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NOTES

Skeletal Isomerization of 3,3-Dimethylbut-1-ene on OH-Free Alumina

Extensive studies of olefin isomerizations over Al_2O_3 have revealed many subtleties in the mechanisms for these reactions. Thus, depending on reaction conditions, double bond isomerization may proceed predominantly by either an intra- or an intermolecular pathway (*1–6*). In the case of skeletal isomerization (e.g., of 3,3-dimethylbut-1-ene, designated 33-DMB-1) or of isomerization of olefins that can form tertiary carbonium ions, the reaction involves an associative mechanism on Brønsted acid centres (*7–11*).

It might be expected that experiments using an OH-free Al_2O_3 could contribute additional information concerning the mechanism. Surface OH groups can be destroyed by reaction with organometallic compounds. The use of $Al(C_2H_5)_3$ with Al_2O_3 has the advantage that foreign cations are not introduced. It may also be used at lower temperatures (0–60°C) to determine OH-group concentration (*12*).

Al_2O_3 used in these experiments was prepared by hydrolysis of aluminium isopropylate with subsequent heat treatment of the hydroxide in air at 600°C for 24 h. The Al_2O_3 had a surface area of 140 $m^2\ g^{-1}$ and was activated for catalytic tests at 600°C for 5 h. The surface concentration of OH-groups was found to be 2.3 OH nm^{-2}, in agreement with literature data. The complete dehydration of the surface using $Al(C_2H_5)_3$ at 200°C was demonstrated by subsequent exposure at 100°C to $Zn(CH_3)_2$/THF.

Olefin isomerization activity was studied in a pulse reactor using 100 mg catalyst and with dried, O_2-free He as carrier gas. The skeletal isomerization of 33-DMB-1 was studied. The pulse size of the olefin was generally 1 μl. The surprising result was obtained that dehydroxylation of the Al_2O_3 did not change the activity for skeletal isomerization of 33-DMB-1 (Fig. 1).

Additional information was obtained using deuterated catalysts, both as prepared (activation in He, treatment with D_2O at room temperature, and reactivation (*15*)) and following de-deuteroxylation with $Al(C_2H_5)_3$. The deuterium content of the reactant and product olefin molecules was determined by GC/MS.

Significant deuterium uptake in both 33-DMB-1 reactant and 23-DMB-1 and 23-DMB-2 product molecules was observed during isomerization over the deuterated Al_2O_3 (Table 1). The significant D-content in 33-DMB-1 shows that simple exchange rather than isomerization causes D-uptake from surface OD groups. The deuterium uptake of the olefin was 2.4×10^{18} D-atoms for the first pulse and the cumulative D-uptake after 6 pulses was 1.2×10^{19} deuterium atoms, i.e., 7.4 and 38% of the initial D-content of the catalyst, respectively. Following surface de-deuteroxylation with $Al(C_2H_5)_3$ no D was detected in reactant or products, as expected, and again no influence on isomerization activity was recorded (Table 1).

The lack of D-incorporation in DMB-s after reaction on the deuterated Al_2O_3 following treatment with $Al(Et)_3$ again shows the success of this treatment.

The insensitivity of the skeletal isomerization rate to OH concentration is surprising but is in agreement with earlier work (*10, 16*). Our results are consistent with the explanation proposed in the literature (*10, 11, 15*) that reaction occurs over Brønsted acid centers produced from the adsorbed

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TABLE 1

Skeletal Isomerization of 3,3-Dimethylbut-1-ene on Deuterated Al_2O_3 Catalyst

Experiment *number*	Reaction *temperature* (°C)	Olefin	Composition (↓)	d_0	d_1	d_2	d_3	d_4	d_4
1	200	33-DMB-1[a]	68	73.5	20.0	6.5	—	—	—
		23-DMB-1[b]	7	78.5	16.5	5.0	—	—	—
		23-DMB-2[c]	25	44.5	26.0	17.5	8.0	2.5	1.5
2[d]	200	33-DMB-1	69	100.0	—	—	—	—	—
		23-DMB-1	6	100.0	—	—	—	—	—
		23-DMB-2	25	100.0	—	—	—	—	—

[a] 33-DMB-1, 3,3-dimethylbut-1-ene.

[b] 23-DMB-1, 2,3-dimethylbut-1-ene.

[c] 23-DMB-2, 2,3-dimethylbut-2-ene.

[d] Catalyst deuterated and dehydrated with aluminium-triethyl.

olefin, possibly via C–H bond dissociation.

It can be explained in this way how it is possible that although alumina exhibits certain properties for olefin isomerization characteristic for a Brønsted acidic catalyst, the surface OH groups are not part of the active sites for this catalytic reaction, as demonstrated in this work.

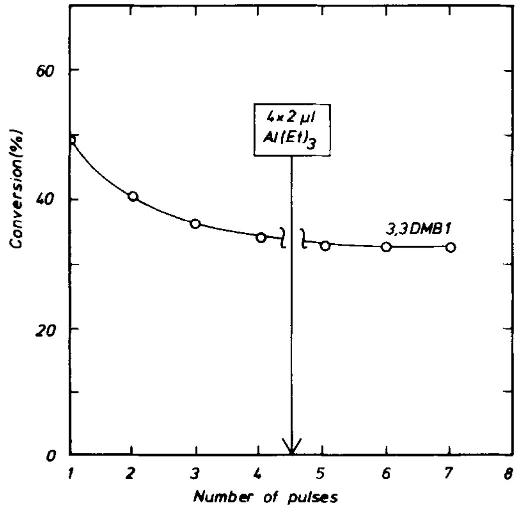

FIG. 1. Effect of aluminium-triethyl on the activity of Al_2O_3 catalyst for isomerization of 3,3-dimethylbut-1-ene. Temperature of reaction, 200°C. Temperature of treatment with $Al(Et)_3$, 200°C. 3,3DMB1, 3,3-dimethylbut-1-ene; $Al(Et)_3$, triethyl-aluminium.

In principle it is possible that skeletal isomerization takes place on OH groups which are present in very small concentration and are undetectable by our methods. In this case we must suppose that these OH groups, while being very active in olefin isomerization, are completely inactive toward $Al(C_2H_5)_3$. We must keep in mind that all other OH groups react promptly with $Al(C_2H_5)_3$. Thus we consider this hypothesis as very unlikely.

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