

Figure 9. Proposed formamide decomposition mechanism on the Ni(111) surface.

a significant dynamic dipole moment perpendicular to the plane of the metal surface. Our proposed  $\eta^1_{(N)}$ -HCONH<sub>2</sub> agrees with this IR result.

As a result of our TDS and RAIR studies we now have a general picture of the formamide decomposition process following multilayer-coverage adsorption on Ni(111). After the initially adsorbed multilayers film are heated to about 220 K,  $\eta^{1}_{(N)}$ -HCONH<sub>2</sub> species are observed, which favors NH and CH bond cleavage, leading to the production of HNCO<sub>(a)</sub>. Two parallel decomposition channels have been directively observed. One channel produces surface NH2(a) species, which desorb as ammonia between 230 and 300 K, as well as surface formyl groups (HCO), which further decompose by 285 K yielding hydrogen  $(H_2)$  desorption at 300-400 K and carbon monoxide (CO) desorption at 350-450 K. The other decomposition channel results in the production of isocyanic acid at  $\sim$ 285 K. The isocyanic acid then desorbs at 325 K. These reaction mechanisms are summarized in Figure 9.

#### 5. Conclusion

Two reaction channels for formamide decomposition on Ni(111) have been observed. One reaction channel is the production of CO and NH<sub>3</sub>, which has also been observed on other metal substrates. The other reaction channel is the production of isocyanic acid (HNCO), which is a first report to our knowledge. Comparing the results of formamide adsorption and reaction on Ru(001) and Ni(111), it is clear that the formamide decomposition chemistry is substrate dependent. On the Ni(111) surface not only ammonia and carbon monoxide are formed but isocyanic acid HNCO is also produced as well. It is proposed that the isocyanic acid results from an  $\eta^{1}(N)$ -HCONH<sub>2</sub> bonding configuration. This product has not been observed for other substrates such as Ru-(001),<sup>1</sup> Ru(001) with preadsorption of hydrogen,<sup>2</sup> and Ru- $(001)-p(1\times 2)-O.^{3}$ 

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# Vibrational Infrared Spectroscopic Studies of 1-Butene Skeleton Isomerization at the Surface of a Silicated Alumina in a Micro Plug Flow Reactor

## L. Basini,\* A. Aragno, and A. Raffaelli

Snamprogetti S.p.A., Via Maritano 26, 20097 San Donato Milanese, Milano, Italy (Received: November 22, 1989; In Final Form: April 30, 1990)

The skeletal isomerization of 1-butene to obtain 2-methylpropene is catalyzed by the interaction at high temperatures with solids having acidic properties. The nature of the solid-gas interaction is investigated through some vibrational infrared spectroscopic experiments aimed at highlighting the perturbation of the surface molecular groups and the formation of surface complexes on a silicated alumina under different conditions of pressure and temperature. The spectra recorded during the interactions lead us to propose that the catalytic isomerization occurs through a temperature-dependent proton-transfer equilibrium between an OH surface group and an H-bonded internal olefin.

### 1. Introduction

This work deals with the skeletal isomerization of 1-butene to obtain 2-methylpropene catalyzed at 400 °C by the interaction with silicated alumina (hereafter referred to as SA).

Molecular interactions of gaseous alkenes with electron-withdrawing sites on solids can produce surface complexes. These could be involved as intermediates in many heterogeneous catalytic reactions. Vibrational spectroscopies are sensitive to the perturbations of the bond orbitals of both solid and gaseous phases when the interactions occur<sup>1</sup> and have often been used in the studies of alkene adsorption on metal oxides or metal-supported catalysts,<sup>2</sup> zeolites,<sup>3</sup> and other inorganic acidic solids.<sup>4</sup> In some experiments, metal-olefin interaction has been investigated at low temperature by using the matrix isolation technique aimed at understanding how olefin double bonds coordinate to transitionmetal centers.<sup>5</sup> Further adsorbed olefin reactions such as polymerizations<sup>6</sup> and oxidations<sup>7</sup> have been described with spectroscopic studies at higher temperatures.

The catalytic properties of SA for the skeletal isomerization of linear butenes have been studied in detail by Nielsen et al.<sup>8</sup> and are covered by several patents quoted in ref 9. These describe

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catalysts prepared by the condensation reaction of tetraethoxysilane, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, with the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The hydrolysis of the ethoxylic groups anchored in this way to the surface results in the formation of SiOH groups. Catalytic tests performed by the same authors, at temperatures between 400 and 550 °C, revealed the good activity of SA toward the skeletal isomerization reaction and the low activity of the catalyst toward the olefin oligomerization reactions. Nielsen et al. also investigated the surface composition of SA by X-ray photoelectron spectroscopy and the surface acidity of SA by infrared spectroscopy with adsorbed pyridine. The authors concluded that silicon-containing groups formed on the alumina surface at less than monolayer coverage induce a strong acidity on the SA. Accordingly, Brønsted and Lewis acid sites were detected.

The main object of this work is to study solid-gas interaction phenomena during the catalytic reaction by vibrational spectroscopic experiments. This has been done both with transmittance experiments on self-supported wafers of solid samples and with diffuse reflectance investigations inside the catalytic reaction environment in a micro plug flow reactor.

We have found that hydrogen-bond formation and chargetransfer reaction occur at the surfaces to a different degree at different temperatures. We propose that reversible proton-transfer reactions between the OH groups of the solid and the double-bond carbon atoms of the olefin catalyze the isomerization.

Spectroscopic studies on the SA OH group perturbations due to the interaction with 1-butene and ammonia highlighted steric hindrance effects at the surface. This suggests that the acid-base properties of the catalyst are dependent on the structure of the gaseous molecules and on the "geometry" of the solid-gas interaction.

The reaction investigated is important due to the key role of isobutene in the production of MTBE (methyl *tert*-butyl ether), which is actually the main additive among the oxygenated compounds for lead-free gasoline.

## 2. Experimental Section

SA containing 1.5% (w/w) SiO<sub>2</sub> was prepared according to the procedures described in ref 8 and 9. The primary reaction between ethyl silicate and alumina is supposed to follow the scheme

$$Si(OC_2H_5)_4 + n-AIOH \Rightarrow (Al-O)_n - Si(OC_2H_5)_4 + nC_2H_5OH$$

Then the resulting material was thermally treated in a stream of nitrogen saturated with gaseous water to hydrolyze the unreacted ethoxysilicon groups and subsequently heated to 600 °C in a nitrogen stream. The surface area of the resulting material was about 200 m<sup>2</sup>/g; the SiO<sub>2</sub> content (determined by elemental analysis) is 1.5% (w/w). Since it has been demonstrated that under these conditions silicon is dispersed in a submonolayer coverage of the surface<sup>8</sup> and is not present in the bulk, we have calculated a surface concentration of 0.75 silicon atom/nm<sup>2</sup>.

Gas adsorption was studied after a thermal pretreatment of the samples at 500 °C. Self-supported wafers were heated under vacuum conditions while powdered SA was heated in a flowing nitrogen atmosphere.

"Active site" adsorption properties at the surface of SA have been studied by solid-gas interaction experiments with ammonia and 1-butene. All the gaseous reagents were furnished by Ucar (Union Carbide) and used without any further purification; their purity was 99.998% (w/w) for ammonia and over 99.95% (w/w) for 1-butene.

Spectra were recorded with a Nicolet 20SXC spectrometer equipped with an auxiliary sampling bench. Data manipulations were made using standard software furnished by Nicolet. Rapid scan data collection was also used in recording high-temperature spectra of the adsorbed species. TGS and MCT detectors were used for transmittance and diffuse reflectance experiments, respectively. Spectra were recorded at a resolution of 4 cm<sup>-1</sup> with



Figure 1. Scheme of the catalytic environmental cell used for the diffuse reflectance spectroscopic experiments.

the number of scans between 100 and 500 depending on the experimental conditions. Transmittance spectroscopic experiments were performed by an evacuable and heatable cell furnished by Specac. The cell can be heated up to 500 °C and was connected with two lines, one for gas manipulation and the other for evacuation by a diffusive vacuum pump. Self-supported wafers of SA were placed between the inlet and outlet line. With this arrangement it was possible to evacuate the cell at a pressure of about  $10^{-3}$  Pa or alternatively to maintain a gaseous stream through the cell at pressures lower than  $10^4$  Pa. Under these two different conditions, pressure was monitored by Penning and Pirani gauges.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic experiments were performed by a catalytic environmental cell furnished by Spectra-Tech; the cell is represented in Figure 1. A similar device has been recently used by Moser et al. in an experimental work reported in ref 10 and by others in previous years.<sup>11</sup> The cell has zinc selenide windows and all the main features of a micro plug flow reactor; it has temperature capabilities up to 900 °C and can be pressurized up to 7 MPa. Pressure and space velocity of the gaseous streams were measured by manometers and a mass flow meter and were regulated by grove and flow control valves.

In Figure 1 the optical path inside the catalytic environmental cell is schematically represented. Light absorption phenomena in the gaseous phase, modeled by Lambert-Beer equations, are due to the reagent molecules before their interaction with SA. Light absorption in the solid phase is due to SA and to the adsorbed species and is modeled by the Kubelka-Munk equations (hereafter referred to as KM).<sup>12</sup> The two treatments are related to each other by the concept of absorptivity.

The spectra in the catalytic environmental cell at the different temperatures were obtained by using as background the single beams of SA collected in a nitrogen atmosphere at the same temperatures. In this way SA has been considered as the dilution matrix often used in diffuse reflectance experiments.<sup>13</sup> Absorptions of the gaseous phase and of the surface complexes appear in the spectra as positive bands. The perturbations of the bond orbitals in the "active sites" of the solid surface are revealed by

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Figure 2. (a) Spectrum of the SA self-supported wafer treated with gaseous ammonia. (b) Difference spectrum obtained by subtracting from (a) the SA absorption bands. The negative bands are due to the perturbations to the OH groups which react with ammonia.

bands with a negative polarity due to the disappearance of the unperturbed chemical bonds of SA.

Mass Spectrometric Analysis. Information on the gaseous reagents before interaction with SA and on the surface complexes was obtained from the DRIFT spectra, while the chemical composition of the output stream was studied by mass spectrometric analysis. Unfortunately, the mass spectra of the linear butenes and of the 2-methylpropene are very similar both in the m/e values and in the intensity of the peaks. In this work mass spectrometric analysis has been used (1) to detect products other than the butenes and 2-methylpropene, (2) to monitor variations in the composition of the output stream during the collection of the infrared spectra, and (3) to follow the desorption of adsorbed species in time when the flow of reagents was switched to nitrogen. This was made possible by connecting a Carlo Erba Strumentazione quadrupole mass spectrometer with the output line. The mass spectrometer data station was also equipped with software for TPD (temperature-programmed desorption) analysis.

#### 3. Results

3.1. Thermal Pretreatment of Silicated Alumina. The spectra of the SA OH groups recorded at 500 °C on a self-supported wafer at  $10^{-3}$  Pa and on a powdered sample in a flowing nitrogen atmosphere show the same bands, which consist of one shoulder near 3760 cm<sup>-1</sup> and three peaks near 3720 (sharp), 3675 (broad), and 3590 cm<sup>-1</sup> (broad). The intensity of the last band is lower in the transmittance experiments due to the more drastic dehydration conditions obtained at  $10^{-3}$  Pa. These spectral features gain contributions due to the silanol OH groups on the surface of the SA and to unreacted OH groups bonded to aluminum atoms.

3.2. Interactions with Ammonia. Figure 2 shows the absorbance and the difference spectra (recorded at  $10^{-3}$  Pa) of the stretching zone for OH and NH bonds of a sample of SA treated with a gaseous ammonia. The difference spectrum, obtained by subtraction of the SA absorptions from those of the material with adsorbed ammonia, clearly shows three negative quite sharp bands at 3763, 3725, and  $3672 \text{ cm}^{-1}$ . This is a clear indication that adsorbed ammonia interacts with the OH groups which vibrate at the corresponding frequencies in the unperturbed SA surface. The broad positive peaks centered near 3550, 3350, 3260, and 3160 cm<sup>-1</sup>, can be associated, on the basis of existing literature,<sup>14</sup> with (a) vibrations of hydrogen-bonded OH groups probably superimposed on vibrations of unprotonated adsorbed ammonia (3550 cm<sup>-1</sup>), (b) NH stretchings of adsorbed ammonium species (3260, 3160 cm<sup>-1</sup>) and (c) unprotonated adsorbed ammonia on coordinatively unsaturated aluminum atoms (3350 cm<sup>-1</sup>). These assignments are sustained by the examination of the NH bending



Figure 3. (a) N-H and O-H bond stretching vibrations range: temperature-induced variations in the difference spectra of SA treated with gaseous ammonia. (b) N-H and O-H bond bending vibrations range: temperature-induced variations in the difference spectra of SA treated with gaseous ammonia.



Figure 4. Integrated intensity variations with temperature of the N-H bending bands of the adsorbed ammonia.

zone of the difference spectra in the sequences shown in Figure 3b. Here peaks near 1600 and 1470 cm<sup>-1</sup> can be assigned to unprotonated and protonated adsorbed ammonia, respectively;<sup>14</sup> in addition, two other absorption bands, a broad and small peak centered near 1550 cm<sup>-1</sup> and a shoulder near 1670 cm<sup>-1</sup>, are shown. We are unable to assign these two peaks unambiguously to additional normal modes of the species responsible for the 1600-and 1470-cm<sup>-1</sup> absorptions or to other adsorbed species interacting with different electron-withdrawing sites. However, we point out that by plotting the integrated intensities of the bands at 1600,

<sup>(14)</sup> Knozinger, H. Hydrogen Bonds in Systems of Adsorbed Molecules. In *The Hydrogen Bond*; Schuster, P., Zundel, G., Sandorphy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. III, pp 1263-1364.



Figure 5. Difference spectra obtained flowing at 25  $^{\circ}$ C gaseous 1-butene (a) through a SA self-supported wafer and (b) through powdered SA.

1550, and 1470 cm<sup>-1</sup> versus temperature, we obtain parallel curves for the intensities of the last two peaks (Figure 4). In Figure 3a, the difference spectra of the stretching vibrations of the adsorbed species can be followed between 30 and 500 °C.

3.3. Interactions with Butenes. 3.3.1. Transmittance Spectroscopic Experiments. The adsorption experiment on SA selfsupported wafers started at room temperature after the usual thermal pretreatment of the sample. The spectrum in Figure 5a has been obtained at 25 °C by subtraction of the SA absorptions from the spectrum recorded when 1-butene is flowing through the cell at a pressure of 10<sup>4</sup> Pa. A negative peak near 3750 cm<sup>-1</sup> and a broad positive band centered near 3550 cm<sup>-1</sup> reveal the formation of hydrogen-bonding interaction which perturb the hydroxyl groups of SA. The CH stretching and bending vibration bands are assignable to gaseous 1-butene.<sup>15</sup> If the butene stream is stopped and the cell is evacuated at 10<sup>-3</sup> Pa, no clear evidence of adsorbed species is found in the spectra. The same results were obtained by repeating the same experimental sequences at 100, 200, 300, and 400 °C. Aiming at obtaining oligomerization at the surface and the vibrational spectra of the oligomers to be compared with the spectra obtained in the catalytic reaction conditions, we chose to enhance the contact time between the solid and the gaseous species. The first spectrum in Figure 6 was obtained at 25 °C after flowing 1-butene at 10<sup>4</sup> Pa at 400 °C for 1 h, slowly cooling the sample at room temperature in a static atmosphere of the gaseous olefin, and evacuating again the cell. Only the 1800-1200-cm<sup>-1</sup> range is shown in the figure because in the CH stretching zone a broad and unresolved multiplet is revealed. A broad band centered near 1645 cm<sup>-1</sup>, a multiplet centered near 1480 cm<sup>-1</sup> (where a shoulder near 1460 cm<sup>-1</sup> and a maximum at 1390 cm<sup>-1</sup> can be distinguished), and a band at 1235 cm<sup>-1</sup> are the absorption features. The following modifications were observed by heating again the sample up to 250 °C (see Figure 6); (a) the peak centered near 1645 cm<sup>-1</sup> is split into a doublet with maxima





Figure 6. Absorption bands in the C = C stretching and C-H bending range for the 1-butene oligomers formed at the SA surface.

near 1680 and 1625 cm<sup>-1</sup> (this is more and more resolved by increasing the temperature), (b) the intensity ratio  $I(1480 \text{ cm}^{-1})/I(1390 \text{ cm}^{-1})$  decreases, and (c) the band at 1235 cm<sup>-1</sup> gains intensity with respect to the other spectral features.

It seems reasonable to think that at 400 °C and during the slow cooling period in the static atmosphere of the gaseous olefin, oligomers were formed at the surface of SA. The spectra of the adsorbed species, recorded after the evacuation of the cell, were further transformed by the second thermal treatment under vacuum conditions (see Figure 6). The absorption band at 1235 cm<sup>-1</sup> can be assigned to skeletal vibrations of the oligomers that should contain unsaturated carbon-carbon double bonds responsible for the absorption bands in the 1700-1600-cm<sup>-1</sup> region. The peak at 1390 cm<sup>-1</sup> can be assigned to methyl group deformation while the multiplet centered at 1480 cm<sup>-1</sup> gains contributions of both methyl, methylene, and vinyl group deformations.<sup>15</sup> The sequence of the spectra in Figure 6 indicates that during the second thermal treatment the adsorbed oligomers are partially desorbed (overall reduction of the band intensities), that the adsorbed species increase their molecular weight (increase of the ratio between the intensity of the band at 1235 cm<sup>-1</sup> and the intensity of the other bands), and that more methyl branched species are formed (decrease in intensity ratio  $I(1480 \text{ cm}^{-1})/I(1390 \text{ cm}^{-1})$ cm<sup>-1</sup>)).

3.3.2. Diffuse Reflectance Spectroscopic Experiments. These experiments were performed both flowing a gaseous stream of nitrogen containing 1-butene (1% v/v) and flowing pure 1-butene; in both cases we obtained the same information. The spectra recorded by flowing pure 1-butene will be shown hereafter.

The spectra of the catalytic environment obtained at 25, 100, 200, 300, and 400 °C when a gaseous stream of 1-butene flows through the powdered sample show that the solid-gas interaction occurs with a perturbation of two OH bonds of SA. When the gaseous butene atmosphere is replaced by a flowing nitrogen stream, peaks assignable to adsorbed species are revealed. The temperature-induced changes inside the catalytic environment when 1-butene is flowing can be followed in Figures 7A,C,E,G and 8A,C,E,G, while the spectra of the adsorbed species at the different temperatures are illustrated in Figures 7B,D,F,H and 8B,D,F,H.

The spectrum obtained at room temperature when 1-butene is flowing through the cell has been reported in Figure 5b. A



Figure 7. (A, C, E, G) Difference spectra in the C-H and O-H stretching vibration range recorded in the catalytic environment at different temperatures: (A) 100, (C) 200, (E) 300, and (G) 400 °C. (B, D, F, H) Difference spectra in the C-H and O-H stretching vibration range of the surface complexes recorded after the gaseous butenes were pumped off by nitrogen: (B) 100, (D) 200, (F) 300, and (H) 400 °C.

negative peak at 3720 cm<sup>-1</sup> with a shoulder at 3760 cm<sup>-1</sup> can be distinguished. The spectrum of the adsorbed species in nitrogen atmosphere at room temperature has not been reported because it has the same features as the spectrum recorded at 100 °C shown in Figure 7B discussed hereafter.

The positive bands in the spectrum recorded at 100 °C when 1-butene is flowing throughout the cell (Figures 7A and 8A) can be assigned to a mixture of gaseous butenes.<sup>15</sup> The doublet at 1656 and 1640  $cm^{-1}$  clearly shows that at least a double-bond isomer of 1-butene is formed (Figure 8A). By stopping the flux of gaseous 1-butene and flowing nitrogen to eliminate the gaseous olefins from the cell (as was checked by mass spectrometric analysis on the output flow), we revealed infrared absorptions assignable to adsorbed species. The corresponding spectrum in Figure 7B shows again the doublet with a negative polarity at 3760 and 3725 cm<sup>-1</sup> (but the two bands have now approximately the same absolute intensities) and positive bands similar to the gaseous 1-butene ones. The splitting of the C=C stretching is no longer observable (Figure 8B), and only one peak at 1635 cm<sup>-1</sup> is shown. It is noteworthy that the intensity of the C=C stretching band of the adsorbed species is enhanced with respect to the other spectral features as it has already pointed out by Busca et al.<sup>16</sup>



Figure 8. (A, C, E, G) Difference spectra in the C-H and O-H bending vibration range recorded in the catalytic environment at different temperatures: (A) 100, (C) 200, (E) 300, and (G) 400 °C. (B, D, F, H) Difference spectra in the C-H and O-H bending vibration range of the surface complexes recorded after the gaseous butenes were pumped off by nitrogen: (B) 100, (D) 200, (F) 300, and (H) 400 °C.

The spectrum in Figure 7C shows that, when temperature is raised to 200 °C, the intensity of the band at 3080 cm<sup>-1</sup> decreases with respect to the other CH stretching bands of the gaseous olefins. The absorptions in the 1800–1300-cm<sup>-1</sup> range shown in Figure 8C consist of a symmetric doublet with peaks at 1656 and 1640 cm<sup>-1</sup> and of a multiplet centered near 1460 cm<sup>-1</sup>, whose multiplicity seems to have increased with respect to the one observed at 100 °C. In a nitrogen atmosphere, other adsorbed species at the surface have been revealed; Figures 7D and 8D show their spectral features. The main innovations with respect to the spectra recorded at 100 °C are a new small and broad peak near 1670  $cm^{-1}$  and a couple of intense bands at 1568 and 1460  $cm^{-1}$ . (The latter grows in the middle of the CH bending vibrations multiplet; Figure 8D.) The intensities of the bands at 1568 and 1460  $cm^{-1}$ increase in time and as the reaction temperature increases (as will be discussed hereinafter); and while all the other absorption bands can be removed by heating the sample in a nitrogen atmosphere, these peaks can be found in the spectrum recorded after a thermal treatment in pure oxygen atmosphere at 500 °C.

At the temperature of 300 °C when the gaseous butene is flowing through the cell, the small peak at  $3080 \text{ cm}^{-1}$  completely disappears (Figure 7E) and the intensities of the bands at 1656

<sup>(16)</sup> Busca, G.; Ramis, G.; Lorenzelli, V.; Janin, A.; Lavallay, J. C. Spectrochim. Acta 1987, 43A, 489.



Figure 9. Vibrational bands in the mid-infrared zone of the surface complexes at 400 °C.

and 1640 cm<sup>-1</sup> are drastically reduced with respect to the intensity of the CH deformation multiplet centered near 1460 cm<sup>-1</sup> (Figure 8E). In a nitrogen atmosphere, only very low bands assignable to hydrocarbon species can be distinguished from the noise of the spectra (see Figures 7F and 8F). On the contrary, the intense bands at 1568 and 1460 cm<sup>-1</sup> are still present and clearly shown in Figure 8F.

At 400 °C, the spectrum of the catalytic environment when the butene is flowing is analogous to the one recorded at 300 °C (see Figures 7G and 8G). On the contrary, in a nitrogen atmosphere, the spectral features of the adsorbed species are quite different from the previous ones. The spectrum in Figure 7H shows negative peaks at 3760 and 3720 cm<sup>-1</sup>, with intensity ratio changed with respect to the lower temperature one. In addition, a broad positive band centered near 3600 cm<sup>-1</sup> is clearly revealed. At lower frequencies, a multiplet with peaks at 3010 cm<sup>-1</sup> (weak) and at 2958, 2929, and 2875 cm<sup>-1</sup> is shown. Figure 8H illustrates the absorptions in the 1850–1250-cm<sup>-1</sup> range. Here only the peaks at 1568 and 1460 cm<sup>-1</sup> are shown. As can be deduced from Figure 9, these two very strong peaks cover the other spectral features of the hydrocarbon-adsorbed species in this spectral range.

#### 4. Discussion

4.1. Hydrogen Bonds and Charge-Transfer Reactions in Low-Pressure Interactions with Ammonia and 1-Butene. Experimental results have shown that ammonia and 1-butene are both adsorbed at the surface, but the strength of the interactions is different and the SA OH groups participate in the formation of the surface complexes with the two molecules to a different extent.

The transmittance spectra recorded between 25 and 400 °C have shown that weak HB are formed when gaseous 1-butene is flowed for a few minutes through the cell (Figure 5a). However, it was sufficient to evacuate the measurement cell at  $10^{-3}$  Pa to obtain a clean surface on the solid.

Three OH groups, whose stretching vibrations have been localized by the difference spectra at 3763, 3725, and 3672 cm<sup>-1</sup>, are strongly perturbed when ammonia interacts at 25 °C with the self-supported wafer of SA (Figure 2). In this case, ammonium species are also formed, together with Lewis bonded ammonia, and they can be removed from the surface only by a thermal treatment under vacuum conditions up to 500 °C. These different results can be discussed by considering the different "basic properties" of the proton acceptor (for this purpose the proton affinities of ammonia and 1-butene can be considered a measure) and the different steric hindrance effects (or, from another point of view, the different electrostatic repulsion effects) involved in the interactions. The 1-butene molecule does not perturb the more acidic OH group which vibrates at 3670 cm<sup>-1</sup>, while it interacts with the less acidic OH groups which vibrate at 3760 and 3720 cm<sup>-1</sup>. The butene has a low proton affinity and is expected to interact more strongly with the more acidic OH group. Steric hindrance due to the structure of the surface site where the more acidic group is located can prevent this effect. Experimental and theoretical studies indicate that the proton donor A-H bond is perpendicular to the carbon-carbon double-bond axis in  $\pi$  complexes.<sup>17</sup> If the acidic OH group is located inside a "hole" of the surface, this spatial arrangement can be prevented for steric reasons. The two less acidic groups which vibrate at 3760 and 3720 cm<sup>-1</sup> must be more easily reachable by the  $\pi$ -electron of 1-butene since weak HB are originated.

Returning to ammonia adsorption, we observe that three OH groups are perturbed by the interaction with the gaseous molecule. This is due to the smaller dimensions of the molecule with respect to 1-butene and to the more compact and symmetrical arrangements of the atoms of ammonia. However, the stronger interactions that produce the ammonium species through chargetransfer reactions are due to the greater "basicity" of ammonia.

HB formation is often the first step in the proton-transfer reactions that we have represented in (1). It is worthwhile to

$$[\mathbf{A}\mathbf{H}\mathbf{\cdot\cdot\cdot}\mathbf{B}] \rightleftharpoons [\mathbf{A}^{-}\mathbf{\cdot\cdot\cdot}\mathbf{H}^{+}\mathbf{B}] \tag{1}$$

point out that the equilibrium (1) is strongly influenced by the environment in which the reactions take place.<sup>18-21</sup> At the solid surfaces, the equilibrium (1) is often shifted to the right also with moderately acid-base systems. In this case, the effects of the surroundings should be similar to the liquid-phase ones, but they are certainly strongly anisotropic. (See the works by Sheppard and Knozinger in refs 2 and 14).

To summarize, we observe the following results obtained from low-pressure transmittance spectroscopic experiments: (a) Not all the OH groups can react with the gaseous 1-butene and ammonia to produce H bonding and charge-transfer reactions; in particular, steric hindrance effects prevent the interaction of the olefin with the more acidic group which is available to ammonia. (b) The interaction with the butene is weak and the oligomerization reactions at the surface of SA can be observed only at high temperature and after a long reaction time. (c) On the contrary, ammonia is strongly adsorbed and ammonium species are originated; in this case three OH groups (one more than for 1-butene) are perturbed by the interaction.

4.2. Catalytic Environmental Chemical Transformations. The skeletal isomerization reaction is usually performed at temperatures between 450 and 500 °C<sup>8,9</sup> in order to obtain a high conversion of the linear olefins and a high selectivity to 2-methylpropene. The reactions do not occur on SA at temperatures lower than 300 °C; in this temperature range oligomers of the linear olefins are the favorite products. Cracking reactions occur at temperatures above 500 °C. These features are described in ref 8 and 9 and were studied in our laboratories during catalytic tests that are not described here. The discussion of the spectroscopic information is related to these experimental results.

(a) Perturbations at the SA OH Groups during the Catalytic Reaction. In the recorded spectra, we have always found traces of H-bonding formation between the same two surface hydroxyls

(22) The terminal methylene CH stretching vibration at 3080 cm<sup>-1</sup> of the external olefin is weakened by raising the temperature, and it nearly disappears at 300 °C. At the same temperature a shoulder at 3010 cm<sup>-1</sup>, typical of the CH stretching of the internal olefin, is revealed (Figure 7A,C,E,G). Accordingly, the C=C stretching band of the external double bond at 1640 cm<sup>-1</sup> is weakened and a peak at 1656 cm<sup>-1</sup>, assignable to the C=C stretching of asymmetrical internal olefin, grows by raising the temperature to 300° C. At higher temperatures the absorption band intensities in the 1700-1600-cm<sup>-1</sup> range are reduced with respect to the other spectral features. These results are related to an increase in the concentration of the symmetrical *trans*-2-butene in the gaseous phase (see also: Egloff, G.; Hulla, G.; Komarewski, V. I. *Isomerization of Pure Hydrocarbons*; Am. Chem. Soc. Monograph Ser.; Reinhold: New York, 1942).

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with the olefin double bond. We argue that the negative bands at 3760 and 3720 cm<sup>-1</sup> and the broad positive bands in the 3600-3400-cm<sup>-1</sup> range can be assigned to this phenomenon. Moreover, we observe that the involvement of the two OH groups in the surface complex formation depends on both the temperature and the presence of the gaseous butene atmosphere. The hydroxyl group that vibrates at 3720 cm<sup>-1</sup> is much more perturbed than the 3760-cm<sup>-1</sup> one if 1-butene is flowing through the cell. While the cell was evacuated from the gaseous butene, the perturbation of the OH surface groups produced a negative doublet having peaks of the same intensity at temperatures below 400 °C (Figure 7A,C). At 400 °C, it is the less acidic group that participates to a greater extent in the surface complexes formation (Figure 7H).

(b) Thermal-Induced Modifications in the Gaseous Phase. The spectra recorded when 1-butene is flowing through the cell, with a gas hourly space velocity (GHSV) of 10000 h<sup>-1</sup>, give information on the gaseous-phase composition before interaction with SA (See Figure 1 and the description of the catalytic environmental cell in the Experimental Section.) They show that temperature-induced double-bond isomerizations of gaseous 1-butene occur at high temperature also in the gaseous phase.<sup>22</sup>

(c) Surface Complexes. Surface-bonded complexes were revealed after flowing 1-butene through powdered SA at 25, 100, 200, 300, and 400 °C in a nitrogen atmosphere. At a temperature lower than or equal to 100  $\circ C$ , the absorption bands are quite similar to the gaseous 1-butene ones. However, the C=C stretching vibration frequency is dramatically enhanced with respect to the other spectral features (Figure 8B). At 200 °C, the absorption bands show the formation of other adsorbed species with absorption peaks at 1670, 1568, and 1460 cm<sup>-1</sup> (Figure 8D). The band at 1670 cm<sup>-1</sup> could be associated with an adsorbed internal olefin C=C stretching vibration. The decrease in the 3080-cm<sup>-1</sup> band intensity with respect to the other spectral features of the adsorbed species is also related to the disappearance of the terminal double bonds. Alternatively, the absorption at 1670 cm<sup>-1</sup> could be assigned to the stretching vibration of a carbonyl group. This hypothesis was discussed by Corado et al.<sup>23</sup> during the spectroscopic study of olefin adsorption and double-bond isomerization over alumina and by others who studied the same phenomena over transition-metal oxides.7 Corado et al. obtained DR UV spectra of the adsorbed species at 175 °C showing an absorption band at 266 nm typical of the  $n \rightarrow \pi^*$  electronic transitions of the adsorbed carbonyl species. During our experiments, we could not find in the mass spectra any peak sequences of carbonylic species when the butenes were flowing through the cell, nor did we reveal in the infrared spectra any band in the 2800-2700-cm<sup>-1</sup> region assignable to CH stretching of aldehydic groups. However, we cannot exclude the formation of carbonylic surface complexes, since we have not performed specific experiments dedicated to this purpose. On the contrary, we can assign the two bands at 1568 and 1460 cm<sup>-1</sup> to oxygen-containing species. The high thermal stability, also in oxidizing environment, supports the attribution of these two peaks to polydentate carbonates.<sup>24</sup> The formation of olefin H-bonded surface complexes is not affected by the redox reactions which originate the carbonates. This was experimentally demonstrated by flowing nitrogen at 300 and 400 °C until the vibrations of the weak H-bonded surface complexes disappear from the spectra, while the absorption at 1568 and 1460 cm<sup>-1</sup> remains unchanged. The initial Pi complex spectral features were obtained again by flowing the 1-butene at 200 °C for 10 min and by replacing the gaseous olefin atmosphere with nitrogen. These results indicate that at least two kinds of reaction occur at the surface. In the first kind of solid-gas interaction, H-bonded surface complexes are formed without other chemical reactions occurring on the adsorbed olefins. At nearly 200 °C, a second

this case, polydentate carbonates are formed on surface molecular sites that should have oxidizing properties. It is not the aim of this work to investigate the oxidizing properties of SA, but it should be stressed that Weller and Montagna<sup>25</sup> experimental with  $\gamma$ - and  $\eta$ -alumina, a high-temperature hydrogen uptake which they attributed to the formation of nonstoichiometric aluminas through the reduction of surface aluminum atoms.

H-bonding formation was also revealed at 300 °C (Figure 7E) when the gaseous 1-butene flowed through the SA, but not when the nitrogen stream evacuated the cell from gaseous olefin (Figure 7F). These spectroscopic observations indicate that the  $\pi$  complexes are not stable enough at this temperature to be revealed by our spectroscopic experiments, even if the collection of the interferograms started immediately after the evacuation of the cell from the gaseous butenes. We point out that to obtain the spectra of Figures 7 and 8 it was necessary to accumulate 500 scans. This required from 1 to 5 min depending on the speed of the scansion of the movable mirror. During this time delay desorption phenomena occur, but we found no qualitative differences between the spectra obtained by processing rapid scan data collections and the spectra obtained with the normal acquisition mode.

At 400 °C (Figure 7H), new surface complexes are formed. The CH stretching bands of the multiplet in Figure 7H can be associated with the  $\nu_{as CH_3}$  (2958 cm<sup>-1</sup>),  $\nu_{as CH_2}$  (2929 cm<sup>-1</sup>), and  $\nu_{s CH_2}$ ,  $\nu_{s CH_3}$  (2875 cm<sup>-1</sup>) vibrations, while the very weak band at 3010 cm<sup>-1</sup> can be assigned to the stretching of a CH group pertaining to an internal double bond.<sup>15</sup> The measured ratio  $I(v_{as CH_2})/I(v_{as CH_3})$  at the band maxima gives the value of 1.18. These spectral features are very similar to those measured for cis platinum dibutyl compounds<sup>26</sup> and in studies of surface complex formation during butene hydrogenation reactions over transition metals containing catalysts (see the works of Morrow and Sheppard and of Campione and Ekerdt in ref 2). In this case the measured ratio of the antisymmetric stretchings of the methylene and methyl groups was 1.20. The CH bending vibrations of the adsorbed species could not be observed due to the overlapping with the absorptions of the carbonate groups (see also Figure 9). As previously observed, the spectrum in Figure 7H shows that the OH group that vibrates at 3760 cm<sup>-1</sup> on the free SA is now much more perturbed by the interaction with butenes than the 3720-cm<sup>-1</sup> one. In addition, the broad and intense band of the very strong vibration of the H-bonded OH groups has changed its shape and shifted its maximum near 3600 cm<sup>-1</sup>.

The discussion on the molecular phenomena that produce these spectral features at 400 °C will be developed by considering two hypotheses. The first one is that, in the conditions described, the surface-adsorbed species consist of a few branched oligomers, as it could be inferred by the low intensity of the absorption bands and by the low value of the intensity ratio  $I(v_{as CH_2})/I(v_{as CH_2})$ . In this case the oligomers should be bonded to the surface through the same two OH groups which form H bonds with the gaseous monomeric olefin. Following this hypothesis we have looked for peaks assignable to species different from the butene isomers in the mass spectra. As previously mentioned, we have collected 500 scans to obtain the IR spectra of the surface complexes in a nitrogen atmosphere. During the acquisition time the desorption of the adsorbed species occurs; the mass spectra obtained in this time delay have shown only peak sequences assignable to the butenes. We also followed in the course of time the intensity variations of eight peaks (m/e = 2, 14, 27, 28, 39, 40, 41, 56)in the mass spectra, corresponding to the six stronger peaks due to the fragmentation of the butenes and to the ionization of  $H_2$ and N<sub>2</sub>

The plots of the peak intensities (expressed as partial pressures of the species with the different m/e values) versus time show six flat parallel curves during the catalytic reaction conditions. When nitrogen is flowed in the catalytic cell, the six curves drop stepwise from partial pressure values around 10<sup>-3</sup> Pa to values around 10<sup>-5</sup>

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Figure 10. Symmetric (a) and asymmetric (b) double-minimum potentials for the proton-transfer reaction.

Pa. During the collection of the interferograms (about 3 min), the peak intensities further decrease, reaching the lowest value obtainable by our mass spectrometer  $(10^{-6}$  Pa). In this period the six curves have a negative slope but still remain parallel. Hydrogen formation has never been detected in the mass spectra during the experiments. We can exclude that these results were due to olefin residue that remains in the input lines since these had a very low volume and were evacuated and washed with nitrogen before admission of the inert gas to the cell. Moreover, no gaseous olefins were revealed by the IR spectra in the cell atmosphere. (Surface species are desorbed in the cell output line, and they cannot be detected by infrared spectroscopy but are revealed by the mass spectra.)

These findings indicate that, during the desorption phenomena, no further reactions occur, and they do not sustain the assignment of the IR bands to butene oligomers.

The second possibility that we have considered is that, at 400 °C, a proton-transfer reaction from the OH surface groups toward the H-bonded olefin occurs, thus shifting equilibrium (1) to the right. It is known that the proton-transfer equilibria (1) along a reaction coordinate often give double-well potential energy curves<sup>27</sup> (Figure 10). In this case, the extent of the proton transfer could be small at low temperatures, when the H-bonded complex cannot reach the activation energy necessary to overcome the barrier between the two wells. When the temperature reaches 400 °C, the population of the vibrational excited energy levels increases according to the Boltzmann law and the activation energy for the proton-transfer reaction is reduced if the energy of the H-bonded excited species is near or over the maximum value of the energy barrier that separates the two minima.<sup>28</sup> The equilibrium (1) is than shifted to the right, provided that the lifetime of the excited H-bonded system is longer than the time necessary for the proton-transfer reaction. In this way the charged species could prevail over 400 °C, while the unprotonated one prevails below 300 °C.

The variations of the perturbations of the two OH groups could then be related to the shifting of the equilibrium (1) with the temperature. This seems to indicate that the OH group that vibrates at  $3760 \text{ cm}^{-1}$  is transferred from the solid to the olefin in the high-temperature charge-transfer reaction. If incipient primary or secondary carbocations are formed in this way, skeletal isomerization occurs to give a tertiary carbocation. This will result in the modification of the potential energy curves of the equilibrium (1); consequently, the proton could be pulled back to the donor OH group and isobutene desorbed from the surface. This hypothetical reaction mechanism can be represented schematically by the following equations. (For the sake of simplicity, the three possible linear isomers of the olefin and the interactions with more

than one OH group have not been considered here.)

$$A-OH\cdots \int = A-O\cdots \int \delta^+ \qquad (3)$$

$$A\overset{\overline{b}}{\overline{\phantom{b}}}\cdots\overset{\overline{b}}{\overline{\phantom{b}}}^{*} \implies A\overset{\overline{b}}{\overline{\phantom{b}}}\cdots\overset{\overline{b}}{\overline{\phantom{b}}}^{*} \qquad (4)$$

$$A \xrightarrow{\delta} \cdots \xrightarrow{\delta^+} = A \xrightarrow{OH} + (5)$$

If we assume that the desorption step in (5) is very fast with respect to the other reactions and that equilibrium (4) is shifted to the left, the bands of the spectrum of Figures 7H and 8H should be due to the absorptions of the species of the proton-transfer equilibrium (3). On the basis of these assumptions, the peak at  $3010 \text{ cm}^{-1}$  can be assigned to the stretching of a CH bond of a H-bonded 2-butene, while the other stretching bands can be assigned to the vibrations of the CH bonds of methyl and methylene groups of both species of the equilibrium (3).

## 5. Conclusions

Surface complex formation was observed during the interaction of linear butenes with SA. The involvement of the SA surface groups was revealed by the perturbation of two OH stretching vibrations. The extent of the perturbations changes with temperature and is correspondingly followed by modifications in the spectral features of the adsorbed organic molecules. These experimental findings were interpreted assuming that the interaction leads to the formation of H-bonded species. A proton-transfer equilibrium can be thus established between the solid and the organic molecule. The spectra obtained suggest that near 400 °C the proton has a remarkable probability to be pushed toward the double bond of the olefin. This can be explained with the hypothesis that the proton-transfer equilibrium along a reaction coordinate describes a "double-well" potential energy curve with two minima, corresponding to the formation of the structures with the proton near the donor and near the acceptor group. At high temperature, the population of the excited vibrational levels increases and the energy barrier between the two minima could be lowered if the energy of the excited species is near or over its maximum. We propose that the proton, traveling toward the acceptor, in analogy with some byochemical catalytic reactions,<sup>29</sup> brings the necessary energy for the skeleton isomerization of the charged alkyl group that is formed. The proton is subsequently pulled back to the solid surface, and the isobutene molecule is desorbed. The increase in electrostatic repulsive effects between the catalytic site chemical groups and the branched alkyl group could be responsible for this.

It has also been observed that a redox reaction produces adsorbed carbonate groups at temperature above 200 °C. This reaction does not modify the reactivity of the solid with respect to the skeletal isomerization reaction and should involve different surface molecular groups that possess oxidizing properties.

We have found that SA is able both to coordinate ammonia by Lewis acid sites and to form adsorbed ammonium species through proton-transfer reaction with surface OH groups. In the latter case, ammonia reacts with the same two OH groups which interact with linear butenes and, in addition, with a third more acidic OH group which is not available to olefins. This experimental finding indicates that steric hindrance effects influence solid interactions with the gaseous butene and suggests that any evaluation of the acid-base properties of the catalysts should be referred to the reactions in which they are involved.

<sup>(27)</sup> Pimentel, G. C.; McClellan, A. L. The Hydrogen Bond; W. H. Freeman: San Francisco, 1960.

<sup>(28)</sup> It results that at 400 °C  $(E_1 - E_0)/kT = 278$  (cm<sup>-1</sup>). Since the librational modes in many XH-C<sub>4</sub>H<sub>8</sub> complexes were observed in the 500-300-cm<sup>-1</sup> range, it follows that a substantial amount of complexes will be in the first excited vibrational level in accordance with the Boltzmann distribution function  $n_1/n_0 = \exp[-(E_1 - E_0)/kT]$ .

<sup>(29)</sup> Sheiner, S.; Redfern, P.; Hillenbrand, E. A. Int. J. Quantum Chem. 1986, 39, 817.