I.R. Spectra of Hydrogen Adsorbed on ZrO_2

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I.r. bands due to dissociative adsorption of hydrogen onto ZrO_2 at room temperature were observed by Fourier transform i.r. spectroscopy at 3780 and 3668 cm^{-1} for ZrOH and at 1562 and 1371 cm^{-1} for ZrH and ZrHZr, respectively.

The dissociative adsorption of hydrogen over ZnO,[1] MgO, CaO, and SrO[2] has been observed by i.r. spectroscopy. Recently we have found that the hydrogenation of CO over ZrO_2 proceeds to form methanol at 423 K and isobutene at 523 K in a selective manner.[3] In the search for a mechanism for CO hydrogenation, hydrogen adsorption over ZrO_2 has been studied by Fourier transform (F.T.) i.r. spectroscopy and i.r. bands due to Zr–H species have been observed for the first time.

The catalyst was prepared by precipitation from a solution of zirconium oxynitrate with NH_4OH and calcination of the hydroxide at 973 K for 3 h. A pressed disk sample was placed

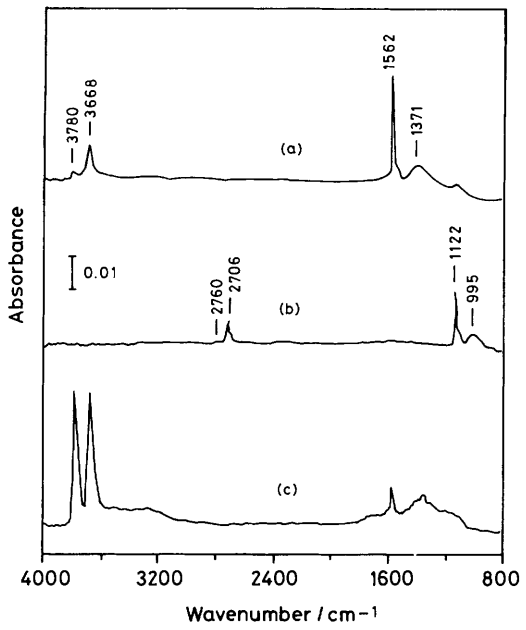

Figure 1. I.r. spectra of hydrogen (deuterium) adsorbed on ZrO_2: (a) H_2 at 298 K; (b) D_2 at 298 K; (c) H_2 at 473 K.

in an i.r. cell which was connected to a vacuum system. I.r. spectra were recorded on a JEOL JIR-100 FT-IR spectrometer with 256 scans at 4 cm^{-1} resolution.

When hydrogen (or deuterium) gas at 27—53 kPa was introduced at room temperature, four bands due to adsorbed hydrogen were observed as shown in Figure 1. A sharp band at 1562 (1122) cm^{-1} and a broad band at 1371 (995) cm^{-1} appeared in the spectra at room temperature in the presence of hydrogen and disappeared gradually when the hydrogen was evacuated. On the basis of the values of the isotope shifts (Table 1) and the i.r. data from hydrogen adsorbed on ZnO,[1] the sharp band at 1562 cm^{-1} is assigned to the Zr–H stretching vibration. The broad band at 1371 cm^{-1}, which is more stable than the band at 1562 cm^{-1}, is assigned to a different Zr–H species, such as ZrHZr, because of the band shape and the position.

Table 1. I.r. bands due to hydrogen (and deuterium) adsorbed on ZrO_2 at room temperature.

H_2	D_2	Isotope ratio	Assignment/v
3780(w)	2760	1.37	OH (OD)
3668(m)	2706	1.36	OH (OD)
1562(s)	1122	1.39	Zr–H (Zr–D)
1371(m)	995	1.38	ZrHZr (ZrDZr)

Bands at 3780 (2760) and 3668 (2706) cm^{-1} as shown in Figure 1(a) can be assigned to the OH stretching vibrations. When hydrogen was introduced onto ZrO_2 at 473 K, these two bands increased in intensity while the bands due to the Zr–H species were reduced, Figure 1(c). The OH species which gives an i.r. band at 3780 cm^{-1} is more reactive towards CO than the species which gives rise to the band at 3670 cm^{-1}, as reported by Tanabe *et al.*[4] The formation of formate ion on the surface has previously been observed at 373 K.[5]

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