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FT-IR Studies on Light Olefin Skeletal Isomerization Catalysis

I. The Interaction of C4 Olefins and Alcohols with Pure γ-Alumina

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The skeletal isomerization of *n*-butene to isobutene and the interaction of the four butene isomers and of *sec*-butanol and *tert*-butanol with a pure γ-alumina sample were investigated. γ-Al_2O_3 is quite active (>34% conversion) and a selective catalyst for *n*-butene to isobutene isomerization at 753 K (>80% selectivity). FT-IR spectroscopic experiments show that the C4 olefins are involved in two different interactions on the alumina surface at room temperature: (i) H-bonding over surface hydroxy groups and (ii) reactive adsorption giving rise to allyl species. Both species have been fully characterized spectroscopically for all four butene isomers. At higher temperatures, carboxylates appear, some of which are aromatic. Alcohol adsorption shows that 2-butoxy and *tert*-butoxy groups decompose to give gaseous *n*-butene and isobutene, respectively, near 473 K. Moreover, traces of *tert*-butoxy species are observed starting from 2-butoxides. H-bonded olefin species are assumed to be precursors for carbenium ions that give rise to double-bond and skeletal isomerization at high temperature. Butoxy groups are proposed to act as the unstable intermediate adsorbed forms for carbenium ions. Allyl species are identified as intermediates in double-bond isomerization at low temperature and in the formation of by-products and coking agents (aromatics and carboxylates) at high temperature.

INTRODUCTION

The skeletal isomerization of *n*-butenes to isobutene may help to meet the increasing demand for isobutene, whose availability was foreseen as the bottleneck of a growing request for ethers (MTBE, ETBE) for reformulated gasoline (1). Two main catalyst types have been proposed for this reaction (2): those based on aluminas and those based on protonic zeolites. Of alumina-based catalysts, interest has focused mainly on chlorided aluminas (3), fluorided aluminas (4), and tungsta alumina (5, 6), while pure aluminas are also active and rather selective catalysts for this reaction (2, 5, 6). Silicated aluminas were patented in 1977 by Snamprogetti (7), and the mechanism of their activity in *n*-butene skeletal isomerization has been the subject of some papers (8–10). Snamprogetti recently reported the development of new alumina-based catalysts for this reaction (11). The use of protonic zeolites, such as ferrierite (12, 13) and ZSM22 (14), as very efficient catalysts for this reaction has been emphasized recently.

The skeletal isomerization of olefins can also occur in the liquid phase with sulfuric acid or superacids like $HF \cdot SbF_5$ as the catalysts (15, 16). It is believed that the transposition of the *sec*-butyl carbenium ion to the *tert*-butyl carbenium ion, either via protonated methylcyclopentane (16, 17) or via a previous dimerization (12) followed by isomerization and cracking of a C8 carbenium ion (18), is the key step. This implies the use of a rather strong Brønsted acid catalyst, as is the case with protonic zeolites and halided aluminas. Conversely, pure alumina is generally believed to be a strong Lewis solid acid (19, 20), but is assumed to lack Brønsted acidity. Silicated aluminas, in spite of their excellent catalytic behavior in this reaction, were found recently to be not strongly Brønsted acidic (10). Thus, the question arises as to whether olefin skeletal isomerization on "pure" and modified alumina occurs through the same mechanism as that for typical Brønsted acids, or via a different way, like through π-allyl species formed over Lewis sites (5, 15).

Following an investigation aimed at understanding the basic chemical features of the *n*-butene skeletal isomerization process (10), we studied the interaction of C4 olefins with different potentially useful catalytic materials. We present our data on the interaction of C4 olefins and alcohols with "pure" γ-alumina.

EXPERIMENTAL

A commercial γ-Al_2O_3 powder (190 $m^2\ g^{-1}$, pore volume 0.48 ml g^{-1}, medium pore radius 85 Å, Na < 100 ppm; Si < 0.2%, from Akzo) was used as the catalyst. This material was the subject of a previous characterization study (10) where it was found to behave as a typical very pure transitional alumina.

The IR spectra were recorded on a Nicolet Magna 750 Fourier transform instrument. The adsorption experiments

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were performed using pressed disks of the pure powders, activated by outgassing at 300–1070 K in the IR cell.

The catalytic tests were performed at 1 atm (101.3 kPa) with pure butene or butene diluted by isobutane with a fixed-bed tubular reactor (internal diameter of 12 mm, with a coaxial internal thermocouple with 5 mm external diameter, 1.5 g catalyst weight). The catalyst granulometry was 20–25 mesh. The products were integrally recovered during a given period (usually 20 min) after 20 min time on stream and were analyzed by on-line gas chromatography (HP 5890) using a FID detector and a 50-m Chrompack PLOT Al_2O_3/Na_2SO_4 capillary column for 1-butene/isobutene separation and a 50-m PONA capillary column for the analysis of all other products.

RESULTS

(a) Catalytic Activity

The analysis of the products from a typical experiment are reported in Table 1. Under reaction conditions the equilibrium among 1-butene, *cis*-2-butene, and *trans*-2-butene is nearly established. In effect the data reported in Table 1 show a slight excess of *cis*-2-butene among *n*-butenes with respect to the thermodynamic equilibrium values reported by Kilpatrick *et al.* (21). The overall *n*-butene conversion is 34.6%. The selectivity to isobutene is quite high though definitely lower than that possible in equilibrium with the other butenes (21). Table 1 shows that the main side reactions give rise to C3 and C5 hydrocarbons (mainly propene and isopentenes and with significant amounts of *n*-pentenes). Among other products, the presence of C8 aromatic compounds (xylenes and ethylbenzene), of C4 paraffins, and of methylcyclopentane and methylcyclobutane seems significant. Coke formation results in catalyst deactivation in experiments performed with time (several hours) on stream. Reactivation completely restores catalytic activity.

TABLE 1

Typical Product Distribution for 1-Butene Isomerization on γ-Al_2O_3

Formula	Name	Inlet (wt%)	Outlet (wt%)	Selectivity (mol%)
CH_4	Methane		Traces	
$CH_2=CH_2$	Ethene		<0.1	0.2
CH_3-CH_3	Ethane		Traces	
$CH_2=CH-CH_3$	Propene		1.2	4.4
$CH_3-CH_2-CH_3$	Propane		Traces	
$CH_2=CH-CH_2-CH_3$	1-Butene	80.5	15.0	—
cis-$CH_3-CH=CH-CH_3$	*cis*-2-Butene		16.0	—
trans-$CH_3-CH=CH-CH_3$	*trans*-2-Butene		21.6	—
$CH_2=C(CH_3)_2$	Isobutene		22.3	80.0
n-C_4H_{10}	*n*-Butane	<0.1	0.1	0.2
Iso-C_4H_{10}	Isobutane	19.5	19.6	0.5
$CH_2=CH-CH=CH_2$	1,3-Butadiene		<0.1	0.1
CH_3-cyclo-C_3H_5	Methylcyclopropane		<0.1	<0.1
$H_2C=CH-C_3H_7$	1-Pentene		0.1	0.4
cis-$CH_3-CH=CH-C_2H_5$	*cis*-2-Pentene		0.2	0.6
trans-$CH_3-CH=CH-C_2H_5$	*trans*-2-Pentene		0.3	1.2
$H_2C=C(CH_3)-CH_2-CH_3$	2-Methyl-1-butene		0.6	2.0
$H_2C=CH-CH(CH_3)_2$	3-Methyl-1-butene		0.1	0.4
$(CH_3)_2C=CH-CH_3$	2-Methyl-2-butene		1.1	4.1
$H_2C=C(CH_3)-CH=CH_2$	Isoprene		<0.1	<0.1
n-C_5H_{12}	*n*-Pentane		Traces	
$(CH_3)_2CH-C_2H_5$	Isopentane		Traces	
CH_3-cyclo-C_4H_7	Methylcyclobutane		<0.1	<0.1
$C_2H_5-C_6H_5$	Ethylbenzene		0.2	0.7
$(CH_3)_2-C_6H_4$	Xylenes mixture		0.1	0.4
Others			1.2	4.2

Note. $T = 753$ K; LHSV 10.2 h^{-1}; products integrally recovered from 20 to 40 min time on stream; catalyst reactivated.

(b) FT-IR Evidence of the Molecular Interaction of the C4 Olefins with the γ-Al_2O_3 Surface

To identify the olefin species adsorbed on alumina, we first recorded their spectra, when condensed over KBr disks, from the vapor at 150 K, thus forming a liquid thin layer. The FT-IR spectra of the adsorbed species arising from the interaction at room temperature of the γ-Al_2O_3 surface, after activation by outgassing at 773 K, with the C4 olefin gases are reported in Figs. 1 to 4. In all cases, the IR spectrum of the olefin species adsorbed on the γ-Al_2O_3 surface in contact with the gas is dominated by a spectrum very similar to that of the liquid. The peak positions for the olefins adsorbed on the γ-Al_2O_3 surface are compared with those of the liquids and of the olefins adsorbed, at low temperature, on silica (22–24) and on HZSM5 zeolite, where the main adsorption occurs on the surface hydroxy groups which can act as Brønsted acidic sites. We also compared the peak positions observed when the C4 olefins are adsorbed on titania, where the interaction is supposed to occur over the Lewis acid sites (22–24). This comparison is shown in detail in Table 2 for 1-butene. Analogous analyses were performed for the other isomers and allowed to detect the overall expected spectrum of the olefin but with some typical perturbations. The most evident are:

(i) the downward shift of the C=C double-bond stretchings;

(ii) the upward shift of the vinylic $=CH_2$ out-of-plane deformation (wagging) fundamental and first overtone modes, for terminal olefins (1-butene and isobutene); and

(iii) the upward shift of combination modes involving the out-of-plane deformations (waggings) of the olefinic $=CH-$ bonds, in the case of nonterminal olefins.

The extent of these perturbations always follows the trend $SiO_2 < \gamma\text{-}Al_2O_3 < HZSM5 < TiO_2$. According to well-known surface chemistry of transitional aluminas (19, 20, 26) as well as our recent characterization of this

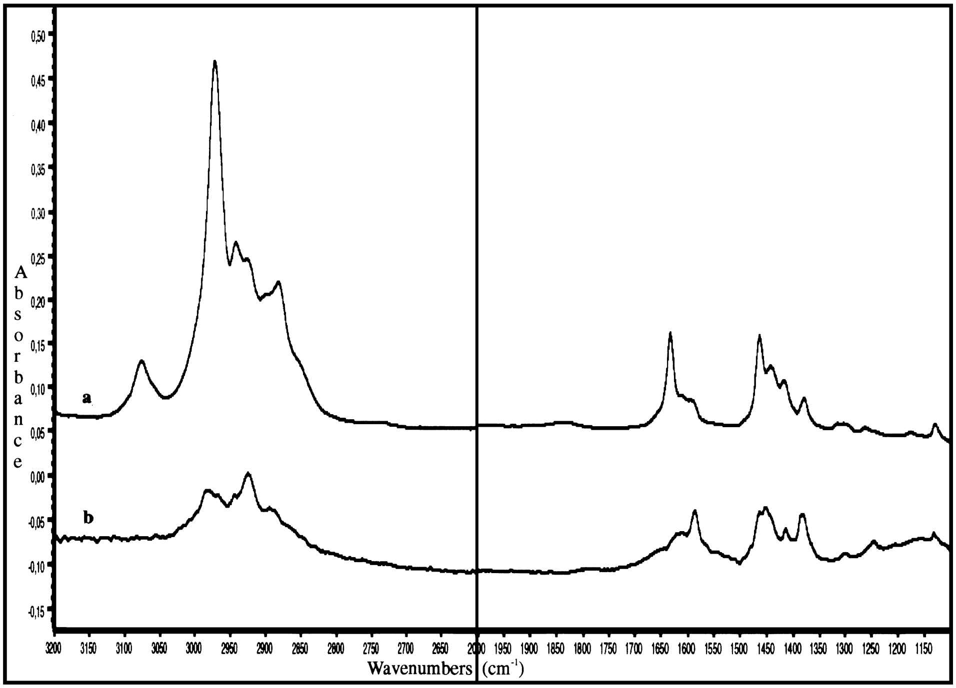


FIG. 1. FT-IR spectra of the adsorbed species arising from 1-butene adsorbed on γ-Al_2O_3 at room temperature in equilibrium with the gas (10 Torr) (a) and after evacuation at room temperature for 10 min (b).

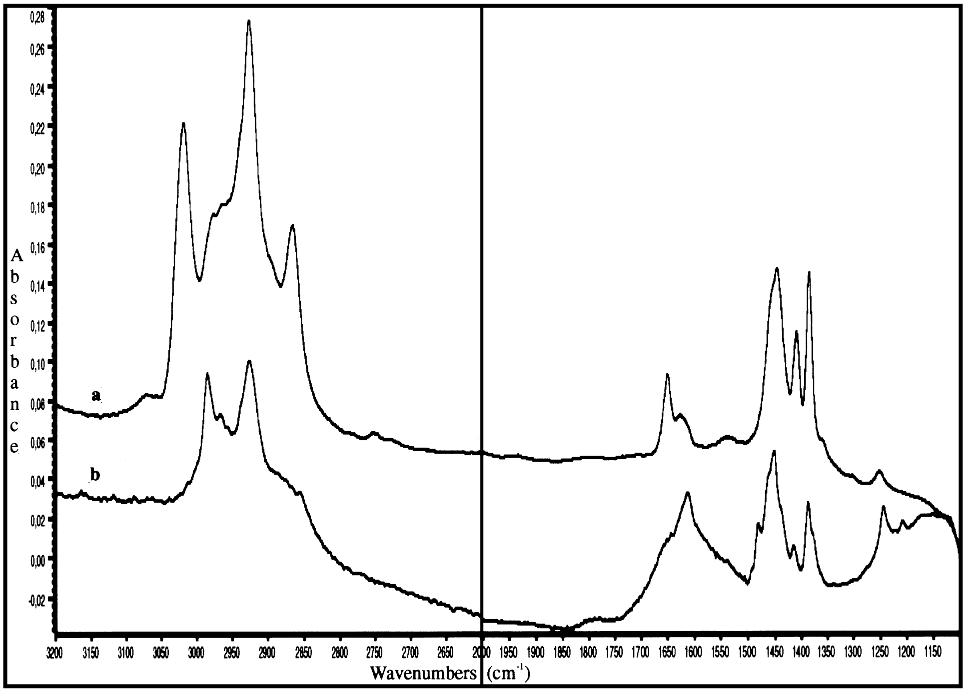


FIG. 2. FT-IR spectra of the adsorbed species arising from *cis*-2-butene adsorbed on γ-Al_2O_3 at room temperature in equilibrium with the gas (10 Torr) (a) and after evacuation at room temperature for 10 min (b).

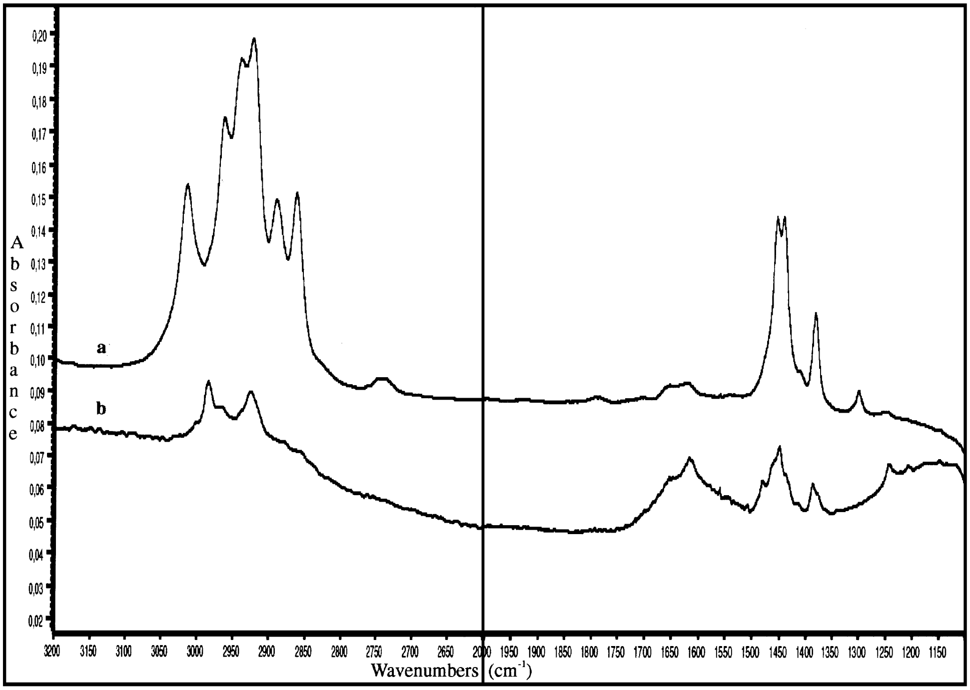


FIG. 3. FT-IR spectra of the adsorbed species arising from *trans*-2-butene adsorbed on γ-Al_2O_3 at room temperature in equilibrium with the gas (10 Torr) (a) and after evacuation at room temperature for 10 min (b).

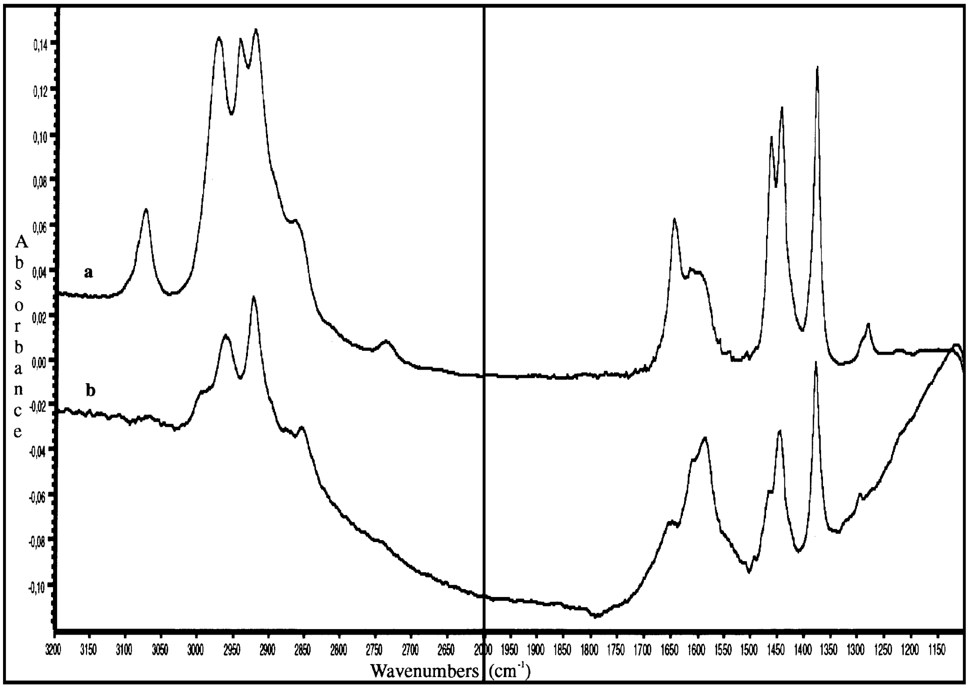


FIG. 4. FT-IR spectra of the adsorbed species arising from isobutene adsorbed on γ-Al_2O_3 at room temperature in equilibrium with the gas (10 Torr) (a) and after evacuation at room temperature for 10 min (b).

TABLE 2

Position (cm^{-1}) of the IR Bands of 1-Butene in the Gas, in the Liquid, and in the Adsorbed State

Vibration	Asymmetry	Symmetry	IR + R gas		IR gas	IR liquid (KBr)	IR SiO_2	IR γ-Al_2O_3	IR ZSM5	IR TiO_2
			s-cis	*gauche*	300 K	150 K	200 K	300 K	150 K	300 K
$\nu 1$	$\nu_{as}{=}CH_2$	a'	3090		3089	3080, 3070	3079	3077	3079	3075
$\nu 2$	$\nu{=}CH{-}$	a'	3019		3022	3006	3008		3000	3000
$\nu 3$	$\nu_s{=}CH_2$	a'	3008		—	3000	2999			2995
$\nu 4$	$\nu_{as}CH_3$	a'	2982		2975	2073	2977	2973	2969	2975
$\nu 20$	$\nu_{as}CH_3$	a''	2978			2965	2970			2971
$\nu 5$	ν_sCH_3	a'	2952	2948	2948	2935	2941	2943	2937	2945
$\nu 21$	$\nu_{as}CH_2$	a''	2936		—	2917	2923	2927	2922	2925
$\nu 6$	ν_sCH_2	a'	2888		2900	2894, 2888	2902	2900	2899	2904
	$2\delta_{as}CH_3$	a'	—	—	2888	2873	2880	2873	2877	2884
	$2\delta_{as}CH_3$		—	—		2848, 2845	2857	2856	2860	
$2 \times \nu 26$	$2wCH_2{-}$		—	—	1833	1828	1850	1850	1861	1875
									1823	
$\nu 7$	$\nu C{=}C$	a'	1643	1647	1648	1641	1637	1634	1641	1625
					1644				1628	1610
$\nu 22$	$\delta_{as}CH_3$	a''	1469		1473	1463	1465		1464	1467
$\nu 8$	$\delta_{as}CH_3$	a'	1460	1463	1463	1458	1460	1464	1459	1462
										1455
$\nu 9$	δ-$CH_2{-}$	a'	1450	1444	1451	1439	1442	1443	1444	1449
					1443	1434	1436		1438	1443
$\nu 10$	$\delta CH_2{=}$	a'	1426	1421	1420	1414	1417	1418	1416	1418
$\nu 11$	δ_sCH_3	a'	1380		1380	1385, 1373	1377	1380	1376	1378
$\nu 12$	w-$CH_2{-}$	a'	1342	1318	1316	1345		1315	1318	1315
						1320				
$\nu 13$	δ-$CH{=}$	a'	1306	1296	1295	1290		1300		1295
$\nu 23$	τ-$CH_2{-}$	a''	1264		—			1262		1264
$\nu 24$	rCH_3	a''	1177					1176		
$\nu 14$	rCH_3	a'	1128			1127		1130		
Refs.			25		This work		22	This work		22

Note. The low-frequency regions for adsorbed species are not available due to the adsorbant skeletal absorptions.

particular alumina sample (10), its Lewis acidity is definitely stronger than that typical of TiO_2 (27). On the other hand, we concluded previously that the molecular interaction of olefins is particularly strong with d_0 transition metal cations where interaction probably occurs between the π-bonding orbital of the olefin and an empty *d* orbital of the cation (24). The *s* and *p* empty orbitals of the main group cations, such as Al^{3+}, seem to be ineffective in interacting with the olefin π-bonding orbitals. Consequently, it is suggested that, on alumina, as on silica and on the HZSM5 zeolite (at low temperature), the molecular interaction occurs at the surface hydroxy groups. For this reason we investigated the perturbation of the IR bands of the surface hydroxy groups of our γ-Al_2O_3 sample upon interaction with olefins.

(c) FT-IR Study of the Interaction of the Surface Hydroxy Groups of γ-Al_2O_3 with the C4 Olefins

As always for well-outgassed spinel-type transitional aluminas (26), the spectrum of our sample outgassed at 770 K (Fig. 5a) shows at least four bands near 3790 (shoulder), 3770, 3730, and 3680 cm^{-1}. A fifth broader band can also be seen after milder pretreatments near 3590 cm^{-1}. According to previous work (20, 28), where the model of Knözinger and Ratnasami (29) was partly modified, the bands at 3790 and 3770 cm^{-1} are assigned to terminal OHs over one tetrahedrally coordinated Al ion, in a nonvacant environment or near a cation vacancy, respectively; the band at 3730 cm^{-1} is assigned to a terminal OH over an octahedrally coordinated Al ion, while the bands at 3680 and 3590 cm^{-1} (the last observed as a broad band after activation at 773 K) are assigned to bridging and triply bridging OHs, respectively.

The spectrum in Fig. 5b is typical for the interaction of γ-Al_2O_3 with the other butenes too. The subtraction spectrum, presented in Fig. 5d, shows that all the surface hydroxy groups are perturbed upon interaction with C4 olefins. In fact, their bands are observed as negative in the subtraction spectra. However, the bands at higher frequencies disappeared completely upon adsorption, while the others seem to be only partially eroded.

The disappearance or decrease in the bands of free surface hydroxy groups corresponds to the formation of a new band, centered near 3480 cm^{-1}. Outgassing causes this band

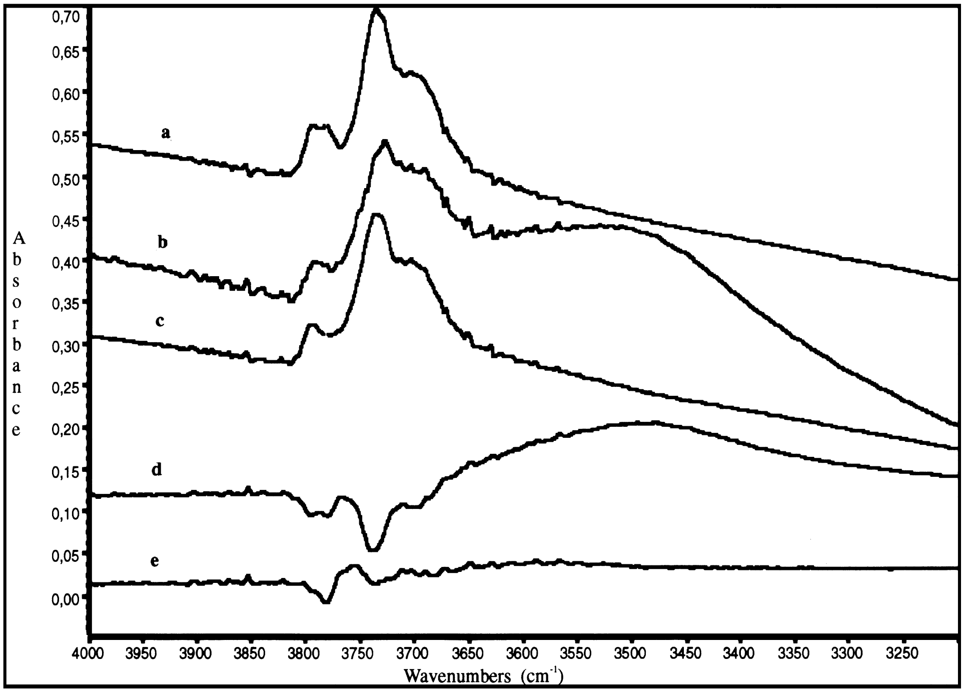
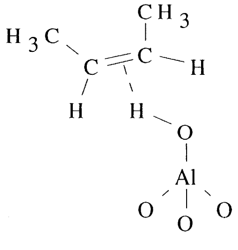


FIG. 5. FT-IR spectra (OH stretching region) of γ-Al_2O_3 after activation (a), in the presence of *cis*-2-butene gas (b), and after outgassing at room temperature (c). Subtraction spectra: (d) = (b) − (a) and (e) = (c) − (a).

to disappear and the bands of the free OHs to be partly restored. This shows that olefins interact with the OHs, giving rise to the above-cited molecular adsorption by H-bonding of the π-type orbitals of the C=C double bond with the hydrogen atoms of the OHs (Scheme I). The shift of the νOH band with this interaction (200–300 cm^{-1}) is greater than that observed previously for the interaction with the OHs of amorphous silica (100–200 cm^{-1} (22)), while it is clearly smaller than that observed on the OHs of HZSM5 zeolite (near 600 cm^{-1}). This confirms that the strength of the H-bonding interaction between C4 olefins and surface OHs is HZSM5 > γ-Al_2O_3 > silica, in agreement with the above conclusions arising from the perturbation observed in the olefin spectra.

As shown in the subtraction spectra (Fig. 5e for *cis*-2-butene), the bands of free surface hydroxy groups are restored by simple outgassing, except for that at 3775 cm^{-1} which remains as a negative band in the subtraction spectrum even after outgassing. This is not very significant, because this band is always perturbed most by all interactions (30).



SCHEME I

These data are evidence of an electrophilic interaction of the surface hydroxy groups of alumina with the olefinic double bond. Under the conditions of our experiments (room temperature), this interaction was too weak to allow the breaking of the C=C double bond and the formation of the carbenium ion due to the weakness of the OHs as Brønsted acids. Thus, it results only in the reversible adsorption–desorption of the olefin on/from the surface hydroxyls.

(d) FT-IR Study of the Reactive Adsorption of the C4 Olefins with the Surface of γ-Al_2O_3 at Room Temperature

As already mentioned, the spectra recorded upon contact with the C4 olefin gases are those of the molecularly adsorbed species. After outgassing, these molecular species desorbed quickly and completely, and their spectra disappeared. In all cases, a weaker spectrum, certainly due to a different, more strongly adsorbed species, was still detectable. The peak positions are reported in Table 3.

The spectra of the strongly adsorbed species, arising from the three *n*-butenes, are exactly the same in the C–H stretching region (3200–2700 cm^{-1}) and in the region below 1500 cm^{-1}, typical of C–H deformations and C–C stretchings. The spectrum of the species arising from isobutene is

TABLE 3

Position (cm^{-1}) of the IR Bands of the Products of the Reactive Adsorption of Butenes and Propene on γ-Al_2O_3 as Compared with Those of Allylmagnesium Bromide

1-Butene on γ-Al_2O_3	*cis*-2-Butene on γ-Al_2O_3	*trans*-2-Butene on γ-Al_2O_3	Isobutene on γ-Al_2O_3	Propene on γ-Al_2O_3	$CH_2{=}CH{-}CH_2{-}MgBr$ Ref. (33)	Assignments Ref. (33)	Assignments This work
		3000			3038 f	$\nu_{as}CH_2$	
2982	2984	2986	2987	2984	2999 M	νCH	
2968	2968	2968	2965	2965	2967 M	ν_sCH_2	$\nu_{as}CH_3$
2925	2926	2925	2923	2924	2923 F	ν_sCH_2	
2895	(2895)						ν_sCH_3
	(2855)		2855	2856	2847	Comb.	
(1616)	1614	1618				}$\nu_{as}C{=}C{-}C$	
1586			1588	1596	1515		
(1481)	1481	1480					
1456	1452	1450	1462				$\delta_{as}CH_3$
1450	1437	1439	1445	1450	1449	δ_oCH_2	
1414	1414	1415		1427			
1385	1387	1387	1379	1376	1372	δ_pCH_2	δ_sCH_3
1300			1285	1295	1261	rCH_2	
1245	1244	1244		1244	1248	rCH_2	
	1222						rCH_3
1204	1207	1207			1228	rCH_2	
					1040	$\nu_sC{=}C{-}C$	

clearly different in these regions, although it can be consistent with species that are closely related.

The analysis of the region 1700–1500 cm^{-1} shows that, in the case of species arising from the two 2-butenes, a broad band is found near 1610 cm^{-1}, while in the case of 1-butene the same band is found but a stronger sharp band is also found at 1586 cm^{-1}. Finally, in the case of the species arising from isobutene a sharp band at 1596 cm^{-1} is found.

The spectra observed are certainly due to closely related species in all four cases. For the species arising from the three linear isomers, the species appear to be exactly or nearly the same. To learn more about the nature of such species, we also investigated the adsorption of propene on γ-Al_2O_3. A strongly adsorbed species is also formed from propene (31), and the position of the corresponding absorption bands are listed in Table 3 and compared with those reported in the literature for the “Grignard-type” compound allylmagnesium bromide (32).

The spectra of the strongly adsorbed forms of propene and of all four butene isomers do not show bands that can be assigned to C=O or C–O bonds (strong bands expected in the region 1750–1650 or 1200–1000 cm^{-1}). They do not contain the typical couple of bands of adsorbed carboxylates. Thus, they are associated with molecules or fragments that are not bonded to oxygen. On the other hand, one band (two for 1-butene) is present in all cases in the region 1615–1585 cm^{-1}, i.e., a region typical of C=C stretching modes (33), shifted to lower frequencies with respect to the value of the “free” olefins by some kind of perturbation. These relatively sharp bands, and their intensities, not stronger than the C–H deformation modes of the same species, also agree with an assignment to C=C stretching modes. The species arising from the 2-butene geometric isomers and from 1-butene appear to be identical except for the additional band at 1586 cm^{-1}, strong only in the latter case. For the species arising from the four butenes, one methyl group seems to be intact, as demonstrated by its characteristic bands (Table 3). However, the lack of splitting of the symmetric deformation mode of the methyl groups in the case of the species arising from isobutene suggests that only one methyl group is still present. Species containing isopropyl or terbutyl groups typically show this band split (33). In all cases, including the species arising from both *cis*- and *trans*-2-butene, quite a strong C–H stretching band near 2925 cm^{-1} was found, where methylene groups typically absorb (33).

All these data, together with the close similarity of the spectrum of the species arising from propene with that of allylmagnesium bromide, strongly support the identification of these species as allyl fragments. These species could be, in principle, cationic, anionic, or radical-like.

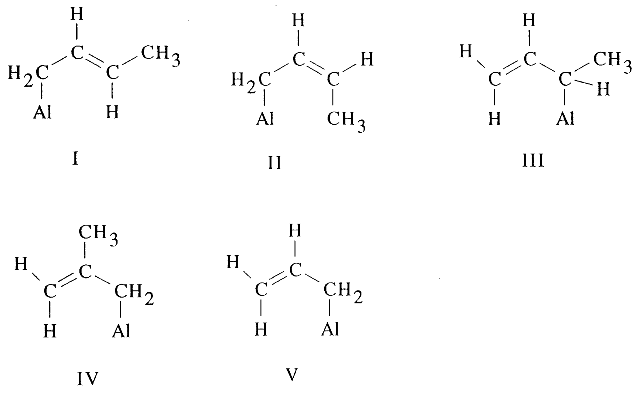
The surface oxide ions on alumina are significantly nucleophilic. In fact, it has been shown that they interact with the electrophilic carbon atoms of, e.g., CO_2 (forming carbonates and bicarbonates (34)) and of formaldehyde (forming dioxymethylene (35)). If the allyl species were cationic, oxide ions would certainly bond with them to form allyloxy species. Nevertheless, the spectrum of the allyloxy species (allyl alcoholates), observed after adsorption of allyl alcohol (31), is definitely different from that observed after propene reactive adsorption. This excludes that the allyl species found after interaction of the olefins are bonded to oxygen and they have a cationic nature.

On the contrary, the position of the C=C stretching, at frequencies lower than that for the "free" olefins but at a frequency higher than that for the anionic allyl species of allylmagnesium bromide and of π-bonded complexes with reduced noble metals (36), strongly favors an identification of these species such as surface organometallic allylaluminum complexes, nearly covalently bonded to surface Al centers. Structures for surface σ-bonded allyl species are proposed in Scheme II.

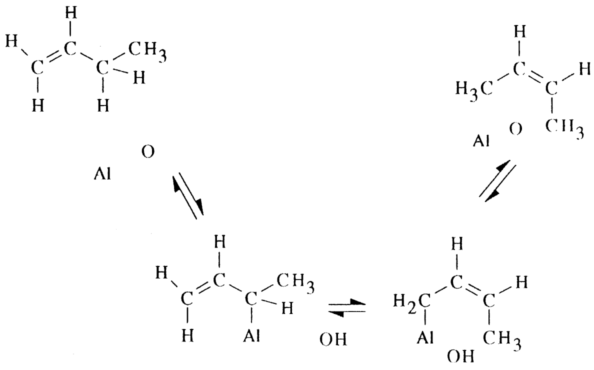
The C=C stretching band is located in the range $1592 \pm 4\ \mathrm{cm}^{-1}$ in the case of the species arising from propene and isobutene, while it is found at $1615\ \mathrm{cm}^{-1}$ in species arising from both *cis*-2-butene and *trans*-2-butene. The C=C double bond is necessarily terminal for allyl species arising from propene (prop-2-en-1-yl species V) and isobutene (2-methylprop-2-en-1-yl species IV), while it is internal for those arising from 2-butenes (but-2-en-1-yl species I or II). The position of the C=C stretching band shifted at frequencies that were higher for internal than for terminal olefins, which are less electron rich.

In the case of species arising from 1-butene, both bands are observed. On the other hand, hydrogen abstraction from the allyl position of 1-butene gives rise to an allyl species with a terminal $C=CH_2$ bond, probably responsible for the band at $1588\ \mathrm{cm}^{-1}$. It is possible that the but-1-en-3-yl species III tends to isomerize to the more stable but-2-en-1-yl species I or II which is also formed by 2-butenes. Thus, we also see the band of this species at 1615 cm^{-1}. In effect, a role of allyl species in the double-bond isomerization of olefins was already suggested by Corado *et al.* (37), Lunsford *et al.* (38), and Guisnet *et al.* (39).

The dissociation of olefins at the allyl position over alumina apparently contrasts with the weak acidity of the allylic hydrogens and the weak basicity of the alumina surface (26). However, it was found that stronger acids, such as methanol (40), also dissociate on alumina at Al^{3+}–O^{2-} couple sites, where the Lewis acidity of the Al^{3+} cationic centers predominates over the basicity of the oxide anion. It seems likely that the C–H bond is broken also for olefins at these sites. This agrees with previous data reported by Lunsford *et al.* (38) showing the role of such Al^{3+} sites in the double-bond isomerization of olefins over alumina. Scheme III gives a possible description of the surface reaction giving rise to allyl species and to *n*-butene double-bond isomerization at low temperature.



SCHEME II



SCHEME III

In conclusion, our data strongly suggest that olefins dissociate over Al^{3+}–O^{2-} "acidic" couples, giving rise to allyl species nearly covalently bonded to aluminum. From 1-butene the but-1-en-3-yl species tends to isomerize to the more stable but-2-en-1-yl species, which is directly formed from 2-butenes. In agreement with the previous literature data (37–39), these surface reactions provide a very reasonable path for low-temperature double-bond position isomerization. However, this reactivity does not seem to be related to the skeletal isomerization reaction, in spite of what has been suggested in the literature (5, 15). On the other hand, these species may play a role in side reactions and in catalyst deactivation by coking.

(e) FT-IR Study of the Interaction of 1-Butene with the Surface of γ-Al_2O_3 at Higher Temperature

The spectra in Fig. 6 are related to the interaction of 1-butene with the γ-Al_2O_3 surface at temperatures higher than 300 K. After contact at 573 K, the features of molecules adsorbed as such are observed again. However, together with the absorptions of adsorbed 1-butene, those of adsorbed 2-butenes are evident too. This is shown, for example, by the presence of a strong band near $3020\ \mathrm{cm}^{-1}$, due to the asymmetric C–H stretching of the H–C=C–H system of 2-butenes. The overall spectrum looks like a mixture of those of the three linear butene isomers, while the presence of isobutene is not evident under these conditions, although

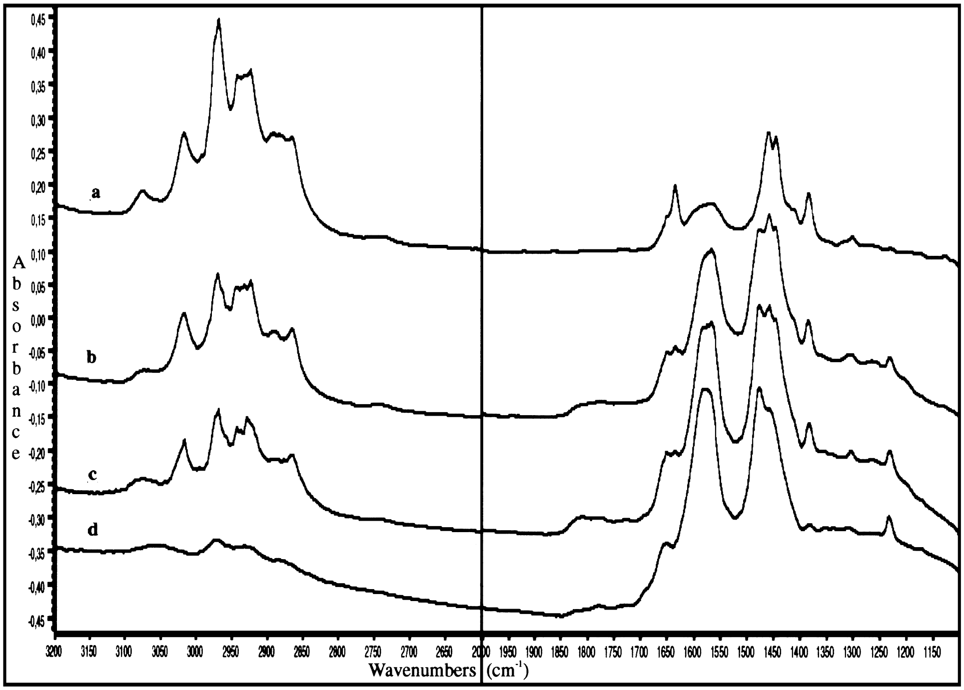


FIG. 6. FT-IR spectra of the adsorbed species arising from 1-butene adsorbed on γ-Al_2O_3 at 573 K (a), 673 K (b), and 773 K (c) (spectra recorded at room temperature in equilibrium with the gas) and after evacuation at room temperature for 10 min (d).

it cannot be completely excluded on the basis of these spectra.

Again, after outgassing the features of the spectra of more strongly adsorbed species appear. However, under these conditions, these species are different from those formed after contact at room temperature. These spectra are now characterized by two strong bands at 1570 and 1480 cm^{-1}, both with shoulders on both sides. Very similar spectra are obtained after adsorption and heating of oxygenated organic compounds on the same surface, and, in particular, after adsorption of carboxylic acids (41). Consequently, we tentatively assign these bands to carboxylates produced from high-temperature adsorption of olefins over γ-Al_2O_3. In effect, a similar spectrum was observed for other alumina-based catalysts after coking (42) and have been assigned to species containing carboxylate groups. In the C–H stretching region, a broad band appeared near 3050 cm^{-1}, typical of νCHs of unsaturated and/or aromatic compounds (33). We suppose, therefore, that strongly bonded carbonaceous species began to grow at the surface after contact under these conditions.

To determine whether these carboxylate species are formed at the expense of the strongly bonded allyl species, we performed another experiment (Fig. 7). We adsorbed *trans*-2-butene at room temperature and then outgassed it, so that only the allyl species remained at the surface, which we then heated. In effect, the spectrum of the allyl species converts progressively to that of the carboxylates. This supports (but does not prove) the idea that the carboxylate species are formed at the expense of the allyl species. In fact, the allyl species could allow the desorption of the intact olefin that later transforms to the carboxylates under these conditions. To allow the formation of carboxylates, it seems unavoidable that hydrogen arising from surface hydroxy groups must be involved in dehydrogenation reactions. These species are probably involved in catalyst deactivation phenomena, and may also participate in the production of side products, such as C8 aromatics.

(f) FT-IR Study of the Interaction of 2-Butanol and tert-Butanol with the Surface of γ-Al_2O_3

γ-Al_2O_3 is known as an efficient catalyst for alcohol dehydration to the corresponding olefins and/or to the corresponding ethers (43–45) as well as for the olefin hydration to the corresponding alcohols. This alcohol–olefin equilibrium reaction is closely related to the olefin isomerization, because it can occur through the same intermediates (e.g., carbenium ions) and with the same products. On the other hand, it has been found that, during alcohol dehydration, skeletal isomerization can also occur (43, 45). In particular, the dehydration of 1-butanol and 2-butanol can give rise to isobutene together with linear butenes. For this reason, we also investigated the interaction of 2-butanol and *tert*-butanol over our γ-Al_2O_3 catalyst.

The interaction of 2-butanol over γ-Al_2O_3 (Fig. 8) gives rise to a spectrum which is dominated in the region

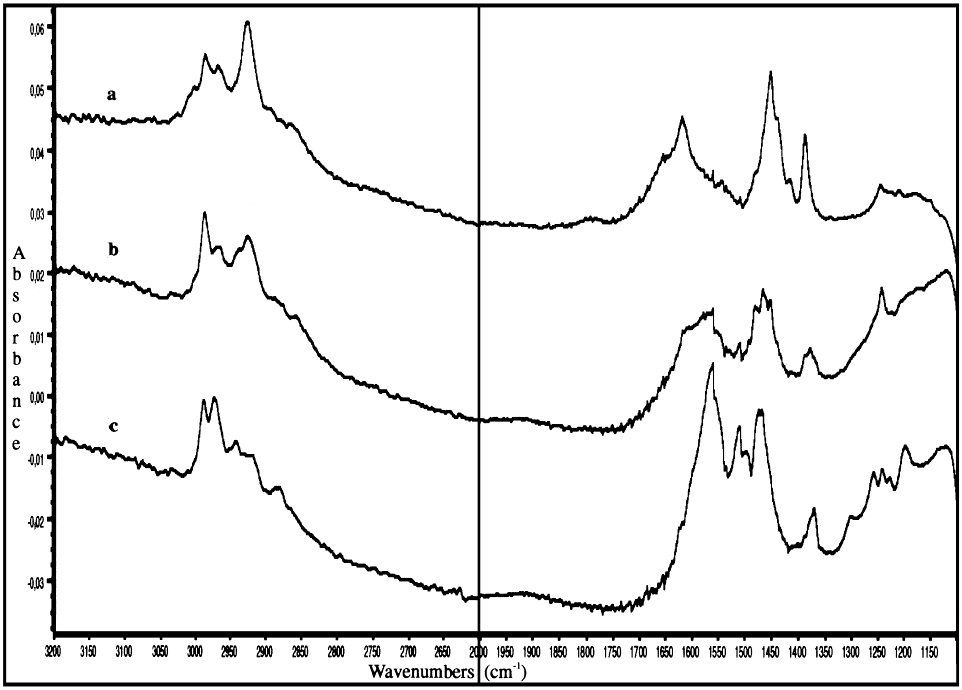


FIG. 7. FT-IR spectra of the adsorbed species arising from *trans*-2-butene adsorbed on γ-Al_2O_3 at room temperature followed by evacuation at room temperature (a), 373 K (b), and 473 K (c) for 10 min.

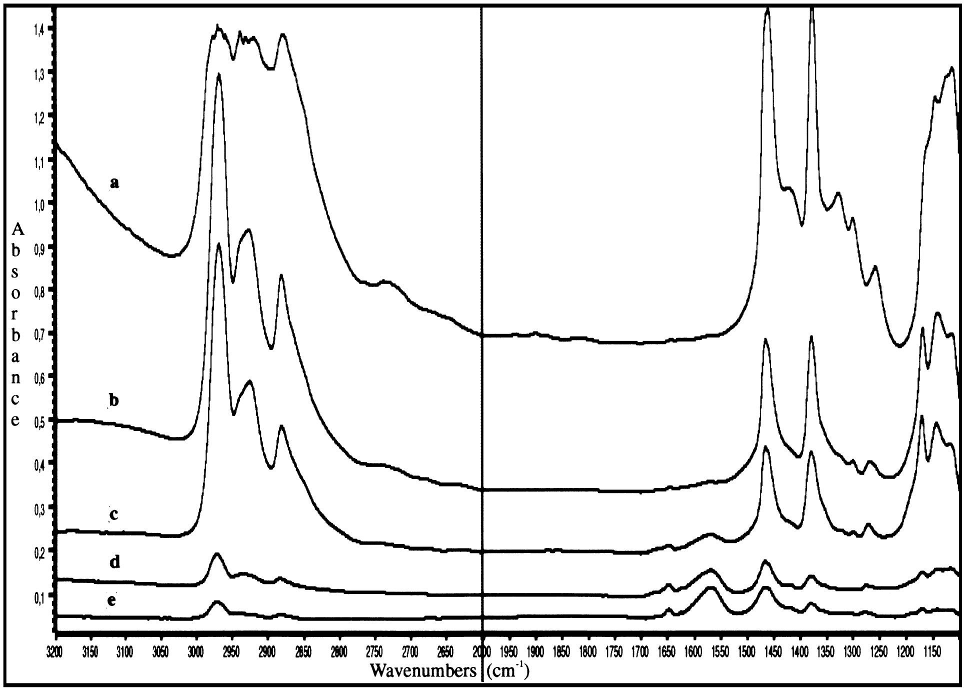


FIG. 8. FT-IR spectra of the adsorbed species arising from 2-butanol adsorbed on γ-Al_2O_3 at room temperature (a) and after evacuation at room temperature (b), 373 K (c), 473 K (d), and 573 K (e).

2000–1000 cm^{-1} by a couple of sharp bands at 1466, 1461 (split), and 1377 cm^{-1}, due to the three deformation modes of the methyl groups, by a strong complex of bands with components at 1166, 1141, and 1125 cm^{-1} and a maximum at 1113 cm^{-1}, and by a further sharp band at 1032 cm^{-1}, which are due, according to the literature (33, 46), to the C–C and C–O coupled stretching modes of the adsorbed undissociated alcohol and of the surface alkoxides, 2-butoxides, formed by alcohol dissociative adsorption. The rather broad band at 1260 cm^{-1} is due to the C–OH in-plane deformation, thus indicating that some of the alcohol is adsorbed in an undissociated form, also responsible for the broad OH stretching mode centered at 3340 cm^{-1}. Under outgassing, these bands decrease in intensity and later disappear, showing that the undissociated alcohol molecules either desorb or transform into the alkoxides. In parallel, the peaks near 1113 and 1032 cm^{-1} (slightly shifted with respect to the pronounced bands of liquid *sec*-butanol at 1109 and 1031 cm^{-1}) decrease in intensity, while the complex band in the region 1200–1000 cm^{-1} becomes dominated by the maxima at 1168 and 1140 cm^{-1}; a rather broad band near 1050 cm^{-1} is still observed. This behavior demonstrates that some of the undissociatively adsorbed 2-butanol dissociates upon outgassing, giving rise to additional 2-butoxide species. Weaker bands at 1422 cm^{-1} (CH_2 scissoring) and at 1300 cm^{-1} (CH deformation) are also detected.

In the CH stretching region a main band is observed at 2971 cm^{-1}, with weaker components at 2935 (weak shoulder), 2928, 2884, and 2856 (shoulder) cm^{-1}.

Outgassing at 373 K hardly perturbs these bands, while outgassing at 473 K causes a substantial decrease; however, even after outgassing at 573 K, all the above bands are still apparent, but with a very weak intensity. Meanwhile, new bands increase in intensity, at least relatively. After outgassing at 573 K, the spectrum is dominated by two strong bands at 1580 and 1470 cm^{-1}. In the CH stretching region the component near 2940 cm^{-1} becomes more pronounced than before. A broad band appears in the region 1200–1080 cm^{-1}, while in the region 1100–1000 cm^{-1} a negative band becomes apparent. These features are typical of alumina and are due to the perturbation of the surface Al–O–Al modes (negative band near 1050 cm^{-1} (47)) and to the formation of new H-bonded OHs (Al–OH in-plane deformation modes, the "positive" band near 1110 cm^{-1} (48)).

The infrared spectra of the species arising from *tert*-butanol adsorption on γ-Al_2O_3 are shown in Fig. 9. In the low-frequency region, the asymmetric deformation modes of methyls are observed with a maximum at 1474 and shoulders at 1461 and 1450 cm^{-1}, while the corresponding symmetric deformations give rise to the characteristic doublet at 1390 and 1367 cm^{-1}. The spectrum is dominated by a strong band with components at 1236 and 1210 cm^{-1},

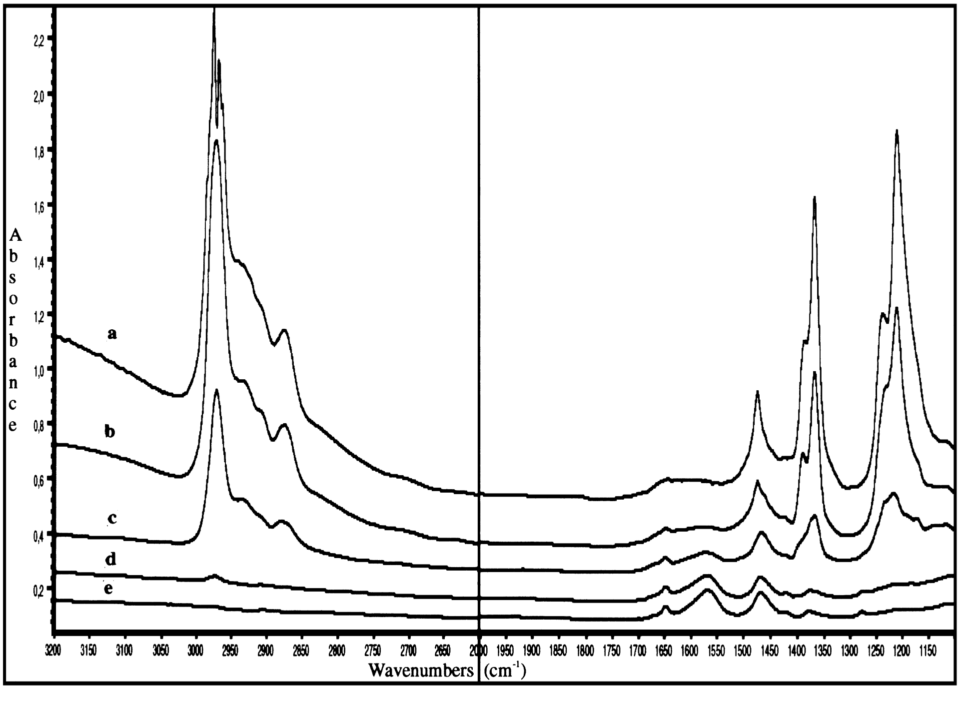


FIG. 9. FT-IR spectra of the adsorbed species arising from *tert*-butanol adsorbed on γ-Al_2O_3 at room temperature (a) and after evacuation at room temperature (b), 373 K (c), 473 K (d), and 573 K (e).

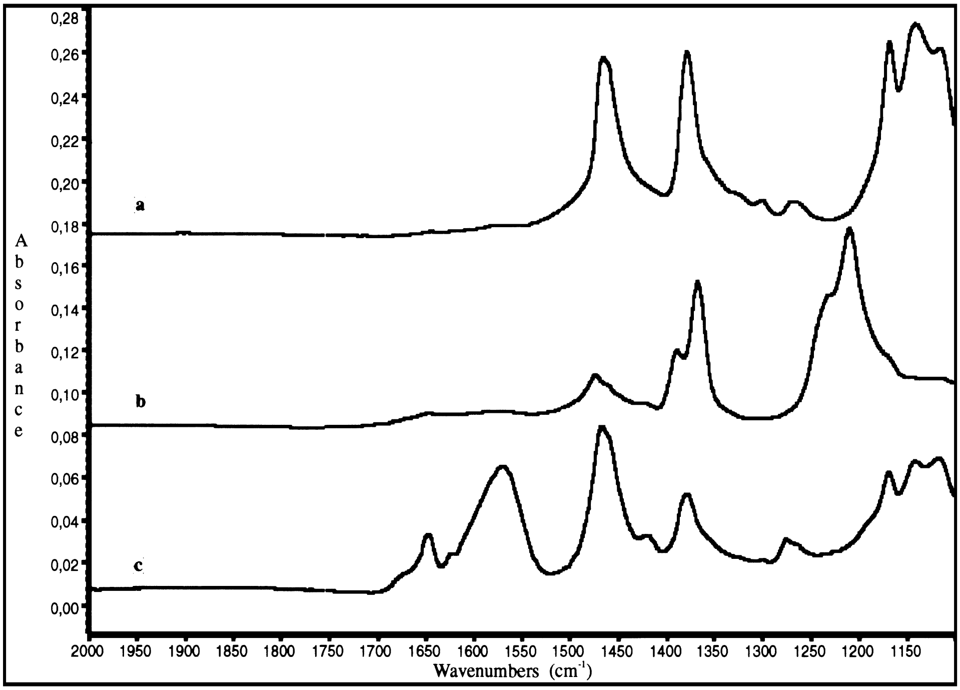
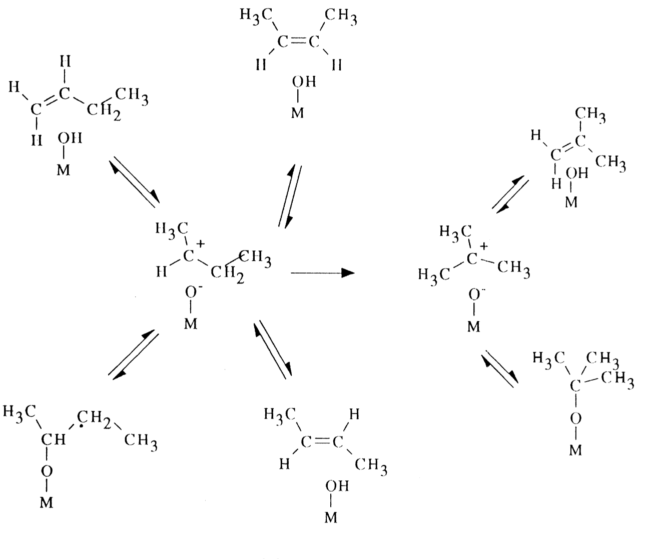


FIG. 10. Comparison of the FT-IR spectra of adsorbed species on γ-Al_2O_3: (a) *sec*-butoxides arising from *sec*-butanol; (b) *tert*-butoxides arising from *tert*-butanol; (c) alkoxides arising from 2-butanol at 473 K.

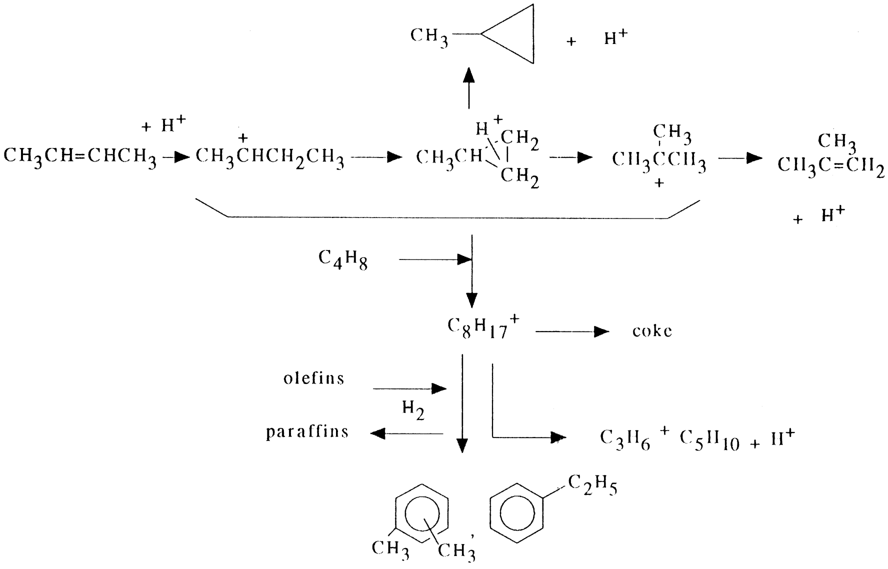
typically due to the coupled C–O and C–C stretchings of the terbutoxy groups according to previous studies of terbutanol adsorption on other oxides (49) and on metal terbutoxides (50). In the C–H stretching region, bands at 2972 cm^{-1} dominate, with weaker components at 2935, 2912, and 2875 cm^{-1}. Only traces of undissociatively adsorbed alcohol were found, according to weakness of the C–O stretching band near 1140 cm^{-1} and to the detection of the OH stretching band near 3350 cm^{-1}. Outgassing at 373 K causes the substantial decrease in the terbutoxy species, while outgassing at 473 K results in their complete disappearance. However, relatively strong bands remain after such outgassing treatments at 1568 and 1470 cm^{-1}, similar to those previously assigned to carboxylate species arising from the olefins.

These data show that both 2-butanol and *tert*-butanol are adsorbed in the dissociated form in the temperature range near 473 K. However, while *tert*-butoxides disappear just above this temperature, probably giving rise mainly to isobutene and an OH group, *sec*-butoxides are more stable, being still apparent up to 673 K. The formation of the olefins by decomposition of the surface alkoxides is in agreement with the literature (44, 45).

In Fig. 10 the spectra of the surface alkoxides produced by 2-butanol and *tert*-butanol adsorption and outgassing at 373 K are compared with each other and with those of the surface species produced by 2-butanol adsorption and outgassing at 473 K. As well as the formation of the bands which assigned to carboxylates, heating of the 2-butoxy species at 473 K also caused the foramation of a shoulder at the lower-frequency side of the CH_3 symmetric deformation mode (near 1370 cm^{-1}) and at the higher-frequency side of the C–C/C–O stretching modes (near 1200 cm^{-1}). This is evidence of the partial transformation of 2-butoxy species into terbutoxy species, i.e., of the skeletal isomerization of the C4 alcoholate (Scheme IV).



SCHEME IV



SCHEME V

DISCUSSION

The data reported in Table 1 show that alumina is an efficient catalyst for *n*-butene skeletal isomerization at 753 K. In Scheme V a possible reaction network that justifies most of the observed products is proposed. As we will discuss below, we believe that skeletal isomerization of *n*-butenes to isobutene occurs via a protonated methylcyclopropane carbenium ion, according to previous literature (16). This species can also give back the proton, leading to methylcyclopropane, which is in fact observed among the products. A C8 dimeric carbenium ion should be produced by alkylation of *n*-butene by the C4 carbenium ion, and can give rise to several products. Its cracking would produce C3 + C5 hydrocarbons, and its cyclization and dehydrogenation would give rise to the C8 aromatics ethylbenzene and xylenes. Further oligomerization can give rise to heavy products that, deposed at the surface, are the precursors for coke. The hydrogen resulting from aromatization and coking should be responsible for the hydrogenation of butenes to butanes.

The results of the IR study show that a hydrogen abstraction from the allylic positions of butenes occurs, and gives rise to σ-bonded allyl species. This interaction was already reported in the literature (37–39) although, to our knowledge, the IR spectra of the allyl species had not been determined with precision. The present study revealed the IR spectrum of the allyl species formed from the four C4 olefins as well as from propene. We propose that the resulting species are σ-bonded to Al centers and form over a Al^{3+}–O^{2-} coordinatively unsaturated couple.

The reversible formation of such allyl species and the interconversion of the but-1-en-3-yl "allyl" species and of the isomeric form but-2-en-1-yl species, we envisaged in particular in the experiments of 1-butene adsorption, provide a likely way for low-temperature double-bond isomerization of *n*-butenes (Scheme IV), according again to the literature (37–39).

Additionally, an electrophilic H-bonding interaction of the surface OHs with the olefinic double bond was observed; it did not, however, result in a substantial reactive transformation at room temperature. According to our previous studies (24), the interaction of catalyst surface hydroxy groups with olefins can give rise to simple hydrogen bonding, to formation of surface alkoxides, or to oligomerization of the olefin. The detection of these three processes is related to the acid strength of the surface hydroxy groups, to the electron density of the olefin (e.g., the olefin reactivity trend is isobutene > propene > ethene), and to the temperature. As we will discuss in the accompanying paper (51), the interaction of the C4 olefins with the acidic OHs of the zeolite HZSM5 gives rise to the formation of polymers at room temperature through the formation of a carbenium ion. Similar results were previously observed on other Brønsted acidic solids such as sulphate- or tungstate-containing oxides (24, 52). However, this reaction does not occur at lower temperatures (e.g., 170 K), and hydrogen bonding only can be detected even on such strongly Brønsted acidic solids. This means that the kinetics of the reaction of the surface OHs with the olefin strongly depends on the temperature, thus being an "activated" process. It is suggested that proton transfer from the weak OHs of alumina to the olefins, although not detected at room temperature, can occur at higher temperatures.

On the other hand, it is likely that the *n*-butene double-bond isomerization process is closely related to the alcohol dehydration reaction. According to the literature, 2-butanol dehydration on alumina takes place readily at 573–623 K, giving rise to the equilibrium mixture of the three linear butenes if the contact time is sufficiently high (43–45). At lower contact times, *cis*-2-butene is favored, while *trans*-2-butene is definitely not favored, in contrast to thermodynamics, because of kinetics. In practice, the product distribution from 2-butanol on alumina in the range 573–623 K is the same as that observed from 1-butene double-bond isomerization in the range 300–600 K (53), supporting the idea that the two mechanisms are closely correlated and that a common intermediate can occur. According to several authors (43, 44) the surface alkoxy groups are the key intermediates in alcohol dehydration. According to Moravek (54), such alkoxy groups are formed from the alcohol on alumina by substitution of surface hydroxy groups and retaining the alcohol oxygen atom. If this is true, the alkoxy groups formed by alcohol dissociative adsorption should be the same as are produced by the interaction of the olefin with the surface OHs. Thus, it is reasonable to propose that olefin double-bond isomerization can also take place through alkoxy group formation and elimination of the alkoxide. After alkoxy group formation, the alcohol dehydration process and the olefin isomerization process are expected to be identical.

2-Butoxides are expected to be formed by the reaction of all three *n*-butenes with acidic OHs, according to the Markovnikov rule and also to experimental data on surfaces (52). According to our data (24, 55), the reaction of isobutene with slightly acidic OHs instead gives rise to *tert*-butoxy species. Our data relative to alcohol adsorption indicate that the substantial decomposition of surface 2-butoxides on alumina takes place in the temperature range 373–673 K, while *tert*-butoxides are slightly less stable. On the other hand, evidence of isomerization of 2-butoxides to *tert*-butoxides was found.

This strongly supports the idea that the protonation of the olefins from the alumina surface OHs to give the surface alkoxides, which is certainly an exothermic process and thermodynamically more favored at lower temperature, is increasingly kinetically inhibited at low temperature. This is more evident if the OHs Brønsted acidity is weak. This is understandable, because the conversion of an olefin to a carbenium ion (intermediate in alkoxy group formation) implies the breaking of the olefin π orbital, the rehybridization of at least one carbon atom from sp^2 to sp^3, and the establishment of a new C–H σ bond. This process can become fast at higher temperatures (above 473 K) where, however, the exothermic formation of the C–O bond can become unfavorable from the point of view of thermodynamics. This means that, as the reaction of OHs with the olefin becomes possible from the point of view of kinetics, the lifetime of the carbenium ion becomes longer. Consequently, skeletal isomerization becomes possible, and isobutene can be formed from *n*-butenes, according to their equilibrium.

That skeletal isomerization of olefins may occur on surface OHs of alumina too (as proposed in Scheme V), in spite of their weakness as Brønsted acids, is strongly supported by the role of water in enhancing catalyst activity and increasing selectivity and catalyst lifetime. In fact, water is cofed with butenes in relevant amounts by most researchers (2). The number of active OHs is in fact increased by cofeeding water, while the Lewis sites are partly poisoned. Lewis sites may be involved in unselective butene transformations, giving rise to by-product formation and catalyst deactivation.

According to this picture, the catalytic activity of γ-Al_2O_3 as a catalyst for the skeletal isomerization of *n*-butenes is due to its weak Brønsted acidity, sufficient to catalyze skeletal isomerization, although at rather high temperatures. On the other hand, its acidity is not sufficient to enhance too much the rate of the oligomerization and cracking reactions. Consequently, catalyst coking also is relatively slow. In contrast, the Lewis acidity, typical of transitional aluminas, should be involved in the double-bond olefin isomerization at low temperatures (according to Lunsford *et al.* (38)) but would play a negative role in high-temperature skeletal isomerization, because it would favor the production of allyls that would be intermediates in coking and aromatics production.

These results agree with the scenario we previously proposed for silicated aluminas (10) which are more effective than pure alumina for the skeletal isomerization of *n*-butenes and were found to be very weakly Brønsted acidic too, although perhaps slightly stronger Brønsted acids than aluminas. It is not excluded that an additional effect of silication is the killing of the active sites for allyl species formation.

This also explains why the real intermediates in the skeletal isomerization process on γ-Al_2O_3 (the carbenium ions) escape detection and could not be detected directly. However, the present investigation seemed to justify the proposal of a complete and self-consistent understanding of the chemistry of this reaction on alumina. More insight into the details of the carbenium ion mechanism and of its transposition was obtained by using strongly Brønsted acidic catalysts such as zeolite ZSM5 and will be discussed elsewhere (Part II of this series, Ref. (51)).

CONCLUSIONS

The main conclusions of the present work are as follows:

1. γ-Alumina is a good catalyst for *n*-butene skeletal isomerization to isobutene at 753 K. Main by-products are propene, pentenes, and C8 aromatics.
2. C4 butenes interact at room temperature with the surface hydroxy groups of alumina via H-bondings.
3. Additionally, they react with Al^{3+}–O^{2-} couples, giving rise to allyl species probably bonded to aluminum ions.

4. Alkoxy groups are produced by adsorption of 2-butanol and of *tert*-butanol. These species decompose to *n*- and isobutene respectively around 473 K.

5. 2-Butoxy groups partly isomerize to *tert*-butoxy groups around the decomposition temperature.

6. On the basis of the analysis of these data and other published data, it is proposed that skeletal isomerization of *n*-butenes to isobutene on alumina occurs via the slow formation of 2-butoxy groups, followed by their faster skeletal isomerization and the fast decomposition to isobutene. Such alkoxy species are indeed not detected from butenes because at the temperature at which they are formed (>473 K) they decompose even faster.

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