JOURNAL OF CATALYSIS 14, 213–219 (1969)

Infrared Spectrum of 1-Butene on Mixed-Oxide Catalysts

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Received August 27, 1968

The adsorption of 1-butene onto synthetic mixtures of silica with boric oxide, zirconia, and alumina has been studied using infrared spectroscopy. The gas is physically adsorbed onto hydroxyl groups on the surface of each sample. Slight polymerization of the gas occurs over silica-zirconia and rapid isomerization and polymerization was found over silica-alumina.

These results are compared with studies of the adsorption of 1-butene onto porous silica glass. It is considered that the catalytic activity of the porous glass towards olefins is mainly due to the presence of aluminum atoms in the glass.

The adsorption of ammonia onto porous silica glass has been the subject of many investigations (*1*, *2*). It is found that ammonia is physically adsorbed onto surface hydroxyl groups on the glass and is more strongly chemisorbed onto other sites. Small concentrations of boric oxide, aluminum oxide, zirconium dioxide, and possibly other oxides are present in porous glass and it is considered that these can act as Lewis acid sites to chemisorb ammonia (*3*).

Isomerization, polymerization, and cracking of *n*-butenes were found on porous silica glass (*4*). It was considered that the catalytic activity of the porous glass depended upon the presence of the alumina and perhaps also the zirconia rather than boron atoms which were the principle chemisorption sites for ammonia. After reducing the concentration of alumina and zirconia in the glass, the rate of isomerization of 1-butene was greatly decreased (*4*).

The aim of the present study was to determine which of the oxides in porous silica glass would catalyze the isomerization, polymerization, and cracking of *n*-butenes. Infrared spectroscopic studies were made of the interaction of 1-butene with samples of boric oxide, alumina, and zirconia supported in silica and these were compared with studies of the interaction of 1-butene with samples of porous glass. 1-Butene was chosen since its infrared spectrum undergoes marked changes as isomerization proceeds.

EXPERIMENTAL

Samples of Corning Glass Works Code 7930 porous glass were supplied by Corning Glass Works, Corning, New York in the form of tubes 1 mm in wall thickness and 2 cm in diameter. Similar samples have been shown to contain 2–3% B_2O_3, 0.3–0.4% Al_2O_3, and 0–0.4% ZrO_2 in addition to silica [ref. (*4*) and information supplied by Corning Glass Works]. A second tubular sample was specified by the manufacturers to contain 3% B_2O_3, 0.03% Al_2O_3, and almost no zirconia.

Solutions of boric acid, aluminum nitrate, and zirconium nitrate were prepared from laboratory grade materials and to each of these was added Cab-O-Sil HS-5 silica powder (supplied by Godfrey L. Cabot Corporation, Boston, Massachusetts) to form slurries. These were dried at 130°C and calcined at 400°C for 8 hr. The residues were ground to a fine powder which had an oxide concentration of approximately 5%. Cab-O-Sil HS-5 silica has a surface area of

340 m^2/g and it has been shown that supported adsorbents prepared in this way have surface areas similar to that of the pure support (*3*).

The mixed-oxide powders were compressed under a pressure of 10 tons/sq inch to form rectangular pellets of between 10 and 15 mg/cm^2, which were transparent to infrared radiation. Anhydrous ammonia (99.99% pure) and CP grade 1-butene gases were obtained from Matheson Company, Inc., and were used without further purification.

All spectra were recorded in the frequency range 4000 to 2000 cm^{-1} on a Perkin-Elmer Model 521 spectrophotometer. Two types of infrared cells were used and these have been described elsewhere (*1, 4*). The samples were first heated in a stream of oxygen at 450°C for 2 hr to remove hydrocarbon impurities and again heated in oxygen within the infrared cell. They were then evacuated at 400–450°C for 8–10 hr to remove adsorbed water and aligned in the infrared beam. A silica tube was arranged in the reference beam to compensate for absorption by the cell when the silica cell was used and a spectrum was recorded from 4000 to 2100 cm^{-1}, below which frequency the cell absorbed all radiation. A known pressure of gas (between 20 and 30 torr) was admitted to the sample while it was still aligned in the infrared beam and spectra were recorded at intervals. Gases in the cell could be condensed into a cold finger (cooled to liquid air temperature) to permit spectroscopic observation of adsorbed species without interference from gas absorption. Weakly adsorbed molecules were desorbed by this operation and could be accounted for by subtracting the gas phase spectrum from the composite spectrum of the gas plus the adsorbed species. In each case, band intensities were expressed as optical densities before subtraction and converted back to percentage transmission to provide spectra of the physically adsorbed species shown in Figs. 2–4. Care was taken to exclude mercury vapor from the system and a Bourdon gauge was used to measure approximate gas pressures.

RESULTS AND DISCUSSION

It has been found (*4*) that *n*-butenes isomerize very rapidly over a porous glass catalyst and attain an equilibrium composition of 2.4% 1-butene, 74.2% *trans*-2-butene and 23.3% *cis*-2-butene. The infrared spectrum of 1-butene has a strong band at 3080 cm^{-1} corresponding to the asymmetric stretching vibration of the $=CH_2$ group while the $=CH-$band for 2-butene occurs at 3020 cm^{-1} (Fig. 1a). Therefore the progress of the isomerization of 1-butene can be followed by comparison of the intensities of these bands in the infrared spectrum of either adsorbed or gaseous material.

Within 10–15 min after admitting 1-butene (10 torr) to a sample of porous silica glass, a strong band indicating the presence of 2-butene appeared at 3020 cm^{-1} in the combined spectrum of gas plus sample. Meanwhile the band at 3080 cm^{-1} due to the 1-butene decreased progressively and had completely disappeared after 50 min, at which stage equilibrium had almost been reached (Fig. 1b). After evacuation at 20°C for 30 min, the infrared spectrum showed an olefinic species remaining on the surface of the sample. This was considered to be a mixture of physically adsorbed 2-butene, bound by the interaction of the π-electrons of the olefin with surface hydroxyl groups of the catalyst, and a polymeric species adsorbed onto the surface,

When 1-butene was admitted to the same cell containing a sample of porous glass having only 0.03% alumina and almost no zirconia, a large amount of the gas was physically adsorbed to the sample but no evidence was found for isomerization. There was no change in the band intensities of the combined spectrum of gas plus sample, even after the gas had been in contact with the sample for 50 hr (Fig. 1c). The adsorbed species could be almost completely desorbed by evacuation for 45 min at room temperature. It appears that negligible isomerization or polymerization of the gas had occurred over this sample.

Admission of ammonia gas to both the samples of porous silica glass discussed

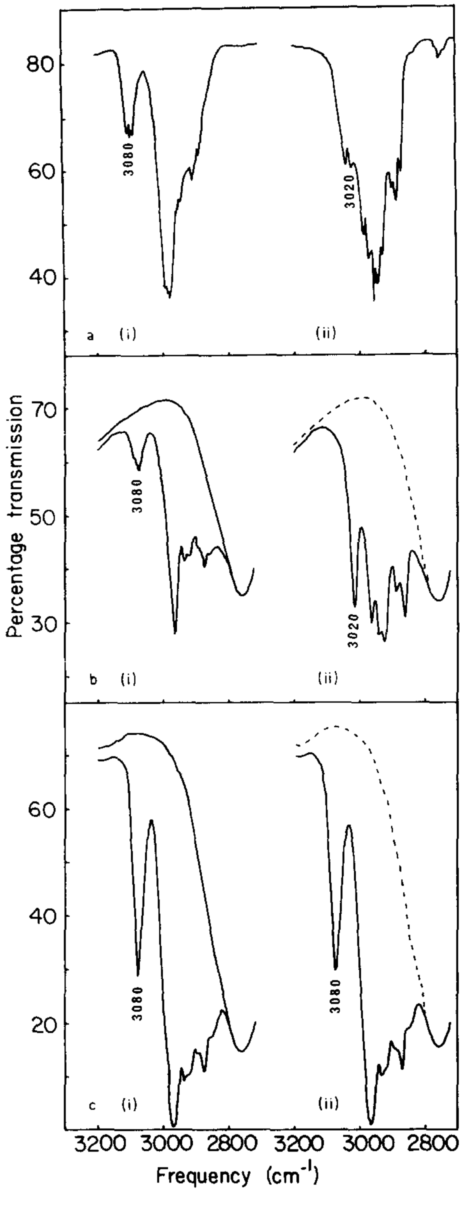

FIG. 1. Infrared spectra: (a) gaseous (i) 1-butene and (ii) *trans*-2 butene (20 torr, 5 cm cell); (b) 1-butene adsorbed on porous silica glass after (i) 10 min (ii) 50 min (gas pressure 10 torr); (c) 1-butene adsorbed on porous glass of low alumina content (gas pressure 20 torr) (i) 20 min after admission, (ii) 50 hr after admission.

above produced similar results to those obtained by previous workers (*1*, *2*), indicating both physical adsorption onto surface hydroxyls and chemisorption onto other sites. Both of these samples contained approximately 3% boric oxide and both chemisorbed ammonia. However, the second of these samples would not catalyze the isomerization of 1-butene, suggesting that boron atoms are not active sites for the isomerization of olefins. It would appear that the presence of other oxides is responsible for the catalytic activity of porous glass towards olefins.

The inactivity of boric oxide and the activity of alumina and zirconia for isomerization and polymerization of olefins is supported by studies made on the adsorption of 1-butene onto synthetic mixtures of silica with boric oxide, alumina, and zirconia.

The infrared spectrum of a sample of 5% boric oxide in Cab-O-Sil (Fig. 2,a) contained two very sharp bands at 3747 and 3704 cm^{-1} corresponding to the O–H streching vibration of free surface hydroxyl groups bonded to silicon and boron atoms, respectively (*5*), and a shoulder between 3700 and 3600 cm^{-1} due to internal and hydrogen-bonded hydroxyls. When 1-butene (25 torr) was admitted to this sample, the intensities of both these bands were reduced while the intensity of the shoulder increased, indicating hydrogen bonding between surface hydroxyl groups and the π-electrons of the olefin (Fig. 2,b). After the gas had been condensed into a liquid air trap, the spectrum of the sample (Fig. 2,c) was almost identical to the original, showing that the gas was only weakly adsorbed and could be completely desorbed by condensation.

The infrared spectrum of the gas in the cell is shown in Fig. 2,d. By subtraction of the band intensities of the gas in Fig. 2,d from those of the gas plus adsorbed species in Fig. 2,b, it is possible to construct a spectrum of the species which is physically adsorbed onto the surface of the sample (Fig. 2,e) and which is desorbed by condensation into a liquid air trap. No spectral evidence for changes in the composition of the gas phase or the adsorbed phase could be found with the sample of boric oxide–silica, even after the gas had been in contact with the sample for 67 hr. However, after the 1-butene was evacuated at room temperature, this same sample was able to physically

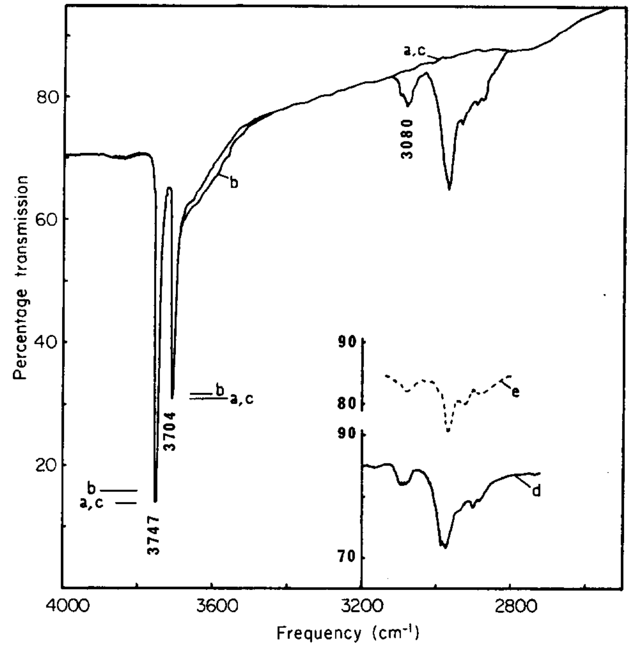

FIG. 2. Infrared spectra of the adsorption of 1-butene on boric oxide–silica: (a) before gas admission; (b) 39 hr after gas admission (25 torr); (c) gas condensed; (d) gas spectrum; (e) physically adsorbed species [by subtraction of (d) from (b)].

adsorb and chemisorb ammonia, giving infrared bands similar to those obtained by Cant and Little (*3*), indicating that boron atoms were exposed to the surface.

Spectra of a sample of 5% zirconia in Cab-O-Sil before and after the addition of 1-butene (30 torr) are shown in Fig. 3,a and b. The interaction of the gas with hydroxyl groups on the surface of the sample was similar to the interaction found with the boric oxide–silica sample. In addition, however, a very weak band due to an adsorbed hydrocarbon species was present in the spectrum after the gas had been condensed. Initially this band could only be distinguished by amplification of the ordinate scale of the spectrum, but after 39 hr, three distinct bands were evident (Fig. 3,c). The strongest occurred at 2965 cm^{-1}, corresponding to the asymmetric stretching vibration of a $-CH_3$ group. Weaker bands appeared at approximately 2935 and 2878 cm^{-1}, corresponding to the asymmetric $-CH_2$ streching vibration and the symmetric stretching vibration of the $-CH_3$ group, respectively. These bands could be produced by a surface polymeric species having a high proportion of $-CH_3$ groups and hence a high proportion of chain branching.

The spectrum of the gas phase above the sample is shown in Fig. 3,d. Subtraction of the intensities of bands of this spectrum from those of the spectrum of the gas plus the physically adsorbed species (using Fig. 3,c of the chemisorbed species as a background spectrum), provided the spectrum of the physically adsorbed gas (Fig. 3,e). It appears that the extent of physical adsorption of 1-butene by the silica-zirconia sample is greater than for the silica–boric oxide sample. No spectral evidence was found for the isomerization of 1-butene over the zirconia-silica sample after 70 hr.

The spectrum of a sample of 5% alumina in Cab-O-Sil, evacuated for 12 hr at 440°C is shown in Fig. 4,a. Admission of 1-butene (25 torr) to this sample caused a greater perturbation of the surface hydroxyl groups (Fig. 4,b) than that observed for the previous mixed oxides. After the gas had been standing over the sample for 10 min, the composite spectrum of gas plus sample

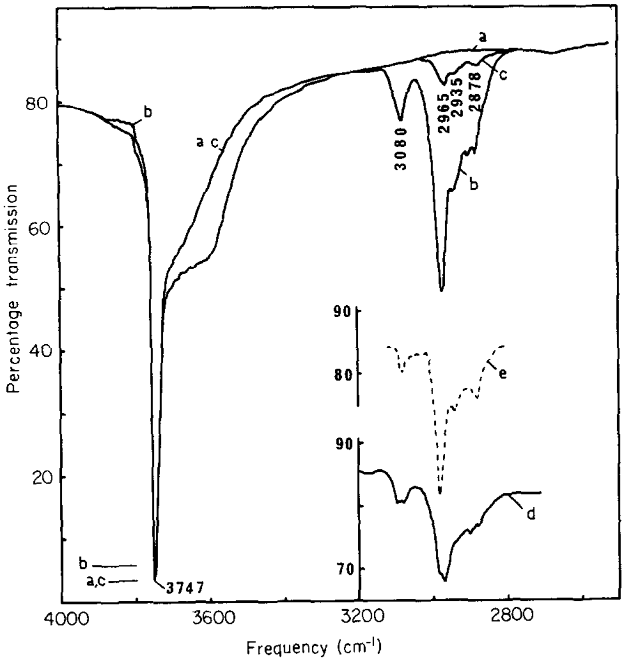

FIG. 3. Infrared spectra of the adsorption of 1-butene on silica–zirconia: (a) before gas admission; (b) 39 hr after gas admission (25 torr); (c) gas condensed; (d) gas spectrum; (e) physically adsorbed species [by subtraction of (d) from (b) with (c) as background].

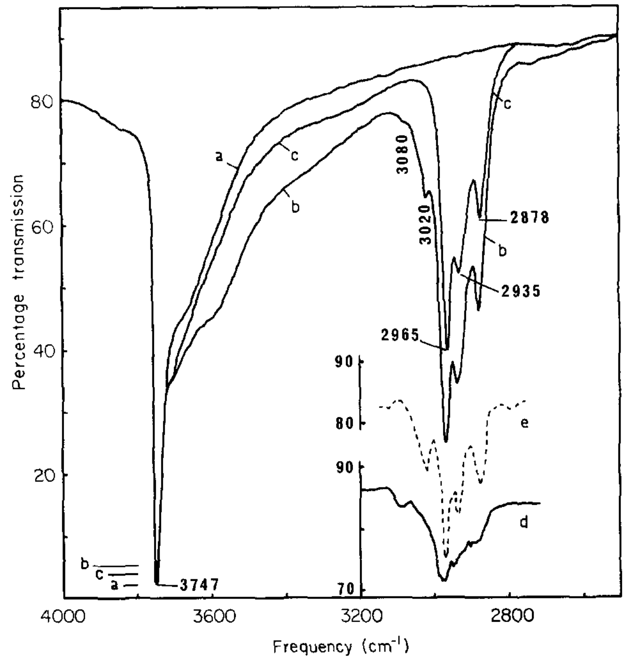

FIG. 4. Infrared spectra of the adsorption of 1-butene on silica–alumina: (a) before gas admission; (b) 10 min after gas admission (25 torr); (c) gas condensed after 20 min; (d) gas spectrum after a total of 25 min exposure to sample; (e) physically adsorbed species [by subtraction of (d) from (b) with (c) as background].

plus adsorbed species contained a very weak band at 3080 cm^{-1} and a more intense band at 3020 cm^{-1} (Fig. 4,b) showing that rapid isomerization was taking place. There were also three intense bands at 2965, 2935, and 2878 cm^{-1}.

Condensing the olefin after 20 min removed most of the surface hydroxyl perturbation in the spectrum and the bands at 3080 and 3020 cm^{-1} also disappeared. The three sharp bands remained at 2965, 2935, and 2878 cm^{-1} and were thought to be due to a saturated polymeric species adsorbed onto the surface (Fig. 4,c). The gas was allowed to evaporate and a spectrum of the gaseous species in the cell after a total of 25 min exposure to the sample is shown in Fig. 4,d. Since the band at 3020 cm^{-1} is not present in this spectrum, the isomerized 2-butene must have existed mainly on the surface. The spectrum of the species physically adsorbed on the sample [obtained by subtraction of the gas spectrum of Fig. 4,d from the gas plus sample (Fig. 4,b) with the chemisorbed species of Fig. 4,c as background] most closely resembles a 2-butene-like species and supports this conclusion (Fig. 4,e).

The isomerized 2-butene adsorbed on the surface and shown by the constructed spectrum in Fig. 4,e was very rapidly consumed in the surface polymerization reaction to produce saturated hydrocarbons responsible for the bands at 2965, 2935, and 2878 cm^{-1} in Fig. 4,c. This is suggested by the fact that the isomerized 2-butene was not apparent in the gas spectrum which Fig. 4,c shows to be almost entirely 1-butene, and also because the 3020-cm^{-1} band of 2-butene was absent from the spectrum (Fig. 4,c) of the material remaining on the surface after condensation.

On standing, the intensities of the bands due to the polymeric chemisorbed species increased at approximately equal rates, showing that a similar number of $-CH_3$ and $-CH_2$ groups were formed and indicating much chain branching. The spectrum of this species resembles that of the polymer formed when 1-butene was admitted to the

TABLE 1
RESULTS OF AMMONIA AND 1-BUTENE ADSORPTION ON MIXED OXIDES

Catalyst	Adsorbate	Chemical reaction	Chemisorption site	References
Cab-O-Sil (pure silica)	Ammonia	Nil	—	*7*
	1-Butene	Nil	—	*4*
Porous silica glass	Ammonia	Coordination	Boron	*1, 2*
	1-Butene	Isomerization and polymerization	Alumina and possibly other oxides	*4*
Acid-leached porous silica glass	Ammonia	Coordination	Boron	*8*
	1-Butene	Nil	—	*4*
Porous silica glass low in alumina	Ammonia	Coordination	Boron	[a]
	1-Butene	Nil	—	[a]
Boric oxide–silica	Ammonia	Coordination	Boron	*3*
	1-Butene	Nil	—	[a]
Zirconia–silica	Ammonia	Coordination and slight protonation to form NH_4^+	Zirconium	*3*
	1-Butene	Slight polymerization, no isomerization detected	Zirconia	[a]
Alumina–silica	Ammonia	Coordination and protonation to form NH_4^+	Aluminum	*3*
	1-Butene	Rapid isomerization and polymerization	Alumina	[a]

[a] Present investigation.

silica-zirconia adsorbent. However, the silica-alumina sample is a much more active polymerization catalyst and will also catalyze the isomerization of the 1-butene.

After the gas had been standing over the sample for several hours, a broad weak band appeared at 3700 cm^{-1} in the composite spectrum of the gas plus sample. This band remained in the spectrum of the sample when the gas was evacuated at 20°C but after evacuation at 100–150°C, the band disappeared and the intensity of the bands due to the adsorbed hydrocarbon species decreased. Peri and Hannan (*6*) found that surface hydroxyls on pure alumina give rise to three major bands at 3795, 3737, and 3698 cm^{-1}. The species which produces the low-frequency band can be deuterated most easily and when deuterated, will reexchange with hydrogen from adsorbed 1-butene. This Al-OH species is quite stable to evacuation at 800°C. Thus it seems unlikely that the band at 3700 cm^{-1} in the spectrum of the silica-alumina sample plus adsorbed species is due to a hydroxyl group attached to a surface aluminum atom because it is removed by evacuation at 150°C. Since the band becomes evident only after polymer concentration has reached a certain level and disappears when the polymer is removed, it may be produced by interaction of surface hydroxyl groups with the adsorbed material.

A similar sample of 5% alumina in Cab-O-Sil was evacuated at 670°C for 8 hr. The spectrum of this sample showed a very low concentration of hydrogen-bonded hydroxyls remaining on the surface. When 1-butene (25 torr) was added to this sample, rapid polymerization occurred but the band at 3020 cm^{-1} in the spectrum of the gas plus sample did not appear. Even after the gas had been in contact with the sample for 1½ hr, no isomerization of the 1-butene was evident although the bands due to the polymer had increased. A broad weak band appeared at 3700 cm^{-1} once more and isomerization of the gas was evident after several days. It can be concluded that the catalytic activity of silica-alumina for the isomerization of 1-butene depends largely upon the degree of dehydration of the sample, evacuation at higher temperatures greatly retarding the rate of isomerization.

The results of investigations of the adsorption of ammonia and 1-butene onto various related oxide systems are summarized in Table 1. It appears that the presence of alumina in porous silica glass is mainly responsible for the catalytic activity in the isomerization and polymerization of 1-butene. The silica–boric oxide sites on the porous silica glass which chemisorb ammonia are different from the sites (silica–alumina) which react with the olefin.

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