

The Isomerization of *cis*-2-Butene over Silica-Alumina Catalysts

III. Dependence on Alumina Content

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cis-2-Butene isomerization catalyzed by silica-alumina is shown to be affected by dealumination. The initial rate can be broken down into two parts. The first, v_L , corresponding to sites isomerizing in the first minutes of a run, parallels Lewis acidity and the oxidizing and reducing properties of the materials. The second initial rate, v_B , corresponding to sites which undergo only little poisoning, is related to Brønsted acidity and to the reducing properties of the four catalysts. Deactivation occurs and is explained in terms of the Lewis/Brønsted sites ratio. Particular changes in v_L near 2.4% alumina content show the existence of different kinds of aluminum sites in silica-aluminas, as found previously for other properties.

INTRODUCTION

Silica-alumina commercial catalysts in which some aluminum has been chemically removed have modified acidic and catalytic properties (1-3). At least for certain reactions, only about 20% of the aluminum, namely, that relating to tetracoordinated Al, is catalytically active (4). In this report we describe *cis*-2-butene isomerization on such materials, thereby supplementing our previous work on this reaction over silica-alumina (5, 6).

EXPERIMENTAL

Four silica-alumina catalysts containing 14, 9.4, 2.4, and 0.1 wt% alumina, respectively, have been studied. They are designated K-14, K-9.4, K-2.4, and K-0.1, and details may be found in part II (6). The chlorine content of the catalysts has been determined by neutron activation analysis. It decreases from 3.2×10^{-6} atoms/g of K-14 to smaller values for HCl-treated samples (e.g., 0.12×10^{-6} for K-2.4). The isomerization conditions and the method of kinetic analysis have been described previously (5, 6). Aging was studied at 85°C

as a function of time between 2 and 70 min after the start of a run, using a reactant pressure of 30 Torr.

To estimate the Lewis acidity by means of ir spectroscopy, pyridine was adsorbed at room temperature and then pumped off at three temperatures: 150, 350, and 400°C. The optical density of the 1455-cm⁻¹ ir band was taken as being proportional to the pyridine chemisorbed on Lewis acid sites (3). Brønsted acidity was assessed by determining the number of protons exchangeable by Na⁺ ions (5, 6). For dealuminated samples the protons of weak acid strength, exchangeable by sodium ions from Na₂CO₃ solutions, are more thermally stable after a 400°C heating (7).

RESULTS

The initial rates of isomerization, v_T , can be broken down into rates on Lewis (L) sites and Brønsted (B) sites, the latter designated as v_L and v_B , respectively, such that $v_T = v_L + v_B$ (5, 6). Figure 1 shows the characteristics of the Lewis sites by reporting on the same diagram the optical density of the 1455-cm⁻¹ band and the changes in v_L as a function of alumina con-

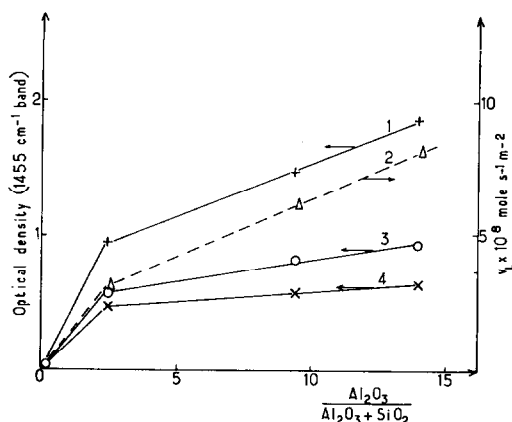


FIG. 1. v_L rate at 85°C (curve 2) and optical density in arbitrary units of the 1455-cm⁻¹ band (coordinated pyridine) (curves 1, 3, 4) against alumina content. Desorption temperature of pyridine: (+) 150°C; (○) 350°C; (×) 400°C.

tent. The oxidizing and reducing properties of dealuminated silica-alumina catalysts were also studied by observing the EPR spectra of perylene (Pe) and tetracyanoethylene (TCNE), respectively (8). v_L rose linearly with the estimated concentrations of Pe⁺ and TCNE⁻ radical ions (Table 1). Regarding the Brønsted sites, Fig. 2 shows the v_B rate as a function of alumina content.

The decay of the catalytic activity is shown in Fig. 3, along with the range of run time during which L + B sites or only B sites are active in the isomerization (5). At $t < 20 \pm 10$ min, L + B sites isomerize *cis*-2-butene, but thereafter the reaction takes place only on B sites. The time at which L sites become inactive, shown in

TABLE I
VALUES OF v_L AND RADICAL ION
CONCENTRATIONS FOR THE
DIFFERENT CATALYSTS

Catalyst	$v_L \times 10^8$ mole s ⁻¹ m ⁻²	[Pe ⁺] ^a	[TCNE ⁻] ^a
K-14	8	10.1	8.3
K-9.4	6	9.1	6.2
K-2.4	3	4.6	3.0
K-0.1	0.3	0.3	

^a Arbitrary units.

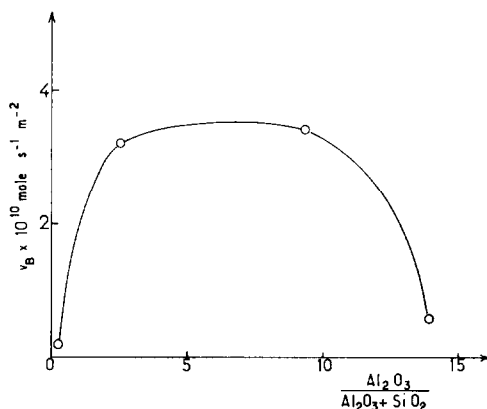


FIG. 2. v_B rate at 85°C as a function of alumina content.

the upper part of Fig. 3, depends on the catalysts and on temperature and pressure (5). During the first 20–30 min, K-14 gave the highest loss in rate and K-0.1 the lowest. The inverted order at short and long run times for three of the catalysts is explained by the v_B and v_L rates analysis just described. Beyond $t = 5-7$ min, the intermediate dealuminated samples gave the

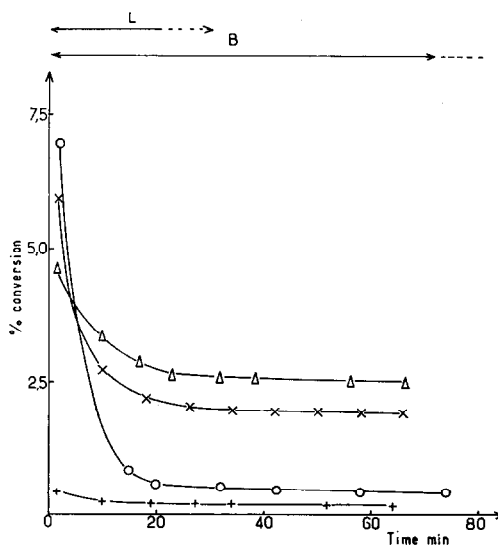


FIG. 3. Percentage conversion of *cis*-2-butene at 85°C as a function of run time ($P = 30$ Torr). (○) K-14, (×) K-9.4, (Δ) K-2.4, (+) K-0.1. The arrows in the upper part indicate times during which B and L sites are working. Lifetime of L sites depends on catalysts.

highest conversion. K-0.1 gave very low conversion at $t < 20$ min, and was about 50% as active as K-14 beyond $t \sim 20$ min.

DISCUSSION

The change in the dependence of v_L on alumina content near the abscissa 2.4% Al_2O_3 (i.e., 20% of the initial alumina content) shown in Fig. 1 confirms the existence of different kinds of aluminum sites in K-14 (1, 4, 8, 9). The sites first eliminated are less active (or not all of them are active), and the Lewis acidity (pyridine band intensity) follows the same pattern. Greater amounts of isomerizing and acidic sites are eliminated in the range 2.4–0.1% Al_2O_3 . Similar changes were noticed in EPR studies (4, 8) and were related (4) to the removal of tetraordinated aluminum atoms. Such a heterogeneity has also been mentioned (10, 11) with other amorphous silica-aluminas.

Several kinds of sites (B and L) are known to be active in butene isomerization on K-14 (5, 6), and the present results indicate that the same kinds of active sites exist also on all dealuminated samples. The data in Fig. 1 and in Table 1 show that v_L isomerization occurs on Lewis-oxidizing sites linked with reducing sites and that v_L depends very closely on the number of these sites. As for the B sites, it is known that isomerization does occur on protonic centers even though they may be very weak (12). It is difficult to measure that part of the protonic acidity which has the strength and stability to follow the isomerizing activity (7) but the correlations between v_B and protonic sites is certain from results of other catalyst poisoning experiments (5, 6). The high catalytic activity of K-2.4 and K-9.4 samples may hence be explained by the high thermal stability of the weak protonic acidity of dealuminated samples (7). Moreover, dealuminated silica-aluminas have more weak acid sites than alumina content suggests (9), which may also account for the high values of v_B . Reducing sites also certainly play a role in isomerization on B sites since K-14 shows a decrease in v_B by poisoning these sites and K-2.4

indicates an interaction between butene and reducing centers (5, 6).

The activity decay (Fig. 3) arises implicitly from properties of v_L and v_B and the lifetimes of B and L sites (5, 6). Butene isomerizes on L sites at the beginning of a run by means of an active polymer which transforms itself into a nonactive polymer residue (5, 6). The main part of the deactivation at $t < 20\text{--}30$ min is then due to the action of L sites, with K-14 strongly affected because of its high Lewis acidity. The decrease with alumina content of the loss of activity during the first 20–30 min (Fig. 3) parallels the decrease in Lewis acidity given in Fig. 1, confirming the role of L sites in the dealuminated samples. The fouling of Lewis acid sites has also been observed in propylene polymerization on silica-alumina catalysts for reaction times higher than 30 min (13), and deactivation in cumene cracking on dealuminated samples was correlated to Lewis acidity (2). Loss of activity at low time range is not at all related to the value, low or high, of the quite constant conversion at higher times since it has been shown that poisoning L sites does not affect the plateau (5, 6). Hence the values of conversion at initial time or after a time > 30 min are completely independent and vary only by changing the catalysts, i.e., the ratio of the number of sites, L/B. This ratio is not constant as alumina is removed from the catalysts, which explains the inverting in the order of the curves in Fig. 3.

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REFERENCES

1. BARTHOMEUF, D., *C. R. Acad. Sci. Paris* **259**, 3520 (1964); BARTHOMEUF, D., BALLIVET, D., DEVAUX, R., AND TRAMBOUZE, Y., *Bull. Soc. Chim.*, 1495 (1967); DE MOURGUES, L., BARTHOMEUF, D., FIGUERAS, F., PERRIN, M., TRAMBOUZE, Y., AND PRETTRE, M., in "Proceedings of the 4th International Congress on Catalysis," paper 61 (1968).

2. BARTHOMEUF, D., PERRIN, M., TRAMBOUZE, Y., AND PRETTRE, M., *Kinet. Katal.* **8**, 115 (1967).
3. BALLIVET, D., BARTHOMEUF, D., AND PICHAT, P., *J. C. S. Faraday I* **68**, 1712 (1972).
4. VEDRINE, J., BARTHOMEUF, D., DALMAI, G., TRAMBOUZE, Y., IMELIK, B., AND PRETTRE, M., *C. R. Acad. Sci. Paris Ser. C* **267**, 118 (1968).
5. BALLIVET, D., BARTHOMEUF, D., AND TRAMBOUZE, Y., *J. Catal.* **26**, 34 (1972).
6. BALLIVET, D., BARTHOMEUF, D., AND Y. TRAMBOUZE, Y., *J. Catal.* **34**, 423 (1974).
7. BARTHOMEUF, D., *C. R. Acad. Sci. Paris Ser. C* **270**, 1549 (1970).
8. NACCACHE, C., BALLIVET, D., AND BARTHOMEUF, D., *C. R. Acad. Sci. Paris Ser. C* **272**, 1616 (1971).
9. BARTHOMEUF, D., URBAIN, H., AND TRAMBOUZE, Y., *Bull. Soc. Chim. France*, 4558 (1967).
10. BOURNE, K. H., CANNINGS, F. R., AND PITKETHLY, R. C., *J. Phys. Chem.* **74**, 2197 (1970).
11. BOEHM, H. P., *Discuss. Faraday Soc.* **52**, 118 (1971).
12. LOMBARDO, E. A., AND VELEZ, J., *Advan. Chem. Ser.* **121**, 553 (1973).
13. SHEPHARD, F. E., ROONEY, J. J., AND KEMBALL, C., *J. Catal.* **1**, 379 (1962).