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Structural and textural factors influencing the rate of butene isomerization on aluminas

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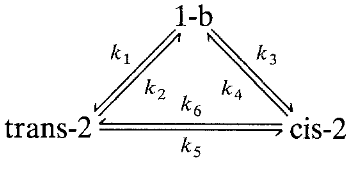
The isomerization of *n*-butene was used as a model reaction on a series of aluminas in order to find relationships between their catalytic activity and their structural and textural characteristics. The results show that the nature of the precursor, either gibbsite or boehmite, from which the alumina is obtained plays an important role in the catalytic activity. If the same precursor is considered the presence of pentacoordinated aluminum on the surface generates sites which influences deeply the product selectivity. Thus, besides structural aspects, detectable by MAS NMR, and textural factors such as surface area and pore size distribution, there are more subtle effects linked to the nature of the precursor which are not explained so far.

Keywords: Isomerization of *n*-butane; model reaction on aluminas; catalytic activity; structural characteristics; textual characteristics

1. Introduction

The isomerization of *n*-butene on aluminas has been extensively studied because of its relative simplicity [1–3]. The three isomers are related by six rate constants as shown in the following triangular diagram:



It is generally accepted that k_3/k_4, k_1/k_2 and k_6/k_5 are the equilibrium constants K_1, K_2 and K_3, respectively, even if the k_i's are apparent rate constants, and that each of the six possible steps is first order. The values of the

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Table 1
Equilibrium constants and compositions at selected temperatures

T (K)	Constants			Compositions (%)		
	K_1	K_2	K_3	1-butene	cis-2-butene	trans-2-butene
268	8.97	42.8	4.98	1.89	17.0	81.1
296	7.30	25.9	3.70	2.93	21.4	75.7
345	5.52	13.0	2.47	5.11	28.2	66.7

K_1, K_2 and K_3 and the equilibrium compositions at selected temperatures are given in table 1.

In ref. [2] several types of aluminas have been compared, but at the time the characterization was based mainly on the X-ray diffraction pattern. Since on aluminas, it is also accepted that the acidity is due to Lewis centers, the overall activity and the selectivity should depend upon the number, the nature, and the strength of the Lewis sites.

With the development of ^{27}Al MAS NMR it is possible to achieve a better characterization from the estimate of the ^{27}Al species in four-, five- and six-fold coordination ($\mathrm{Al^{IV}}$, $\mathrm{Al^{IV}}$ and $\mathrm{Al^{VI}}$, respectively) [4]. In addition, it has been shown that aluminas containing $\mathrm{Al^{V}}$ have stronger Lewis sites than those without $\mathrm{Al^{V}}$. Aluminas with $\mathrm{Al^{V}}$ are obtained by grinding the precursors boehmite and gibbsite before thermal activation [5]. $\mathrm{Al^{V}}$ seems to be metastable since activation above 973 K appears to decrease its relative content with respect to $\mathrm{Al^{VI}}$ and $\mathrm{Al^{IV}}$. More recently [6], in using the proton cross-polarization technique, it has been confirmed that $\mathrm{Al^{V}}$, as well as $\mathrm{Al^{IV}}$ and $\mathrm{Al^{VI}}$ exist in the surface sublayer and that the five-fold coordination shell is the most strained. For instance, in the subsurface layer of a ground boehmite calcined at 550°C and rehydrated in atmospheric moisture, the $\mathrm{Al^{VI}}$, $\mathrm{Al^{V}}$ and $\mathrm{Al^{IV}}$ contents are 1.27, 0.8 and 0.47 times those observed in the bulk, respectively. Accordingly, the $\mathrm{Al{-}\hat{O}{-}H}$ angles are in the ratios 1, 0.94 and 1.09 for $\mathrm{Al^{VI}}$, $\mathrm{Al^{V}}$ and $\mathrm{Al^{IV}}$ in the subsurface layer.

Thus, this work was undertaken with the hope to correlate the activity and selectivity of alumina catalysts with their mode of preparation and thermal activation. Some preliminary results [7] have suggested that the sites linked to the presence of $\mathrm{Al^{V}}$ increase the cis-2 → trans-2 conversion. Here we present a more complete picture in which the textural as well as the structural features are accounted for.

2. Calculation of the rate constants

The calculation procedure is based on two assumptions: (1) the isomerization is a kinetic simple reaction, the six rate constants being first order; and (2) the ratios of the rate constants k_1/k_2, k_3/k_4, and k_6/k_5 in the triangle are equilibrium constants. These are the basic assumptions in the classical papers by Haag and Pines [1] and Hightower and Hall [2]. Therefore, the calculation of the rate constants k_1, k_3, and k_6, all corresponding to the forward reaction towards the most thermodynamically stable product (trans-2-butene), is possible. The fundamental equations are those developed by Haag and Pines [1]:

Concentration of	1-butene	trans-2-butene	cis-2-butene
at time $t = 0$	a	0	0
at time t	$a - x - y$	x	y

$$\begin{aligned} x = {} & \frac{a}{\sqrt{m^2 - 4n}} \left(k_1 - \frac{p_1}{2n} \left(m + \sqrt{m^2 - 4n} \right) \right) \exp\left(-\left(m - \sqrt{m^2 - 4n} \right) \frac{t}{2} \right) \\ & - \frac{a}{\sqrt{m^2 - 4n}} \left(k_1 - \frac{p_1}{2n} \left(m - \sqrt{m^2 - 4n} \right) \right) \exp\left(-\left(m + \sqrt{m^2 - 4n} \right) \frac{t}{2} \right) \\ & + \frac{p_1 a}{n}, \end{aligned}$$

where a = starting concentration of 1-butene, and

$$m = k_1 + k_2 + k_3 + k_4 + k_5 + k_6,$$

$$n = k_1 k_4 + k_1 k_5 + k_1 k_6 + k_2 k_3 + k_2 k_4 + k_2 k_6 + k_3 k_5 + k_4 k_5,$$

$$p_1 = k_1 k_4 + k_1 k_6 + k_3 k_6.$$

An analogous expression has been derived for y. These equations can be adapted if, for instance, the initial feed is cis-2-butene.

Using these fundamental equations, a non-linear least-squares program was written in such a way that values for k_1 and k_3 are allowed to fluctuate within reasonable ranges leading to an optimized k_6, while two additional loops optimize k_3 and k_1, respectively. The program can easily be modified for the isomerization of cis-2-butene or trans-2-butene. It has been checked for the isomerization of 1-butene, in changing k_1/k_6 by more than four orders of magnitude with less than 1% variation on k_3.

3. Experimental

The isomerization reactions were carried out in a recirculation reactor between 250 and 350 K. In all cases the aluminas were calcined at 773 or 973 K for 2 h in O_2 and outgassed overnight at the same temperatures. 0.100 g catalyst was used in each case and about 20 Torr of *n*-butene were diluted in about 600 Torr He. The reaction mixture was analyzed on line by GC. The reactant pressure being low, the k_i's are apparent pseudo-first-order rate constants.

Table 2
Surface area ($m^2\ g^{-1}$) and distribution in micro-, meso- and macro-pores (%)

Sample	T_{act} (K)	Area	Micro	Meso	Macro	Al^V [a]
UB	773	13	7	85	8	no
GB	773	41.8	3	66	31	xx
UB	973	51.3	4	48	48	no
GB	973	39.8	5	90	5	x
UG	773	220	33	36	31	no
GG	773	81.8	3	69	28	x
UG	973	268	6	23	71	no
GG	973	53.5	7.5	70	22.5	(X)

[a] no means not measurable; x means observable amount, xx indicates a higher concentration in Al^V than x; and (X) means initially observable, but not observable after calcination at 973 K.

The specific surface area (BET, N_2 at −196°C) and the pore distribution between micro- (0–2 nm), meso- (2–50 nm) and macro- (> 50 nm) was obtained using the Omnisorp-100 (Coulter Co.) instrument in the static mode. The preparation and characterization of the aluminas used in this work were described thoroughly in ref. [4]. Table 2 summarizes the textural characteristics and it gives a scaling for the contents in five-fold coordinated aluminum (Al^V) in the bulk.

4. Results and discussion

Figs. 1 and 2 show the agreement between the experimental compositions and the theoretical values calculated from the optimized k_i ($i = 1$–6) for the 1-butene isomerization and the cis-2-butene isomerization. After 4×10^3 min at 296 K,

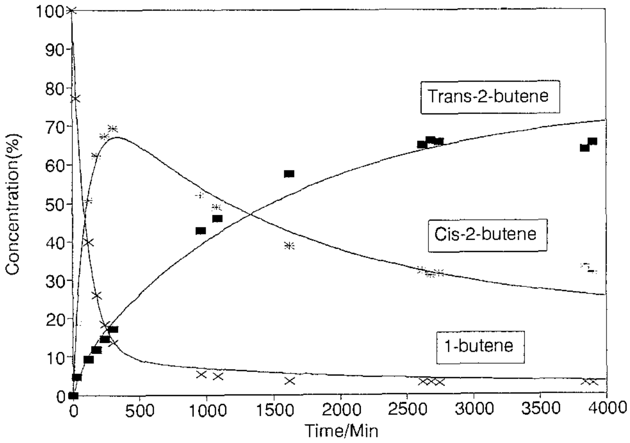

Fig. 1. 1-butene isomerization on the alumina obtained by activating unground gibbsite (UG) at 773 K. Reaction temperature: 296 K. Line: computer simulation. Symbols: experimental data.

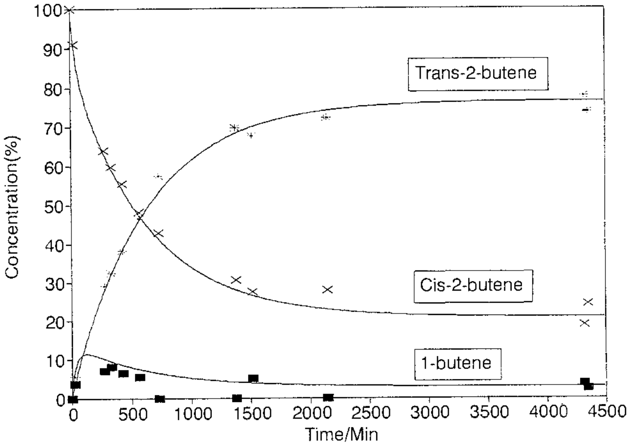

Fig. 2. cis-2-butene isomerization under the same experimental conditions as in fig. 1.

the theoretical equilibrium compositions shown in table 1 are close to the experimental ones when starting from cis-2-butene and are approached within about 10% when starting from 1-butene, indicating some deactivation. For sake of abbreviation, the following symbols represent the various aluminas: UB is the alumina obtained from unground (U) boehmite (B), while GB is that obtained from ground (G) boehmite (B). Correspondingly, UG and GG stand for the aluminas derived from unground or ground gibbsite. It should be outlined that in each case the simulated evolution of the composition, obtained from the k_i's, has been compared to the experimental composition in the reacting system, and that the k_i's in tables 3 and 4 are the best fitting. The validity of the calculated results is further confirmed by comparing them with the rate constant, k, from a linear plot with $-\ln(X_e - X) = kt - \ln X_e$ [8], where X and X_e refer to the conversion of 1-butene at time t and at equilibrium, respectively. Thus, in the case of 1-butene conversion, k should be equal to $(k_1 + k_3) - (k_2 + k_4)$. Indeed,

Table 3

Rate constants k ($\mathrm{min}^{-1}\ \mathrm{m}^{-2}$)$\times 10^3$ calculated for the 1-butene isomerization. T_{act}: activation temperature (K); T_{rxn}: reaction temperature (K)

Sample	T_{act}	T_{rxn}	k_1	k_3	k_6	$\frac{k}{(k_1+k_3)-(k_2+k_4)}$
UB	773	350	0.71	0.48	$<10^{-3}$	0.94
GB	773	350	0.16	0.28	0.72	0.82
UB	973	350	0.14	0.11	$<10^{-3}$	(0.64)
GB	973	350	0.67	0.73	0.85	0.85
UG	773	268	0.012	0.077	0.023	0.92
GG	773	268	0.029	0.16	0.0086	0.95
UG	973	268	0.019	0.16	$<10^{-4}$	0.87
GG	973	268	0.052	0.28	$<10^{-3}$	0.93

Table 4
Rate constant k (min^{-1} m^{-2})$\times 10^3$ calculated for the cis-2-butene isomerization, same legend as in the previous table

Sample	T_{act}	T_{rxn}	k_1	k_3	k_6
UB	773	345	1.8 [a]	$<10^{-3}$	3.8
GB	773	345	0.16 [a]	$<10^{-4}$	0.041
UG	773	296	$<10^{-4}$	1.08	0.059
GG	773	296	$<10^{-4}$	0.83	0.060

[a] Corresponding values of k_2. These values have to be considered since the cis-2 → 1-butene conversion is very small and that 1-butene must be obtained through the trans-2 isomer.

the ratios given in table 3 are between 0.82 and 1 (average: 0.9) with one exception.

The rate constants of the "forward" reactions, k_1 for 1-b to trans-2, k_3 for 1-b to cis-2 and k_6 for cis-2 to trans-2-butene are shown for the six aluminas in table 2. As it can be seen in nine cases out of twelve, grinding the precursors before thermal activation increases the rate constants. Since grinding increases the Al^{V} content it would be tempting to conclude that the presence of surface active sites generated by these species improves the overall activity. However, an increase in the activation temperature from 773 to 973 K provokes a decrease in the amount of Al^{V} both in the bulk [4] and on the surface [6], while the k_i's increase in five cases out of six. In addition, the aluminas obtained from ground and unground gibbsite are more active than those obtained from boehmite, in spite of a lower Al^{V} content. Indeed, at comparable activity the reaction temperature is about 50 K lower on the former than on the latter. Thus, there are obviously other factors than specific site activity which play a role.

Considering the rate constants obtained from the conversion of cis-2-butene in table 4, the aluminas obtained from the unground precursors are more or at least as active than those obtained from the ground precursors. Thus, the trend is opposite to that reported for the isomerization of 1-butene, but again a clear difference between the B and G aluminas is observed. The values of k_3 (or k_4) are very small on the B aluminas, indicating no direct conversion of cis-2 to 1-butene. On the other hand, on the G aluminas the values of k_2 (or k_1) are negligible, ruling out the interconversion between trans-2 and 1-butene.

From the results in tables 3 and 4 it must be concluded that the nature of the precursors plays a more important role than the distribution of the aluminum among its possible coordination shells and/or the pore size distribution reported in table 2.

Two graphic illustrations of the experimental results are represented in figs. 3 and 4. In fig. 3, the selectivity cis/trans, represented by $\ln(k_3/k_1)$, is sketched for the isomerization of 1-butene. As far as the aluminas obtained from boehmite are concerned, grinding the precursors inverts the selectivity at a

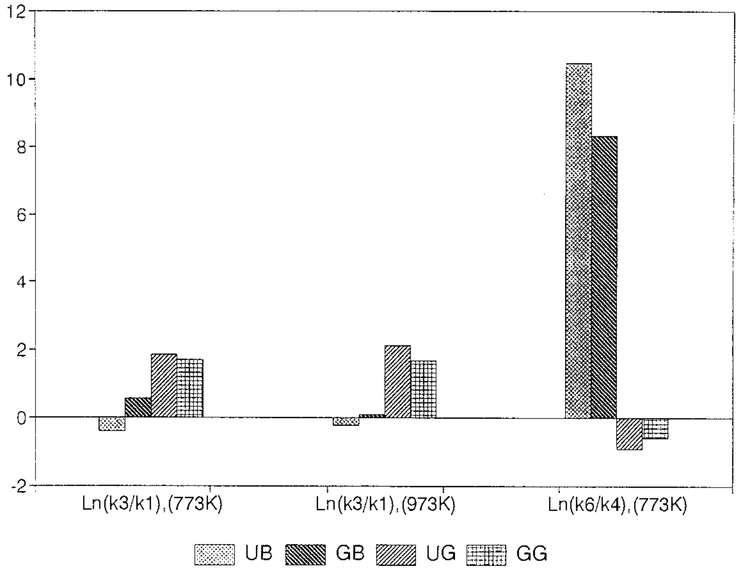

Fig. 3. ln k_3/k_1 is the cis/trans selectivity in the 1-butene isomerization, while ln (k_6/k_4) is the trans-2-butene/1-butene selectivity in the cis-2-butene reaction. UB: alumina from unground boehmite; GB: alumina from ground boehmite; UG and GG: from unground and ground gibbsite. The activation temperatures are shown and the reaction temperatures are 350 K for the B samples and 268 K for the G samples, respectively.

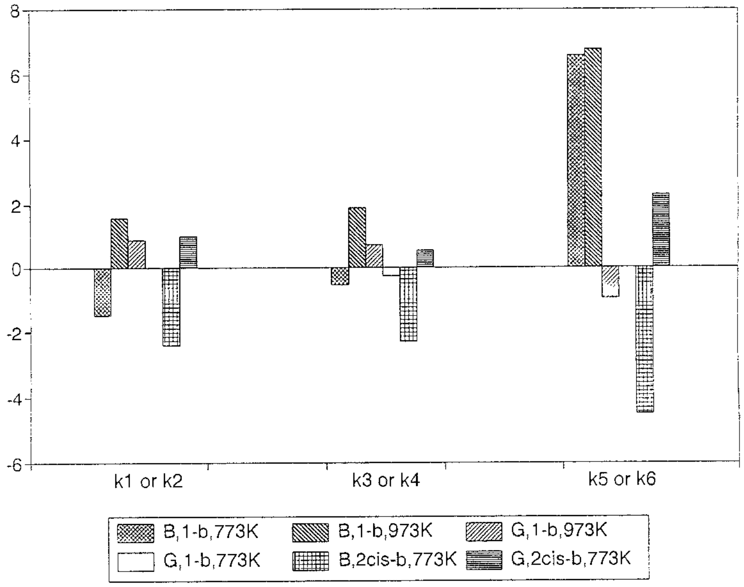

Fig. 4. Δ ln k_i obtained upon grinding the precursor (see text) and activation at either 773 or 973 K, for (i) the 1-butene isomerization at 347±2.5 K on the ex-boehmite aluminas and at 268 K for the ex-gibbsite aluminas and (ii) for the 2-butene isomerization at 296 K on both kinds of aluminas.

greater extent after the activation at 773 K than at 973 K. On the contrary, grinding gibbsite before activation decreases the cis/trans selectivity at a greater extent on GG activated at 973 than at 773 K. In the isomerization of cis-2-butene, the selectivity trans-2/1-butene is high on UB and somewhat lower on GB, but on the aluminas obtained from UG and GG the selectivity is reversed. Note that if the heats of adsorption of the different isomers are not identical, their effect will be included in the expression of selectivity using the apparent rate constants.

In fig. 4 the rate constants of the same step but on different samples are compared in representing

$$\Delta \ln k_i = \ln k_i \text{ (ground + activated)} - \ln k_i \text{ (unground + activated)}.$$

Thus, the emphasis is on the effect of grinding the materials both on the $\mathrm{Al^V}$ content and on the pore size distribution (table 2). Note that $\Delta \ln k_1$ is the same as $\Delta \ln k_2$, even if the k_i's are apparent rate constants. In the same way $\Delta \ln k_3$ equals to $\Delta \ln k_4$, etc. It is clear that grinding + activating boehmite at 773 and 973 K favors k_6 with respect to k_3 and k_1 (in decreasing order). Exactly the opposite effect is observed for gibbsite ground and activated at 973 K, while upon activating the GG at 773 K, the $\Delta \ln k_i$'s are about zero.

As far as the cis-2-butene isomerization is concerned, grinding the boehmite precursors depresses k_5 with respect to k_2 and k_4 (in decreasing order). The effect of grinding gibbsite on the $\Delta \ln k_i$ values follows the opposite trend to that observed in grinding boehmite.

The inversion of trends outlined above might result from differences between the adsorption energy of the different reactants, eventually enhanced by differences in the reaction temperature.

So far, however, there is no hint for what may cause the surfaces of the aluminas obtained from gibbsite or from boehmite to exhibit such differences in activity and selectivity. From the comparison of aluminas obtained from the same precursors, it is clear that the peculiar $\mathrm{Al^V}$ five-fold coordination is not the "Deus ex machina" which solves all the problems. However, $\mathrm{Al^V}$ might be the precursor of sites exhibit activity and adsorption energy different from those linked to other coordination shells. Unfortunately, since the surface concentration in different kinds of aluminum species and the pore size distribution change simultaneously, it is not presently possible to define which factor plays the primary role.

Acknowledgement

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