In situ Infrared Spectroscopic Evidence for Cyclotrimerisation of Acetylene to Benzene over a TiO_2 Catalyst

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The formation of benzene adsorbed species from acetylene over a TiO_2 surface was observed by *in situ* Fourier transform infrared spectroscopy.

Cyclotrimerisation reactions of acetylene to aromatic compounds have been performed by using various catalysts such as transition metal clusters,[1] metathesis catalysts[2] and transition metals.[3,4] The heterogeneously catalysed reaction below 300 K, however, has not been studied so much, except for some spectroscopic studies of transition metal single crystals under ideal conditions.[3,5] Recently, we have found that the reaction proceeds at high selectivity over oxide supported ytterbium–Ti^{IV} halides below 300 K.[6] In this system, it was supposed that the titanium ion plays an important role in the catalytic reaction. In this work, we have studied the reaction behaviour of acetylene over TiO_2; in order to investigate the interaction between the titanium ion and acetylene *in situ* Fourier transform infrared (FTIR) spectroscopy was used. Here we report that benzene adsorbed species are produced over a TiO_2 surface at 300 K.

The TiO_2 used in this work was reference catalyst (JRC-TIO-4) obtained from the Catalysis Society of Japan. A self-supporting disk (*ca.* 60 mg) of the catalyst was set in the infrared cell and oxidised by O_2 at 673 K for more than 10 h and then evacuated at the same temperature for 30 min. C_2H_2 was purified by distillation (several times) in an isovolumetric system *in vacuo*; no impurity was observed in C_2H_2 (as shown by gas chromatography). C_2D_2 (99.7% obtained from Merk Frosst Canada Inc.) was used without further purification. C_6H_6 (Wako Pure Chemical) was used after distillation in Ar atmosphere. Infrared spectra were recorded with an FTIR 7000 (Jasco); all spectra were measured with 256 scans at 4 cm^{-1} resolution and obtained from the ratio of the background spectrum of TiO_2 to that of adsorbed gases.

Time dependence infrared spectra of the adsorbed species formed from adsorption and reaction of acetylene and benzene over the TiO_2 surface at 300 K are shown in Fig. 1. Fig. 1(*a*) shows the spectrum of surface species from the reaction of C_2H_2 after one minute; bands at 3228, 1955, 1698 and 1243 cm^{-1} are mainly observed. The bands at 3228 and 1955 cm^{-1} can be assigned to molecularly adsorbed acetylene (*cf.* bands of free acetylene at 3294 and 1974 cm^{-1}).[7] From the spectrum of the surface species formed from the reaction after 30 min, as shown in Fig. 1(*b*), the production of some new bands at 3092, 3070, 3036 and 1479 cm^{-1} and an increase in the band intensities at 1698 and 1243 cm^{-1} were observed. It was also observed that the intensities of the bands increased with longer reaction times, as shown in Fig. 1(*c*) which was measured after 60 min of reaction time. The infrared spectrum of the surface species formed from benzene adsorption over the surface is shown in Fig. 1(*d*), here bands at 3092, 3070, 3038 and 1481 cm^{-1} were mainly observed, which were attributed to molecularly adsorbed benzene. Comparing the spectrum of Fig. 1(*b*) with that of Fig. 1(*d*), it may be seen that the bands produced by the reaction of C_2H_2 were in agreement with the bands due to adsorbed benzene. The reaction of C_2D_2

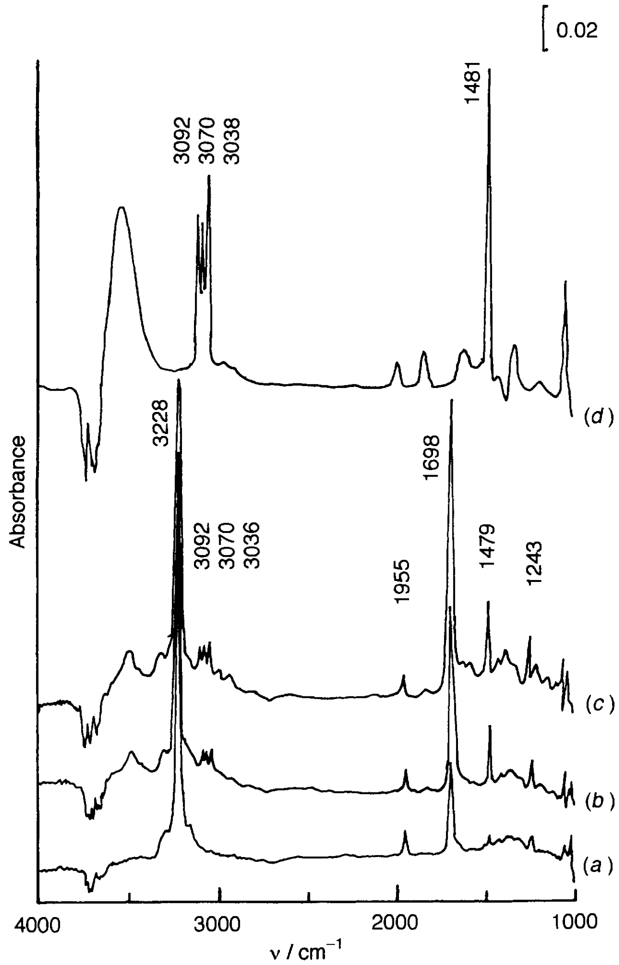

Fig. 1 Infrared spectra of the surface species on TiO_2 formed from adsorption and reaction of C_2H_2 at 300 K after (*a*) 1 min, (*b*) 30 min and (*c*) 60 min and (*d*) infrared spectrum of surface species on TiO_2 formed from adsorption of benzene. Fig. 1(*a*)–(*d*) were measured after contact with benzene (650 Pa) and acetylene (1.3 kPa) for the prescribed time and then the gas phase was trapped by liquid nitrogen.

over the same TiO_2 surface was also observed. It was confirmed that the corresponding bands due to C–H stretching of the adsorbed species produced from the reaction of C_2H_2 after 30 min were shifted to 2284 cm^{-1}. This value is in good agreement with the calculated value for isotopic shift of C–H to C–D. The new bands produced from the reaction of C_2H_2 after 30 min at 300 K can be assigned to adsorbed benzene. It is, therefore, strongly suggested that the cyclotrimisation reaction of C_2H_2 occurred over TiO_2 at 300 K. The cyclotrimerisation reaction over heterogeneous catalysts was carried out at higher temperatures (above 400 K).[2,4] The present communication reports the first observation, using *in situ* infrared spectroscopy, of the cyclotrimerisation of C_2H_2 to form benzene over TiO_2 at 300 K. It suggests that these results reflect the characteristic properties of a TiO_2 surface and are an important insight for utilizing TiO_2 in various catalysts.

The surface species attributed to the bands at 1698 and 1243 cm^{-1} have no corresponding bands in the region due to C–H stretching vibrations around 3000 cm^{-1}. These bands also increase in intensity with increasing reaction time and are accompanied by the bands due to O–H stretching vibration. Nearly the same behaviour was observed with the reaction of C_2D_2. This suggests that the surface species attributable to these bands are formed from the decomposition of C_2H_2 over the surface.

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