts of lanthanum (10 and 11) again showed a remarkable increase in the rate of isobutene formation (up to hundredfold compared with 14 and 15, see Table 2). The observed activities and the rates of formation confirm our assumption, *i.e.*, higher

amounts of La cause lower rates of isobutene formation. Similar behaviour was found for the double bond isomerization rates (see Fig. 2). The rates are much higher, but the same tendency is registered concerning the dependence of the rates on the amounts of lanthanum, although the graduation is not so distinct. Furthermore, our results are in agreement with data reported in the literature.² Finally, it should be emphasized that the results for the double bond isomerization were obtained at 172°C compared to 425°C for the skeletal isomerization.

Experimental

The La-modified silicated aluminas were prepared as follows: Alumina was calcined at 400°C for 18 h before moistening with ethanol and treating with an Si(OEt)₄/ethanol mixture under argon atmosphere. The mixture was kept at room temperature for 5 h. The excess liquid was removed and the carrier was dried under vacuum, first at room temperature for 1 h and later at 200°C for 4 h under nitrogen atmosphere with a stepwise increase of the temperature during a 2 h period. After steaming for 17 h, the catalyst was calcined at 550°C for 5 h in air before treating with a lanthanum nitrate solution. Finally, the mixture was kept at room temperature for 24 h, followed by evaporation of the solvent at 80°C and calcination of the catalyst at 550°C for 5 h in air.

The isomerization of 1-butene (purity 99.8%) was carried out in a fixed bed reactor which was connected on-line to a gas chromatograph (Hewlett Packard 5880). The reaction temperature, weight hourly space velocity (WHSV), amounts of catalyst and helium/1-butene ratio are mentioned in the legends of the Tables and Figures.

The GC analysis of the C₄ fraction were carried out on a 30 m PLOT capillary column operating at the following temperature profile: Initial value: 70°C for 17.50 min, program rate 10°C/min for 3 min, final temperature 100°C during a period of 15 min.

The calorimetric results were obtained by addition of NH₃ ($4.5 \cdot 10^{-6} - 5 \cdot 10^{-5}$ mol/addition · h at 150°C) to 200 mg of the catalysts in a Thermo Analyser calorimeter. The IR measurements were recorded on a Perkin Elmer 580B IR spectrometer, equipped with a pyridine adsorption unit. The spectra were registered at room temperature and at 150°C.

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