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NOTE

Inhibition of Butene Isomerization by Adsorbed Ammonia

The isomerization and polymerization of 1-butene on mixed oxide catalysts and on porous silica glass has been investigated by infrared spectroscopy (*1*, *2*) and the acidic sites on these catalysts have been characterized through adsorption studies using ammonia (*3*–*6*). Oxides that were catalytically active for isomerization were found to chemisorb ammonia in several ways; through coordination of the ammonia molecule, through protonation on Brönsted acid sites (*4*) after high temperature evacuation and through dissociative adsorption as primary amine groups (*5*, *6*). In addition, the surfaces of all oxides contain hydroxyl groups in varying amounts, which hydrogen bond to ammonia (*3*).

In the present investigation, the blocking of the isomerization of 1-butene over porous-silica glass by preadsorption of ammonia has been investigated by infrared spectroscopy. Ammonia adsorbed as $—NH_3$ groups prevents isomerization and polymerization of 1-butene whereas adsorbed $—NH_2$ groups do not. Adsorbed hydrocarbon polymer, resulting from 1-butene reactions, will act as an isomerization site but does not constitute the principal site for olefin reactions over porous glass.

In order to obtain more information about the types of sites present on porous glass which adsorb ammonia and those which react with butenes, the isomerization activities of samples evacuated at 450°C were tested before and after the chemisorption of ammonia. Inhibition of butene isomerization by chemisorbed ammonia and intermolecular interaction between the chemisorbed ammonia and the olefin was observed. The activities of samples dehydrated at 650 and 800°C were also tested.

Figure 1a shows the spectrum of a typical sample of porous glass after evacuation at 450°C with a very strong and broad absorption band at 3800–3500 cm^{-1} due to the stretching vibrations of surface hydroxyl groups and some internal groups within the bulk of the silica sample. When 1-butene is added to such a sample, the gas is isomerized to produce an equilibrium mixture of butenes (97.5% 2-butene) and a polymeric hydrocarbon species forms on the surface of the porous glass (*1*, *2*). The disappearance of a band at 3080 cm^{-1} (due to 1-butene) from the spectrum of the gas indicates that isomerization equilibrium has been reached (Fig. 1b,c). The characteristic adsorption band at 3020 cm^{-1} in Fig. 1c is due to the 2-butenes. For the samples used in the present study, 25 Torr of butene was isomerized completely in less than 8 hr.

The spectrum shown in Fig. 1d was recorded after the addition of 200 Torr of ammonia to a sample of porous glass evacuated at 450°C followed by desorption of physically adsorbed gas at 100°C. The broad bands at 3368 and 3285 cm^{-1} are due to ammonia chemisorbed to boron atoms in the porous glass (*3*–*6*). When 25 Torr of 1-butene is admitted to this ammonia treated sample at 20°C, no isomerization or polymerization of the gas is observed after 20 hr as shown by the constant intensity of the 1-butene band at 3080 cm^{-1} (Fig. 1g).

Ammonia could be slowly desorbed from the sample by evacuation for periods at successively higher temperatures. Following each evacuation of ammonia, the extent of isomerization and polymerization of 25

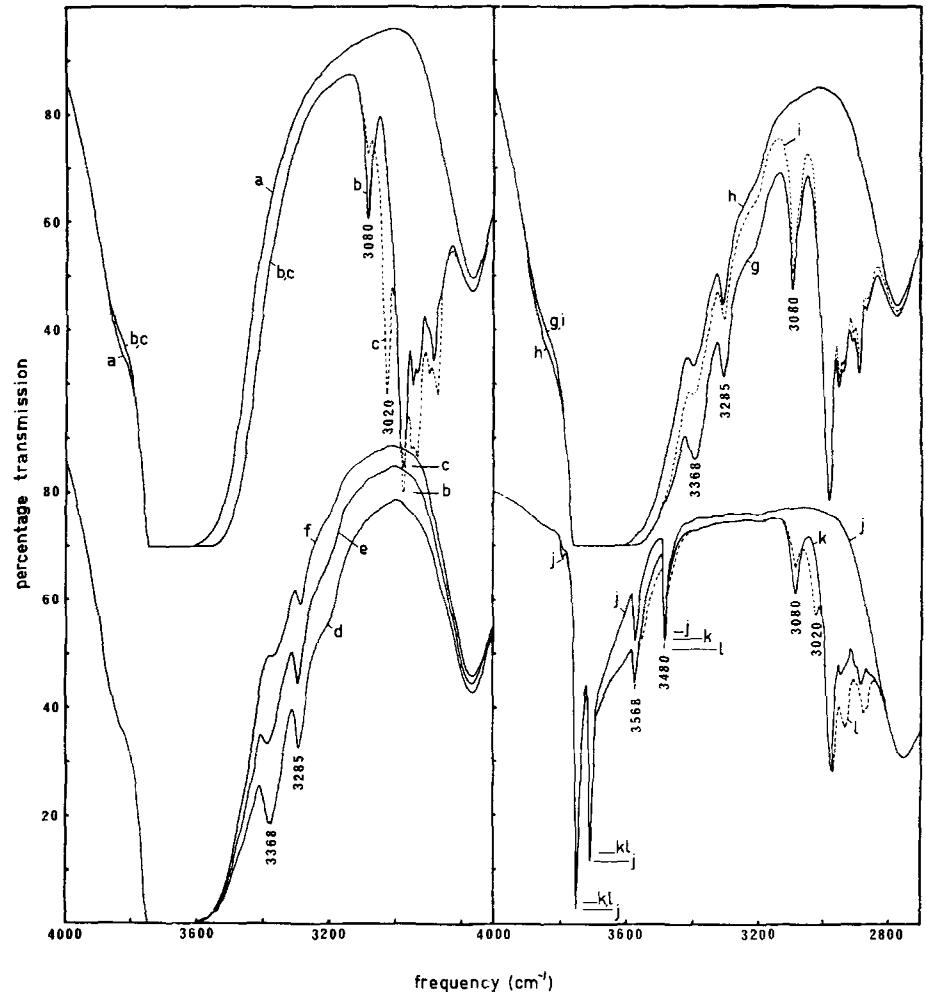

FIG. 1. Infared spectra of porous silica glass: (a) After evacuation for 8 hr at 450°C; (b) after the addition of 1-butene (25 Torr) to the evacuated sample; (c) after standing for $4\frac{1}{2}$ hr at 20°C; (d) after evacuation for 1 hr at 200°C, addition of 20 Torr ammonia and evacuation for 2 hr at 100°C; (e) after evacuation of adsorbed ammonia for 1 hr at 180°C; (f) after evacuation for 15 min at 320°C; (g) 20 hr after the addition of 25 Torr 1-butene to the sample plus adsorbed ammonia which had been evacuated at 100°C; (h) after evacuation of the 1-butene and adsorbed ammonia for 1 hr at 180°C, and (i) 22 hr after the addition of 25 Torr 1-butene to this sample.

The sample was evacuated for 9 hr at 800°C exposed to the atmosphere for 12 hr at 20°C and then evacuated for 12 hr at 450°C. Spectra are shown: (j) After the addition of 100 Torr NH_3 at 20°C followed by evacuation for 4 hr at 450°C; (k) after addition of 25 Torr 1-butene, and (l) 17 hr after standing at 20°C.

Torr of 1-butene was tested after standing with the gas for 20 hr (Fig. 1h,i). After evacuation of some of the ammonia from the sample for 15 min at 300°C (Fig. 1f), slight polymerization and isomerization of 25 Torr of butene was observed in the 20-hr period. When all the adsorbed ammonia was removed by evacuation at 350°C (Fig. 1a), samples were as active for 1-butene isomerization and polymerization at they were before ammonia admission. Thus, preadsorption of ammonia will block sites on porous glass which are responsible for the isomerization and polymerization of

1-butene. Similar results have been observed for isomerization of 1-butene over silica-alumina catalysts, measured by chromatographic methods (*7*).

When 1-butene is isomerized over porous glass evacuated at 450°C, and the gas is evacuated at 20°C, a polymeric hydrocarbon species remains adsorbed to the surface of the sample (*2*). The rate of isomerization of a second dose of 1-butene (25 Torr) is not affected by the polymer and admission of ammonia leads to the formation of chemisorbed ammonia with a spectrum similar to that for ammonia chemisorbed to a fresh sample of porous glass (Fig. 1d). Thus the presence of a hydrocarbon polymer does not prevent chemisorption of ammonia onto porous glass. Over a sample having both adsorbed polymer and chemisorbed ammonia on its surface, isomerization of 25 Torr of 1-butene will take place and is completed within 45 hr of gas admission. But if the adsorbed hydrocarbon is removed by evacuation at 150°C, while the porous glass still has ammonia chemisorbed to its surface, there is only slight polymerization and negligible isomerization of 25 Torr of 1-butene after 7 days. The principal isomerization and polymerization sites were still covered by ammonia.

Thus chemisorbed ammonia is able to block the sites on porous glass (thought to be silica-alumina sites (*1*)) which isomerize and polymerize 1-butene. The principal adsorption sites for ammonia on porous glass are surface boron atoms (*3*, *5*, *6*) but it is most likely that some ammonia is also chemisorbed to the silica-alumina sites (*4*). However, these sites must be of low concentration since ammonia chemisorbed by them cannot be detected in infrared spectroscopy in the presence of the large concentration of gas adsorbed to the boron sites.

When ammonia is admitted to a sample which already has adsorbed polymer on its surface, the gas will be chemisorbed on boron sites (which do not interact with 1-butene) and probably on those silica-alumina sites which are not covered with polymer. Slow isomerization of 1-butene still occurs over such a sample, implying that isomerization sites which do not interact with ammonia are present on the surface of this sample. It has been suggested that the polymeric residue itself can also catalyze isomerization reactions (*7*, *8*) over silica-alumina catalyst and this is consistent with the results we observe. It should be noted that isomerization activity arising from preadsorbed polymer after the addition of ammonia is much less than that found in the absence of ammonia. Adsorbed polymer does not diminish the activity of the bare surface.

In studies of the isomerization of *n*-butenes over silica-alumina, it has been found that the rate of reaction decreases as the concentration of hydroxyl groups on the catalysts is decreased (*8*). In the present study, the isomerization and polymerization of 25 Torr of 1-butene was very slow over porous glass evacuated at 650°C and negligible reaction occurred over samples evacuated at 800°C. Rehydration of samples by exposure to the atmosphere partially restored isomerization activity.

When 25 Torr of 1-butene was admitted to a porous glass sample which had been evacuated at 800°C, exposed to the atmosphere and reevacuated at 450°C, isomerization and polymerization of the gas was observed, although the rate of reaction was less than that before the sample was subjected to high-temperature treatment. Admission of ammonia to such samples produced bands due to NH_3 (3414–3285 cm^{-1}) and NH_2 (3568–3480 cm^{-1}) groups in the spectrum of the sample and these have been discussed elsewhere (*6*). When 1-butene was added to these ammonia treated samples, weak hydrogen bonding between the olefin and the OH groups was observed but no isomerization occurred. In addition, weak interaction between adsorbed ammonia molecules and 1-butene was observed (*6*). Evacuation for 4 hr at 450°C removed all bands due to $—NH_3$ but not those of $—NH_2$ groups from the spectrum of the samples (Fig. 1j) and a further 25 Torr of 1-butene was now seen to isomerize (Fig. 1k,l). Presumably the chemisorbed —NH_2 groups do not affect the silica-alumina sites on the porous glass and therefore cannot prevent isomerization of the 1-butene.

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