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LETTERS TO THE EDITORS

The Mechanism of Isomerization of 1-Butene over La_2O_3

The mechanism of the isomerization of 1-butene over La_2O_3 has been a matter of some controversy in recent years. Minachev and co-workers (*1*) suggested that the overall reaction scheme can be represented as:

$$\text{1-butene} \xrightarrow{k_1} \textit{cis}\text{-2-butene} \xrightarrow{k_2} \textit{trans}\text{-2-butene}. \quad (1)$$

This scheme was deduced from the results of kinetic experiments (carried out in a recirculation system), using 1-butene as shown by the dashed lines in Fig. 1. Note that the curves for the concentrations of *cis*-2-butene and *trans*-2-butene cross as expected for the system moving toward equilibrium. Minachev's catalyst was prepared from $La(OH)_3$ (precipitated with NH_3 from aqueous solution of $La(NO_3)_3$ by calcining at 700°C under vacuum (where it reached maximum activity). The weights of catalyst used varied from 0.12 to 0.30 g; fresh samples were used for each experiment. Rosynek *et al.* (*2*) proposed an alternative scheme, i.e.,

$$\textit{cis}\text{-2-butene} \rightleftarrows \text{1-butene} \rightleftarrows \textit{trans}\text{-2-butene}. \quad (2)$$

This scheme which suggested that the only initial product formed was 1-butene, was based on data such as those represented by the dashed lines in Fig. 2 as well as on experiments using *cis*-2-butene and *trans*-2-butene as reactants. Note that the curves for *cis*- and *trans*-2-butene (Fig. 2) do not cross within the time frame of the experiment. The catalyst used by Rosynek was prepared by hydrolyzing La_2O_3 to $La(OH)_3$ and then subjecting it to a temperature pretreatment (activity maximum at 660°C (*2, 3*)). Because of the high activity of this material the sample weight used was only 10 mg.

It was our purpose to try to understand

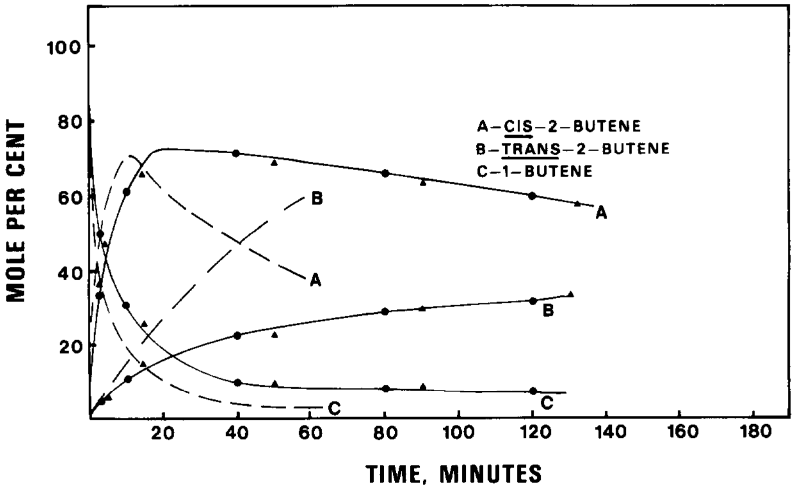

FIG. 1. Product distribution for 1-butene isomerization at room temperature on La_2O_3 (0.130 g). Solid lines with points represent our experimental results using the catalysts of Minachev (●) and of Rosynek (▲). Dashed curves represent the data of Minachev (weight of catalyst used was 0.12–0.30 g), replotted.

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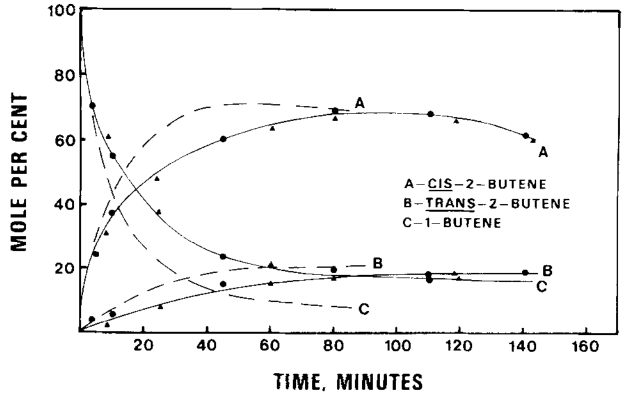

FIG. 2. Product distribution for 1-butene isomerization at room temperature on La_2O_3 (0.026 g). Solid lines with points represent our experimental results using the catalysts of Minachev (●) and Rosynek (▲). Dashed curves represent the data of Rosynek, replotted.

this very basic difference in interpretation. Consequently, we obtained samples of both catalysts from the previous authors and repeated the experments. The experimental points in Figs. 1 and 2 show the conversion of 1-butene at room temperature using 0.130 or 0.026 g, respectively, of each catalyst. Evidently the interpretation reached by the two groups was dependent on the amount of catalyst they used.

Figure 3 shows the *cis/trans* ratio as a function of percentage conversion taken from our experimental data (Figs. 1 and 2); Rosynek published a similar plot (*2*). These data would be consistent with Rosynek's scheme, but not with that of Minachev. Additionally, our experimental results show that there is only one mechanism of isomerization of 1-butene over La_2O_3 and that it is independent of the catalyst preparation. Moreover, the independence of the *cis/trans* ratio on the extent of conversion

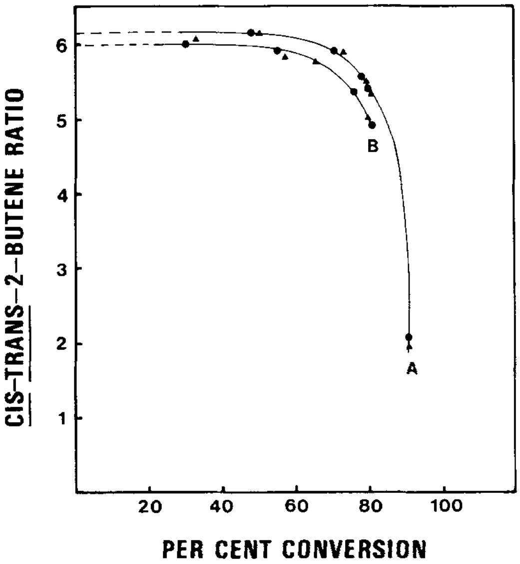

FIG. 3. *Cis/trans* ratio for 1-butene isomerization at room temperature on La_2O_3. (A) 0.130 g of the catalyst of Minachev (●) and of Rosynek (▲). (B) 0.026 g of the catalyst of Minachev (●) and of Rosynek (▲).

up to 80% (Fig. 3) suggests that the maximum in the concentration of *cis*-2-butene (Fig. 1) is simply moved to longer times (becomes less detectable) when smaller amounts of catalysts are used. The constant *cis/trans* ratio (Fig. 3) until very high conversion (80% of 1-butene) is attained would not be possible if a substantial rate of direct *cis*- to *trans*-2-butene conversion was present.

Although Rosynek's reaction scheme appears to be correct, additional work will be required to define the mechanism. Some additional studies to be reported elsewhere bear on this subject. These were carried out using these same two catalysts and involved the hydrogenation of ethylene and butadiene at room temperature. These studies suggest that the catalytic sites on La_2O_3 are similar to those on ZnO (*5*, *6*).

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