Fourier Transform I.R. Detection of Adsorbed Hydrogen on a Cu–Zn–Cr Low Temperature Methanol Synthesis Catalyst

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I.r. bands arising from the activated adsorption of hydrogen on a Cu–ZnO–$ZnCr_2O_4$ methanol synthesis catalyst have been detected in the region 1200—800 cm^{-1}, suggesting the presence of triply bridged hydride species, bonded to Cu sites.

Modern industrial catalysts for the synthesis of methanol from CO + H_2 are typified by complex systems composed of Cu-ZnO–M_2O_3 (M = Al, Cr, or Mn), working in the temperature range 500—550 K.[1—3] The role of the different phases, the structure of the active sites, and several mechanistic features are still unclear or under debate. In particular, the activation mode of hydrogen on these catalysts, believed to involve unreduced copper sites,[1—3] is not known in detail. Heterolytic dissociation of hydrogen has been observed by i.r. spectroscopy on the old 'high temperature' zinc chromite catalysts,[4] and on ZnO,[5] and, indirectly, by n.m.r. on the related copper chromite catalysts.[6] In the present communication we report the results of a Fourier transform (F.t.) i.r. study of hydrogen adsorption on real methanol synthesis catalysts of the system Cu–Zn–Cr-oxide.

The composition, some properties, and behaviour in the low temperature methanol synthesis of the catalysts, all prepared by a coprecipitation method,[7] are reported in Table 1. The F.t.i.r. spectrum of a pellet of catalyst (**3**), the most useful for i.r. investigation in the reduced state, pretreated *in vacuo* at 773 K for 1 h, in hydrogen (1 atm) at 773 K for 1 h, and again *in vacuo* at 773 K for 1 h is shown in Figure 1a. The spectrum of the sample is unchanged if hydrogen (1 atm) is admitted to the cell at room temperature. However, i.r. transmission is markedly lowered if the same contact is carried out at $\geqslant$450 K for even a few minutes, (Figure 1b). After more prolonged contact transmission is almost completely lost. The ratio of the spectrum of the catalyst treated in H_2 at 500 K for 5 min *versus* that of the activated sample shows two broad absorptions (Figure 2a). One is centred near 2000 cm^{-1} and has the character of a continuous absorption in the overall i.r. spectrum. The other is centred between 1000 and 800 cm, with a shoulder near 1140 cm^{-1}, and is superimposed on the absorption bands of the adsorbant, some of which appear to decrease in intensity upon this treatment, so that the ratioed spectra show negative sharp bands in the same region. If contact is carried out with deuterium instead of hydrogen, both the loss in i.r. transmission (owing to the appearance of the continuous absorption) and the decrease in intensity of the bulk bands are again observed, while the band near 900 cm^{-1} is not (Figure 2b). The ratio of the spectrum obtained after contact with hydrogen *versus* that obtained after contact with deuterium evidences the broad band centred near 900 cm^{-1}, with no perturbation (Figure 2c). Evacuation at room temperature does not affect the new absorptions generated by contact with H_2 or D_2 at 500 K, while evacuation at 500 K causes their complete disappearance.

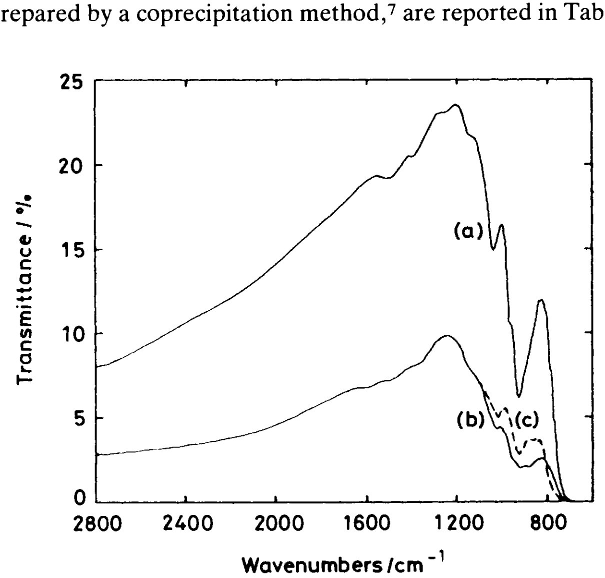

Figure 1. F.t.i.r. spectra (a) of the activated catalyst (**3**); and after contact with (b) hydrogen (1 atm, 500 K, 5 min) and (c) deuterium (1 atm, 500 K, 5 min).

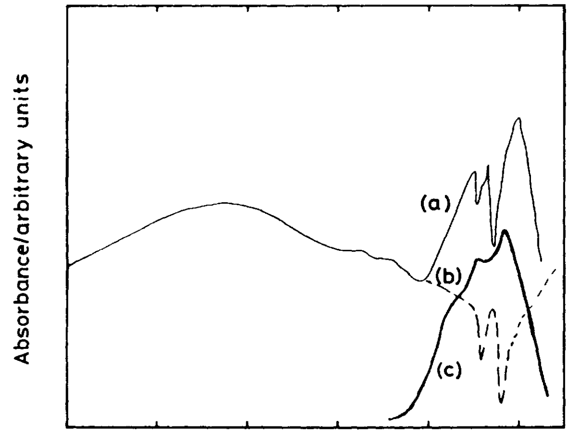

Figure 2. Ratio spectra (a) 1b *vs.* 1a, (b) 1c *vs.* 1a, and (c) 1b *vs.* 1c.

The present data indicate that the continuous absorption shown after treatment with both hydrogen and deuterium is of non-vibrational origin. The same phenomenon, arising from electronic absorptions connected with the semiconducting nature of the system and with the presence of adsorbed (or absorbed) hydrogen, has already been pointed out by Bocuzzi *et al.* on a Cu–ZnO catalyst.[8] On the contrary, the band near 900 cm^{-1} detected after adsorption of hydrogen but not of deuterium clearly arises from metal–hydride stretching. Similar broad absorption bands arising from bridging adsorbed hydrogen have already been observed on several catalyst surfaces.[9,10] The corresponding metal–deuteride stretching absorptons are expected to fall in the cut-off region of our samples, and are consequently inaccessible.

Comparison with data from organometallic cluster compounds indicate that these frequencies are typical of interstitial hydride species which are triply bridged[11] or in octahedral cavities.[12] These features have not been observed in pure ZnO[5] or Zn–Cr oxides[4] and also differ from those of hydrogen adsorbed atomically on Cu single crystals.[13] This thermally activated hydrogen adsorption may involve strong interaction of the copper sites with the oxide matrix. The resulting structure may be similar to that of the first well characterized copper hydride $[(R_3P)CuH]_6$ consisting of a hexameric cluster with triply bridging hydride ligands.[13] The conditions under

Table 1. Composition and behaviour of methanol synthesis catalysts.

	Composition/atom % Cu : Zn : Cr	Area/ $m^2 g^{-1}$	*X*-Ray data (unreduced)	Rate of methanol formation[a] $kg\,h^{-1}\,kg_{cat}^{-1}$	$kg\,h^{-1}\,l_{cat}^{-1}$	$kg\,h^{-1}\,kg_{Cu}^{-1}$	Selectivity/%
(**1**)	38 : 38 : 24	125	CuO, ZnO, spinel[b]	0.393	0.184	1.292	99.9
(**2**)	25 : 51 : 24	94	CuO, ZnO, spinel[b]	0.207	0.044	1.157	99.9
(**3**)	13 : 63 : 24	96	ZnO, spinel[b]	0.035	0.007	0.302	99.9

[a] Reaction conditions: $H_2:CO:CO_2$ = 65:32:3 (v/v); T = 523 K; p = 1.2 MPa; gas hourly space velocity (g.h.s.v.) = 15 500—16 500 h^{-1}. Catalyst reduced according to P. Courty, D. Durand, A. Sugier, and E. Freund, U.K. Pat. 2118061A, 1983. [b] Non-stoicheiometric spinel-like phase, partially evoluted towards a rock-salt type form.

which these adsorbed forms of hydrogen were observed (as well as desorbed) are of the same order as the working conditions of our (Table 1) and industrial 'low temperature' methanol synthesis catalysts,[1—3,15] suggesting that they may represent the active species in CO hydrogenation.

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