Infrared Spectroscopic Evidence for the Formation of an Intermediate Involved in the Zeolite-catalysed Isomerization of n-Butenes upon Addition of Sulphur Dioxide

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Summary The appearance of two new i.r. bands at 1495 and 1245 cm^{-1} is evidence for a sulphone-like intermediate involved in the isomerization of n-butenes by sulphur dioxide adsorbed on zeolite NaCaA.

THE occlusion of various guest molecules into zeolitic cavities can significantly change the catalytic properties of the zeolite.[1] Sulphur dioxide, *e.g.*, adsorbed on a number of solid oxides greatly enhances the rate of *cis–trans*-isomerization of but-2-enes at room temperature and poisons double bond migration. It is believed that an intermediate molecular complex is formed between SO_2 and butene which plays an important role in the reaction.[2]

I.r. spectroscopic observation of the behaviour of n-butenes and SO_2 adsorbed on a type A zeolite of simple, well defined structure confirms this suggestion. The reaction was studied on self-supporting thin wafers of zeolites NaA and NaCaA outgassed for 36 h at 723 K in an ultra-high vacuum system. The spectra were obtained on a Fourier transform i.r. spectrophotometer, DIGILAB FTS 14, by a sensitive technique using the instrument's computer. By means of the arithmetic package, the background spectrum of the outgassed zeolite could be removed from the overall spectrum so that the spectrum of only the adsorbed species was obtained enabling us to observe small spectroscopic changes. The adsorptions of but-1-ene and *cis-* and *trans*-but-2-enes on NaA and NaCaA were studied in the range 295—345 K at coverages up to *ca.* 2·5 butene and 1·5 SO_2 molecules per unit cell. The adsorbed n-butenes can be identified by the positions of the C–H stretching bands. Assignment of all bands in the bending region is rather difficult because they overlap with bands due to asymmetrically distorted carbonates in the zeolitic supercage.[3] From the small frequency shifts with respect to the gas phase, it appears that adsorption is weak. The bandshapes of adsorbed butenes indicate restricted rotation caused by interaction with the zeolitic lattice. The spectra were unchanged after several days at ambient temperature as well as after heating to 345 K, which shows that isomerisation does not take place on NaA and NaCaA in the absence of SO_2. When SO_2 is allowed to be adsorbed on NaCaA simultaneously with n-butenes, isomerization takes place as indicated by the change in the spectrum in the C-H stretching region. New bands appear at 1495 (intense) and 1245 (weak) cm^{-1} which are not observed in the spectra of the butenes and SO_2 adsorbed separately on zeolites NaA and NaCaA or in a gaseous mixture of both, or upon coadsorption of n-butenes and SO_2 on zeolite NaA. In all these cases no isomerization occurs. As these bands are only correlated with isomerization, they must be attributed to by-products or intermediates of the isomerization reaction. Possible by-products are polysulphones, polymers, or fragments of the butenes. Formation of polysulphones and butene polymers may be excluded, since after desorption under mild conditions the two bands are not observed. Fragmentation too is not in accordance with our spectra. We assign these new bands to the ν_3- and ν_1-vibrations of an intermediate molecular complex between SO_2 and butene in the adsorbed state to which a sulphone-like structure[4] must be ascribed. Bands characteristic of S=O vibration are presumably masked by the strong bands of the zeolite lattice vibrations.

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