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Heterolytic Dissociation of Hydrogen on High-Temperature Methanol Synthesis Catalysts

The heterolytic dissociation of hydrogen is thought to constitute the hydrogen-activation step in the mechanism of methanol synthesis (*1, 2*). Heterolytic dissociative adsorption has been proved by infrared (IR) spectroscopy on several pure oxides active in methanol synthesis, such as ZnO (*3–8*), ThO_2 (*9*), and ZrO_2 (*10*). In the case of the industrial low-temperature methanol synthesis catalysts, based on supported Cu/ZnO, the activation of hydrogen is generally thought to take place on the ZnO exposed surface (*2, 11*), although other authors have proposed a different mechanism (*12*), involving surface Cu(I) species stabilized by ZnO (*11*).

No data have been reported until now for the adsorption of hydrogen on the high-temperature methanol synthesis catalysts based on Zn/Cr mixed oxides, with a Zn/Cr atomic ratio higher than 0.5. Although a progressive replacement of the high-temperature and -pressure methanol synthesis technology in favor of lower temperature and pressure processes based on copper-containing catalysts has occurred during the last 2 decades, Zn/Cr catalysts are still of interest because they can be modified to enhance the selectivity toward higher molecular weight alcohols (*13, 14*). In these catalysts the active phase was thought to be ZnO in very small crystallites supported on the $ZnCr_2O_4$ spinel (*15*). However, it has been shown recently that a nonstoichiometric zinc-rich spinel-type phase may be formed, characterized by an expansion of the elementary crystal cell, probably due to the incorporation of excess zinc in octahedral holes (*16*). Such a phase is very active in methanol synthesis (*16–18*).

In the present communication results of an IR study of the adsorption of hydrogen and deuterium on stoichiometric (Zn/Cr = 0.5) and nonstoichiometric zinc-rich spinels (Zn/Cr = 0.6 and 1.0) are reported. X-ray diffraction (XRD) analysis of such samples, whose preparation (*19*), bulk characterization (*16–18*), activation (*18*), and catalytic behavior (*16–18*) have been previously reported, indicates that all samples are monophasic, showing only the presence of the spinel-type phases cited above (Fig. 1). Furthermore, these samples were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), with an energy dispersive X-ray analyzer (EDX), and the presence of particles containing only zinc was not found.

Adsorption of hydrogen (or deuterium) on the Zn/Cr = 1.0 sample caused the formation of a strong and asymmetric IR band, that was sensitive to the isotopic exchange (Fig. 2, full lines). Similar bands, although much weaker, were observed in the same conditions on the Zn/Cr = 0.6 sample (Fig. 2, dashed lines). On the contrary, when either hydrogen and deuterium were put into contact with an activated sample of the stoichiometric Zn/Cr = 0.5 spinel, we were unable to observe any bands in the temperature range of 170–470 K. The frequencies of the bands we observed on the zinc-rich samples are compared in Table 1 with those observed after hydrogen and deuterium adsorption on pure ZnO and MgO–ZnO solid solutions, as well as those of known zinc hydride species. The similarity of the data allows us to assign the bands to Zn–H (D) stretching frequencies. With zinc-rich samples another adsorption band also formed, and

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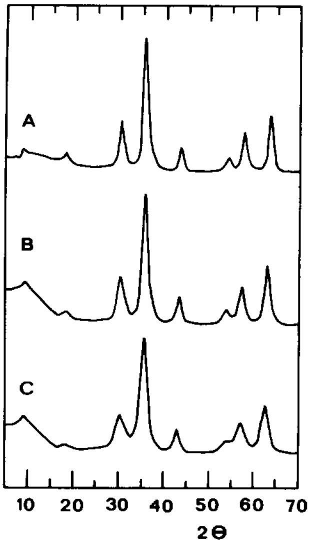

FIG. 1. XRD powder patterns of the samples calcined at 623 K for 24 h: (A) Zn/Cr = 0.5; (B) Zn/Cr = 0.6; (C) Zn/Cr = 1.0. The XRD powder patterns were collected using a Philips goniometer, equipped with a stepping motor and automated by means of a General Automation 16/240 computer. The radiation used was the nickel-filtered Cu$K_{\bar{\alpha}}$ (λ = 0.15418 nm).

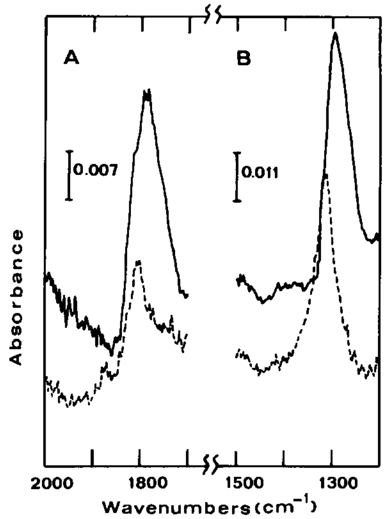

FIG. 2. FT-IR bands appearing after contact of H_2 (A) and D_2 (B) (40.0 kPa at room temperature for 10 min) with Zn/Cr = 1.0 (full line) and Zn/Cr = 0.6 (dashed line) samples. Both samples were previously activated in hydrogen (101.3 kPa) at 673 K for 1 h and later evacuated at 673 K for 1 h. A conventional IR cell was used (*20*).

these observed peaks superimposed those of the "normal" hydroxy (or deuteroxy) groups produced by water dissociation (νOH 3682, 3668, and 3648 cm^{-1}; νOD 2718, 2708, and 2682 cm^{-1} on Zn/Cr = 1.0 sample). This is evidence that heterolytic dissociation of hydrogen occurred on Zn–O pair sites. The shift to higher frequencies of the Zn–H stretching frequency in our catalysts with respect to those observed on ZnO clearly indicates a different state of surface zinc ions. The similarity of the peaks observed with those reported by Ghiotti and Boccuzzi (*21*) on some sites on MgO–ZnO solid solutions, assigned to hydrogen adsorbed on "isolated" Zn–O

TABLE 1

Observed Stretching Frequencies (cm^{-1}) of Terminal Zinc-Hydride and Deuteride Bonds

	νZnH	νZnD	νZnH/νZnD
1. H_2 (D_2) adsorption on Zn/Cr = 1.0 sample	1815 sh	1315 sh	1.380
	1788	1295	1.381
2. H_2 (D_2) adsorption on Zn/Cr = 0.6 sample	1810	1312	1.379
3. H_2 (D_2) adsorption on MgO–ZnO solid solution (*21*)	1786	1280	1.395
	1707	1230	1.388
	1663	1200	1.386
4. H_2 (D_2) adsorption on ZnO (*3–8*)	1740 w	1253 w	1.389
	1712	1232	1.390
	1687 w	1215 w	1.388
5. H-Zn-CH_3 (*22*)	1846		
6. [H-Zn-N(CH_3)C_2H_4N(CH_3)$_2$]$_2$ (*23, 24*)	1825		

Note. sh, shoulder; w, weak.

bonds in the MgO matrix, is noted. In such cases, as in our catalysts, octahedrally coordinated Zn^{2+} ions (in substitutional positions) are probably present. However, the complex dependence of a νM–H frequency on the overall coordination of the metal ion (*25–27*) does not allow us to propose unambiguously a structure for the active sites.

The activity for dissociative adsorption of hydrogen is clearly related to the nonstoichiometric samples. The lack of hydrogen dissociative adsorption on the Zn/Cr = 0.5 sample in fact agrees with the corresponding lack of activity in carbon monoxide adsorption (*28*), as well as with the almost complete absence of catalytic activity toward methanol synthesis over the stoichiometric spinel (*1, 15–17*). The presence of completely new sites on the surface of the nonstoichiometric spinel-type samples is also indicated by the comparison of the spectra of adsorbed pyridine on the samples Zn/Cr = 0.5 and 0.6 (Fig. 3). On the stoichiometric sample, the more sensitive ν8a and ν19b bands are observed at 1594 and 1442 cm^{-1}, typically due to chemisorbed pyridine on weak Lewis sites of basic surfaces as K_2O–TiO_2 (*29*) and ThO_2 (*30*); the medium intensity band near 1610 cm^{-1} is probably due to the 1 + 6a combination that is also sensitive to the strength of the adsorption bond. These vibrational bands are observed at 1636 (1 + 6a), 1612 (8a), and 1451 (19b) on the samples Zn/Cr = 0.6 and 1.0, indicating the presence of sites of relevant Lewis acidity. According to the data obtained by hydrogen adsorption and to the presence of excess zinc, it seems reasonable to identify such sites as exposed Zn^{2+} ions.

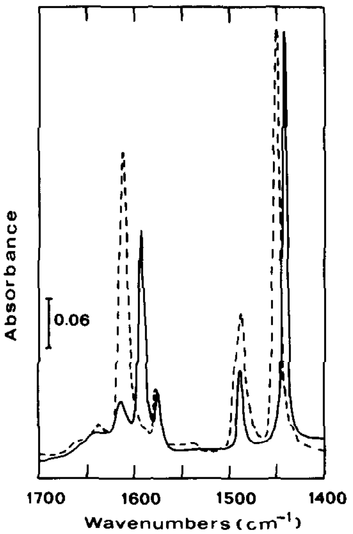

FIG. 3. FT–IR spectra of pyridine adsorbed on Zn/Cr = 0.5 (full line) and Zn/Cr = 0.6 (dashed line) samples. Both samples were previously activated as reported in Fig. 2.

In summary, the present data lead to the following conclusions:

(i) Heterolytic dissociative adsorption of hydrogen occurs on active high-temperature methanol synthesis catalysts only.

(ii) The surface activity is related to the presence of the nonstoichiometric spinel-type phase evidenced previously.

(iii) The active sites involve exposed Zn^{2+} ions in a coordination sphere different from that of exposed zinc sites of ZnO and the unactive $ZnCr_2O_4$ spinel.

(iv) The nonstoichiometric zinc-rich samples show a particular surface activity that cannot be attributed to XRD-undetected ZnO.

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