Infrared and carbon dioxide chemisorption study of Mo/ZrO_2 catalysts

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The interaction of Mo with zirconia has been investigated by infrared spectroscopy (IR) and carbon dioxide chemisorption. Quantitative analysis of the IR results indicated that Mo interacts preferentially with the most basic hydroxyl group (high frequency band at 3775 cm^{-1}). An approximately 79% decrease in the 3775 cm^{-1} band is observed vs. 21% for the low frequency band at 3673 cm^{-1}, with increasing the Mo loading up to 1 wt%. The relative decrease of the IR band at 3775 cm^{-1} was identical to that measured for the CO_2 uptake. The Mo cross-sections estimated from CO_2 chemisorption results were much higher than those typically reported for the Mo system. It was concluded that, as previously reported for the Mo/Al_2O_3 system, CO_2 chemisorption overestimates the surface coverage of Mo/ZrO_2 catalysts.

Keywords: Mo and Zr oxides; CO_2 chemisorption; infrared Mo/ZrO_2; surface coverage

1. Introduction

Zirconium dioxide has recently been used in heterogeneous catalysis in the form of a simple and combined oxides [1,2]. ZrO_2 presents special characteristics such as high thermal stability, extreme hardness, stability under reducing conditions and both acid and base functions, which make its use very appealing as a carrier for several catalytic applications [2].

One of the most attractive features of ZrO_2 is the simplicity of the IR spectrum of its hydroxyl region. It consists, essentially, of two well defined bands at ca. 3780 and 3680 cm^{-1} attributed, respectively, to terminal and bridged hydroxyl groups

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[3–5]. Yamaguchi et al. [4] showed, by using D_2O and different organic molecules, that an almost complete replacement of the original hydroxyl bands (3780 and 3680 cm^{-1}) with new deuteroxyl bands at 2780 and 2705 cm^{-1} occurred, after D_2O treatment. The OH(D) groups associated with the high frequency band were more reactive towards the adsorption of molecules such as chloroform than those associated with the low frequency band. The H–D exchange results, after the D_2O treatment, were later confirmed by He and Ekerdt [6].

The simple IR spectra for the OH region of ZrO_2 make it suitable for studying the deposition of Mo, W, Re, V and Cr oxyanions over this support. These anions are known to anchor onto the surface of various supports by replacing the OH groups [7–10]. Payen et al. [11] studied a series of molybdena–zirconia catalysts. IR results showed a decrease in the intensity of the hydroxyl bands of the support upon addition of the molybdenum species. The more basic hydroxyl groups (higher frequency) were more affected by molybdenum impregnation. However, the above observations were only qualitative in nature. To date, no quantitative analysis of the variation of the OH groups as a function of Mo addition has been reported. This study is important because of its relevance to ongoing assessment of various techniques for measuring the surface coverage of supported oxide catalysts [12]. Also, the type of hydroxyls involved in the interaction with the Mo phase may determine the reactivity of the Mo species.

CO_2 has been very useful for assaying basic sites on surfaces due to the acid nature of the molecule [1]. Moreover, CO_2 chemisorption has also been used to monitor the surface coverage of several metal oxides supported on alumina catalysts. Segawa and Hall [13] reported that CO_2 was selectively chemisorbed on the uncovered alumina portion of the surface of an 8% molybdena–alumina catalyst. For the pure alumina, the chemisorption of CO_2 almost completely eliminated the high frequency OH band present in the IR spectra. The infrared bands of other alumina OH groups were not greatly affected. In a subsequent report [14] the total CO_2 uptake was used to calculate surface coverage of molybdena–alumina catalysts. Recent studies [9,15–17], however, have indicated that this approach leads to a significant overestimation of the surface coverage on molybdena–alumina catalysts. This was explained in terms of CO_2 and the molybdenum species competing for the high frequency (basic) hydroxyl groups of the support, which comprise less than 10% of the total amount of OH groups.

CO_2 chemisorption on zirconia has been thoroughly investigated [18–20]. Bensitel et al. [18] reported the formation of bidentate carbonate species upon addition of 90 μmol/g or less of CO_2. Hydrogenocarbonates, linear species and "perturbed CO_2" or bridged species appeared at higher coverages. The low frequency band (3667 cm^{-1}), due to bridged hydroxyl groups, was not affected by the addition of CO_2. The high frequency band (3776 cm^{-1}) completely disappeared after the CO_2 pressure in the cell reached 2×10^2 Pa. Morterra and Orio [19] studied the interaction between CO_2 and a monoclinic ZrO_2 preparation by IR spectroscopy. Depending on the extent of dehydration of the solid, various types of carbonate-like species were observed. Interconvertible bidentate bicarbonates and bidentate carbonates were also reported. Evidence for the formation of carbonates [3,6] and hydrogenocarbonates [3] species upon addition of CO_2 on the ZrO_2 support has been given by other authors. However, the suitability of CO_2 as a probe for monitoring the surface coverage of ZrO_2 has not been fully investigated. The first step toward this objective is a detailed investigation of the effect of Mo addition on the CO_2 uptake.

Thus the purpose of the present paper is twofold:

(a) To undertake a quantitative analysis of the effect of Mo addition on the relative abundance of hydroxyls over the ZrO_2 support.

(b) To measure the variation of CO_2 chemisorption as a function of Mo loading and to correlate the results with the corresponding changes in the hydroxyl distribution of the support as monitored by IR.

2. Experimental

2.1. CATALYSTS

Degussa ZrO_2 (pore volume: 0.5 ml/g; BET surface area: 36 m^2/g, particle size < 100 mesh) was used as the support. The catalysts were prepared by impregnation of the support with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ via the incipient wetness method. The solids were then dried at 393 K for 12 h and calcined for 16 h at 813 K. The metal loadings are reported in table 1.

2.2. PROCEDURES

The IR spectra were obtained on a Nicolet 800 FTIR instrument. To facilitate data analysis, the spectral data were converted into a PC compatible format and

Table 1
Integrated intensities for the hydroxyl groups of a series of molybdena–zirconia catalysts

Mo loading		Normalized intensities	
wt% Mo	Mo/nm^2 [a]	3775 cm^{-1} [b]	3673 cm^{-1} [c]
0.00	0.00	1.00	1.00
0.25	0.44	0.67	0.88
0.50	0.88	0.52	0.97
0.75	1.32	0.36	0.78
1.00	1.76	0.21	0.78

[a] Molybdenum atoms per nm^2 of the support.
[b] Normalized intensity of the 3775 cm^{-1} band.
[c] Normalized intensity of the 3673 cm^{-1} band.

interpreted using in-house generated software [21]. The IR cell was described previously [22,23]. Samples were mounted in the cell as wafers having a thickness of approximately 18 mg/cm^2. The infrared studies were carried out at room temperature after a pretreatment period of 4 h at 773 K in a flow of dry He/O$_2$ (90 : 10) (30 cm^3/min). Integrated intensities (absorbances) were normalized to unit wafer thickness. Correction of the baseline was performed by a simple subtraction using a completely dehydroxylated ZrO$_2$ sample as the reference.

The CO$_2$ volumetric measurements were performed in a conventional BET system [24]. The procedure is fully described elsewhere [25,26]. In short, after treatment with flowing He/O$_2$ (90 : 10) (30 cm^3/min) for 16 h at 773 K, the catalyst sample was cooled down to room temperature under high vacuum ($< 1 \times 10^{-5}$ Torr). The catalyst was then exposed to 550 Torr of pure CO$_2$ for 15 min. The excess CO$_2$ was condensed in a cold trap (77 K) and measured in the BET line. The amount of chemisorbed CO$_2$ was then obtained by difference. The temperature was then raised to 773 K and the desorbed gas was collected in a cold trap (77 K). The latter amount was used to cross-check the amount of chemisorbed CO$_2$. The values were essentially identical.

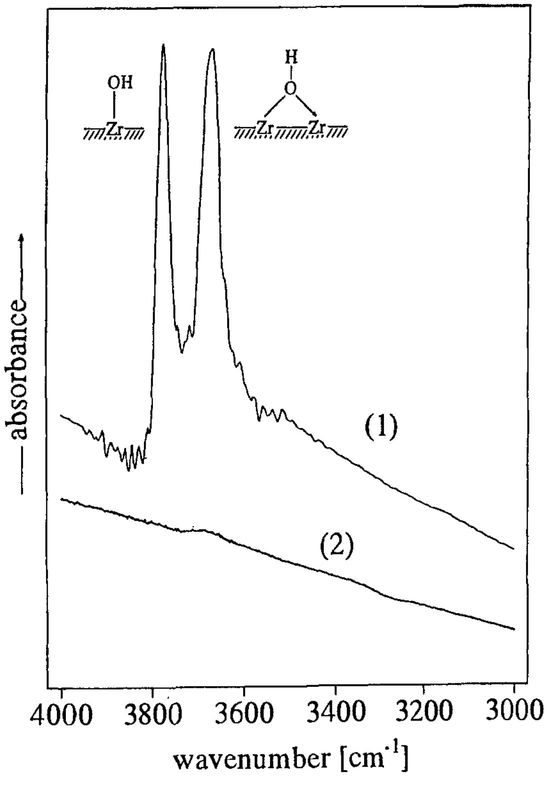

Fig. 1. FTIR absorption spectra of zirconia after dehydroxylation at 773 K (1), and 993 K (2).

2.3. REAGENTS

CO_2 was Matheson high purity. A freeze–pump–thaw technique, described previously [26], was used for purification purposes. The high purity He/O_2 (90 : 10) mixture was passed over an activated molecular sieve trap to remove traces of water.

3. Results and discussion

The X-ray powder diffraction pattern for the ZrO_2 support, after calcination at 873 K in air, showed bands characteristic of the tetragonal and monoclinic forms. The absence of a discrete MoO_3 phase, for all the catalysts, was verified by Raman spectroscopy. No bands characteristic of MoO_3 (816 and 922 cm^{-1}) were observed, in accordance with the literature [27].

Fig. 1 shows the infrared spectra for the hydroxyl region of the pure zirconia support treated at two different temperatures. Dehydroxylation at 773 K (spectrum 1) revealed the presence of two different types of surface OH groups at 3775 and 3673 cm^{-1}, attributed to isolated Zr–OH and bridging Zr–O(H)–Zr centers, respectively [3,4]. At higher temperatures (993 K) the dehydroxylation process is complete (spectrum 2). The latter was used as a reference for baseline correction.

Fig. 2 shows the effect of increasing Mo loading on the IR spectra of zirconia,

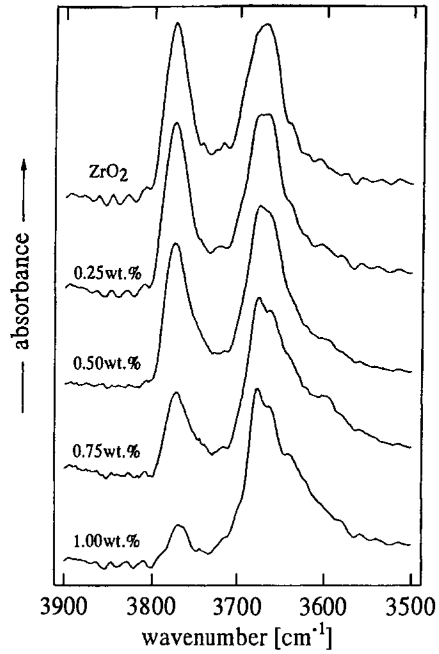

Fig. 2. FTIR spectra of the zirconia and molybdena–zirconia catalysts.

pretreated at 773 K. Clearly, the anchoring of molybdenum species by replacement of the high frequency hydroxyl groups is favored. Table 1 and fig. 3 show a decrease of 79% in the normalized peak area of the high frequency band for the 1% Mo/ZrO$_2$ catalyst vs. a decrease of only 21% for the low frequency OH band. These results agree with early qualitative work by Payen et al. [11] who investigated the effect of molybdenum species on the hydroxyl groups of the zirconia.

The CO$_2$ chemisorption experiments were carried out in order to investigate a possible correlation with the IR data. Carbon dioxide chemisorption is known to selectively involve the high frequency OH band in the formation of bicarbonate species [18]. The low frequency band was practically not affected by the introduction of CO$_2$ [18]. The carbon dioxide uptake for the pure support was 2.15 CO$_2$ molecules per nm^2 of zirconia. This value is approximately 5 times higher than that obtained for alumina [16]. The data in table 2 show a decrease in the CO$_2$ uptake with Mo loading. This result reflects the fact that CO$_2$ only chemisorbs on the free zirconia surface and not on the molybdenum phase. Fig. 4 shows an excellent correlation between the fraction of total CO$_2$ chemisorbed (referred to the zirconia uptake) (table 2) and the normalized peak intensity for the high frequency hydroxyl group of the support (table 2). This correlation can be explained in terms of CO$_2$ and the molybdenum species competing for the high frequency hydroxyl groups of the support. This implies that bicarbonate formed by reaction of CO$_2$ with the high frequency OH groups, is the only species present. However, several reports [18–20] have shown that carbonate bands also appear in the IR spectra. Since the

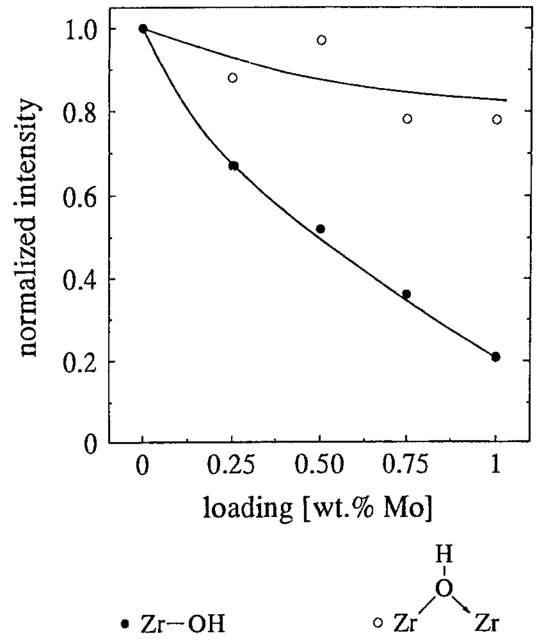

Fig. 3. Plot of normalized IR intensity vs. Mo loading ((●) 3775 cm^{-1}, (○) 3673 cm^{-1}).

Table 2
CO_2 chemisorption on zirconia and molybdena–zirconia catalysts [a]

Mo loading (wt%)	Amount of CO_2 chemisorbed (molec./g_{cat} × 10^{19})	F [b]
0.00	7.74	1.00
0.25	5.50	0.71
0.50	4.05	0.52
0.75	2.79	0.36
1.00	1.41	0.18

[a] Amounts of CO_2 chemisorbed measured volumetrically. For more details see text.
[b] Fraction of the total CO_2 uptake (referred to the zirconia).

total uptake of CO_2 should comprise the contribution of both species (bicarbonates and carbonates), it is reasonable to assume that the observed agreement is due to similar relative changes of both species. This is supported by recent CO_2 chemisorption results on molybdena–alumina catalysts [12].

Finally, we have evaluated the use of carbon dioxide chemisorption for monitoring the surface coverage of molybdena–zirconia catalysts. The Mo cross-sections obtained were 66 and 47 Å^2 per Mo for the 0.25 wt% Mo and the 1 wt% Mo catalysts, respectively. These values are unrealistic and much higher than those obtained by other methods [12,17,28,29]. Thus, as previously reported for alumina supported systems, the use of CO_2 chemisorption leads to a significant overestimation of the surface coverage of molybdena–zirconia catalysts.

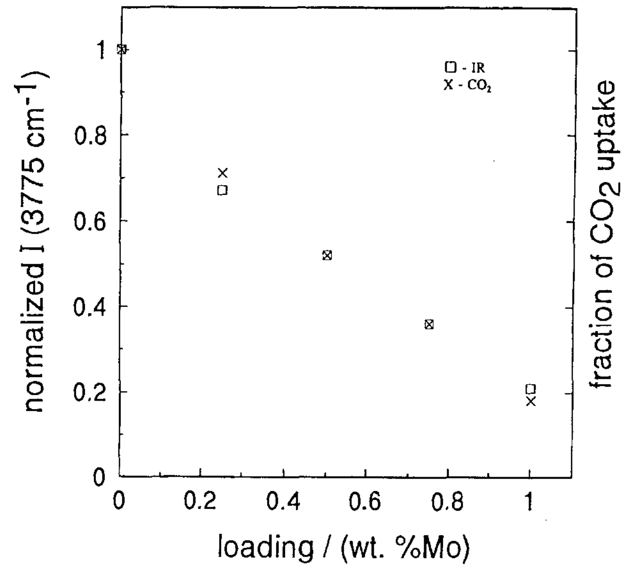

Fig. 4. Normalized intensity of the 3775 cm^{-1} band (left scale) and fraction of CO_2 uptake (right scale) vs. Mo loading.

4. Conclusions

The interaction of molybdenum species with zirconia has been investigated using IR spectroscopy and CO_2 chemisorption. Infrared results showed two well defined bands (3775 and 3673 cm^{-1}) in the hydroxyl region for the zirconia support activated at 773 K, in accordance with the literature. A significant decrease in the intensity of the high frequency band was observed upon addition of molybdenum. The low frequency band was influenced to a much lesser extent. These results suggest that the anchoring of molybdenum species by replacement of the high frequency hydroxyl groups of the zirconia is favored.

CO_2 chemisorption experiments showed a decrease in the carbon dioxide uptake with increasing Mo loading. An excellent correlation was observed between the intensity for the high frequency OH band and the CO_2 uptake. The results also indicate that the use of CO_2 chemisorption leads to a significant overestimation of the surface coverage of molybdena–zirconia catalysts.

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