The IR spectroscopy of methane and hydrogen adsorbed on α-chromia

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The vibrational perturbations induced in the IR spectra of methane and of dihydrogen by the non-dissociative adsorption on the $(01\bar{1}2)$ and $(11\bar{2}0)$ faces of α-chromia are illustrated and compared. It is concluded that both molecules are adsorbed on Cr^{3+} sites and that the involved forces are mainly of the electrostatic type. The resulting situation is compared with that found on the more basic MgO. The problems associated with the C–H and H–H bond activations on transition metal oxides are also discussed.

Keywords: C–H activation, chromium oxide, infrared spectroscopy

1. Introduction

The activation of the C–H bond of saturated hydrocarbons – among the most abundant but least reactive feedstocks for the chemical industry – is one of the most important problems of modern chemical science and the design of appropriate catalytic centres is consequently a challenging topic in both homogeneous and heterogeneous catalysis.

As far as CH activation with homogeneous compounds is concerned, it is sufficient to recall the recent contributions of Jia et al. [1] and Chen et al. [2] where the state of the art of hydrocarbon activation with homogeneous complexes is briefly reviewed: it is shown that the CH bond activation occurs on catalytic centres containing transition metal atoms in an oxidized state (Pd^{2+}, Pt^{2+}, Rh^{+}). The detailed mechanism of the CH bond activation with these homogeneous catalysts is, however, still unknown.

CH bond activation also occurs on heterogeneous systems like metal and oxide surfaces and a comprehensive review of the activity of the metallic and oxidic surfaces can be found in [3]. As far as the activity of oxide surfaces is concerned, the role of the positive (metallic) and the negative (O^{2-}) ions emerging on the surfaces and of their cooperation in CH bond activation is of primary importance. To simplify the problem of the understanding of the elementary steps involved in CH bond activation on oxides, Knözinger et al. [4,5] and Ferrari et al. [6], have studied the interaction of the simplest hydrocarbon molecule (methane) with a model oxide (MgO) with highly ionic character and simple rock-salt structure. In this contribution the prevailing role of low coordinated sites (particularly those with anionic character) in methane adsorption has been evidenced while the extended (100) faces where found to be substantially inert. In particular the adsorption of methane on low coordinated sites was found to be accompanied by the activation of the symmetric stretching mode (which is IR inactive in the free molecule) and by a bathochromic shift of the stretching frequencies. All these data and the results of CH_4–CO coadsorption experiments led to the conclusion that on the basic MgO oxide the main interaction is of the

$$\equiv C\text{–}H \cdots O^{2-}$$

type and that the coordinatively unsaturated basic O^{2-} centres located at defective sites are the most active in CH bond polarization.

Following the Knözinger line and to add further information on this fundamental research topic, we have planned a new investigation concerning the interaction of methane with the polycrystalline transition oxide α-Cr_2O_3 characterized by the simple corundum structure and well defined morphology of the microcrystals [7,8]. With respect to the previous case, the main differences are: (i) the surface metal cations (formally Cr^{3+}) have higher positive charge and hence higher polarizing chararacter; (ii) the coordination state of the metallic centres is different with respect to that of Mg^{2+} on MgO; (iii) the Cr^{3+} cations have d electrons of suitable energy to allow, in principle, an overlap interaction with the σ electrons of the CH bond, α-Cr_2O_3 is less ionic than MgO and the surface oxygens are characterized by a definitely smaller basicity; (iv) α-Cr_2O_3 is an active catalyst in many reactions involving hydrocarbons [9];

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(v) Cr^{3+} centres can interact with saturated hydrocarbons molecules via a

$$\equiv C\text{–}H \cdots Cr^{3+}$$

agostic-type bond [8,10].

All the effects (i)–(v) are expected to appreciably influence the IR spectrum of adsorbed methane and hence to add further information on the factors determining the elementary steps of the hydrocarbon–oxide surface interaction and, ultimately, to help the elucidation of the CH bond activation mechanism on transition metal centres.

In view of the similarity of the C–H and H–H bonds (both of the σ type, covalent and non-polar or only slightly polar) we have considered as relevant for the present discussion to verify wether the surface of α-Cr_2O_3 is also active in H_2 molecular adsorption and to ascertain which sites (Cr^{3+}, O^{2-} or both) are responsible. For this reason in this paper also the results of H_2 adsorption experiments will be briefly illustrated and discussed.

2. Experimental

The microcrystalline α-Cr_2O_3 samples have been synthesized by exothermic decomposition of $(NH_4)_2Cr_2O_7$, as previously described [7]. For FTIR transmission measurements the polycrystalline sample was compressed in form of pellet and inserted in a cell where both high-temperature treatments (needed to sinter the sample and to clean the surface under high vacuum) and *in situ* IR spectra from RT to 77 K could be recorded. The lower temperature limit of 77 K was achieved on cell walls, while the actual temperature on the irradiated sample might have been slightly higher. The sintering temperature was usually 1123 K. After this treatment the specific surface area was lower than 30 $m^2\,g^{-1}$ and the microcrystals had regular habit (as determined by HRTEM) [7,8]. The IR cell was permanently connected to a gas manifold allowing *in situ* gas dosage. The IR spectra where obtained with a Bruker IFS 48 FTIR spectrometer.

3. Results and discussion

3.1. Methane adsorption

The IR spectra in the stretching and bending regions of increasing doses of methane adsorbed at 77 K (nominal temperature) on α-chromia are illustrated in figure 1.

Bands are observed at 3005 (broad), 2979 (broad and asymmetric on the high-frequency side and likely composite), 2888 (narrow, tailed on the high-frequency side), 2840–36 (broad), 1540–36 (broad), 1320–1314 (doublet) and 1304 cm^{-1}. By considering the low surface area of the α-chromia employed in this investigation ($\sim$30 $m^2\,g^{-1}$), the intensity of the strongest bands is remarkable: this indicates that they are associated with methane adsorbed on extended facelets.

The bands at 2979, 2888 and 1314–1320 cm^{-1} are clearly dominating at the lowest coverages: hence they must be assigned to the most strongly adsorbed species (A species). In contrast the peaks at 3005 and 1304 cm^{-1}, which become very strong only at the highest coverages, belong to more weakly bonded species adsorbed on different sites (B species). The weak and broad bands at 2840–36 and 1540–36 cm^{-1} which are apparently growing in a uniform way with coverage (with a shift with coverage of about -4 and $+4$ cm^{-1}) are due to overlapped vibrational features common to both species. As a final comment it must be underlined that at the highest coverages the 3005 cm^{-1} peak shows a distinct tail on the high-frequency side. We think that this is associated with some degree of rotational feedom of the weakly adsorbed B species.

As fully documented in [8], the microcrystals of α-chromia obtained by combustion of ammonium dichromate and sintered at high-temperature (1073 K) have the shape illustrated in figure 2.

The microcrystals usually expose preferentially $(01\bar{1}2)$, $(\bar{2}116)$ and $(11\bar{2}0)$ faces where the Cr^{3+} ions are five-fold ($(01\bar{1}2)$ and $(11\bar{2}0)$) and four- and five-fold coordinated $(\bar{2}116)$. The $(\bar{2}116)$ face tends to disppear upon sintering at $T > 1050$ K and is nearly absent in our case [8]. Faces $(01\bar{1}2)$, $(11\bar{2}0)$ and $(\bar{2}116)$ adsorb CO [7,8], N_2 [11], NO [12], C_2H_4 [8]. The CO adsorbed at full coverage on $(01\bar{1}2)$ and $(11\bar{2}0)$ faces gives two narrow ν(CO) peaks at 2167 and 2160 cm^{-1}, respectively. The $(01\bar{1}2)$ faces are preferentially covered at the lowest coverages with CO because the five-fold cordinated Cr^{3+} are more exposed than those present on $(11\bar{2}0)$ and hence have greater polarizing power [8].

On the basis of these brief considerations we assign the peaks at 2979, 2888 and 1320–1314 cm^{-1} (belonging to the A species) to methane adsorbed on $(01\bar{1}2)$ faces and the peaks at 3005 and 1304 cm^{-1} (B species) to methane adsorbed on $(11\bar{2}0)$ faces. With regard to the bands in the 2840–36 and 1540–36 cm^{-1} intervals, we think they are due to the superposition of two components at 2840–1540 and 2836–1536 cm^{-1} belonging to A and B species.

The frequencies of methane in the gas phase, adsorbed on MgO (used for comparison) [4,6] and on α-chromia are compared in table 1. In this table the shifts of the peaks with respect to the gas phase are also reported.

The following can be commented:

(a) Methane adsorbed on α-chromia shows peaks which are usually IR inactive in the gas phase (see the bands at 2888 and at 1540–36 cm^{-1}). This is due to the reduction of symmetry caused by the adsorption process. The intensification of the IR inactive peaks is remarkably larger than observed on MgO (especially at the lowest coverages): this is likely associated with the larger polarization forces associated with Cr^{3+} ions present on the surface (we shall return on this point in the following).

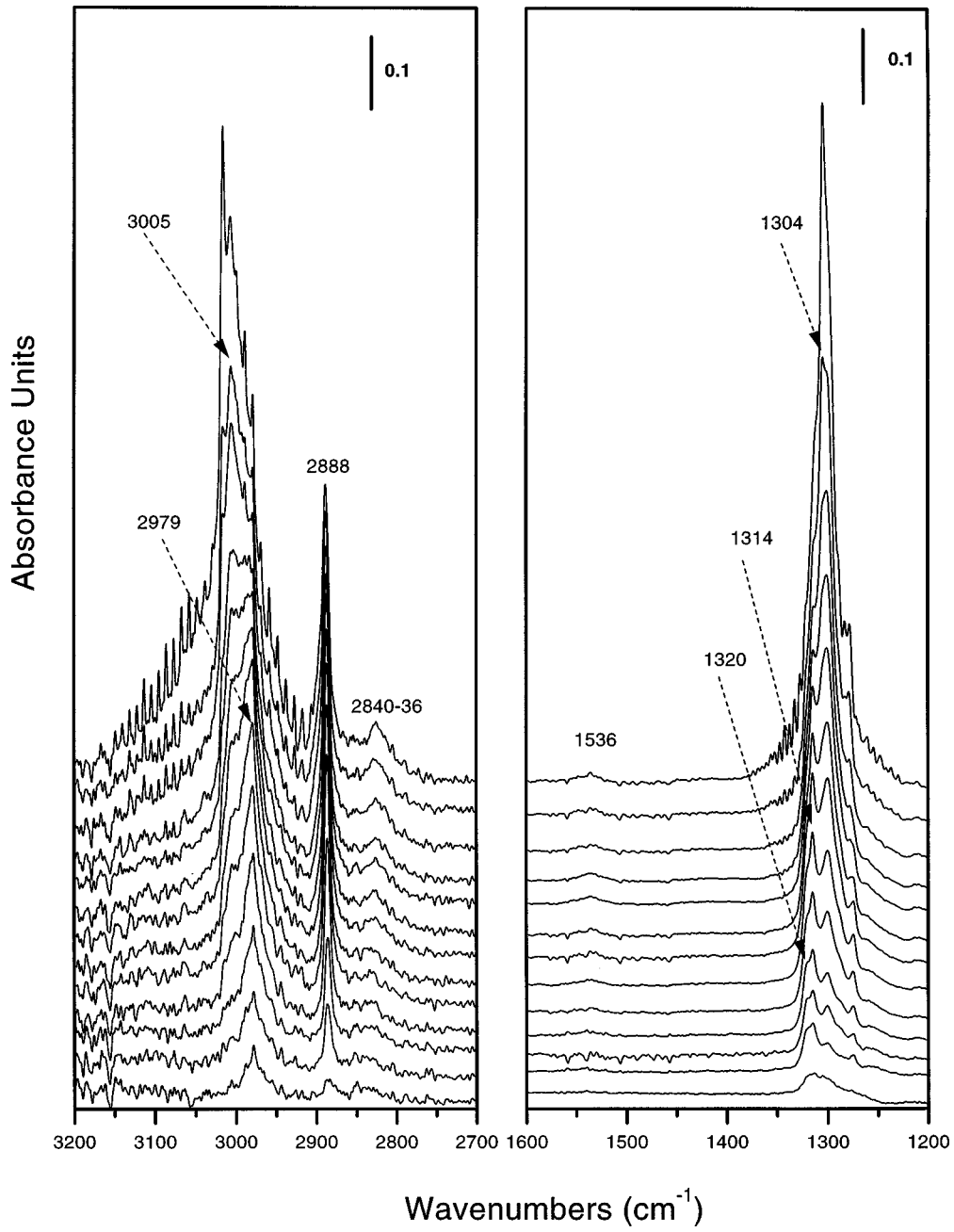

Figure 1. IR spectra in the 3200–2700 (stretching) and 1600–1200 cm^{-1} (bending) ranges of increasing doses of methane adsorbed at 77 K (nominal temperature) on α-chromia. The most intense spectrum corresponds to $p = 2.66$ kPa equilibrium pressure.

(b) The peaks with ν(CH) and δ(CH) character are shifted downwards and upwards, respectively, with respect to the gas phase. The shifts of the A species are definitely larger than those observed for the B species. A similar trend for the shifts has been observed for methane on MgO (the absolute values observed for B species being, however, appreciably larger).

(c) The peaks corresponding to degenerate modes in the gas phase have the largest half width (as expected, because low symmetry perturbations by surface ions remove the degeneracy).

3.2. Methane–CO coadsorption experiments: the structure of the adsorbing sites

So far we have established that the adsorption of methane on $(01\bar{1}2)$ and $(11\bar{2}0)$ faces of α-Cr_2O_3 is accompanied by a remarkable vibrational perturbation associated with the loss of T_d symmetry and C–H bonds polarization. Moreover, being the basicity of surface O^{2-} ions lower than that of MgO, it can be hypothesized that Cr^{3+} ions are the most plausible candidates as methane adsorption centres. However, on the basis of the sole data presented in figure 1, a definite conclusion about this point could not be achieved,

because both positively and negatively charged centres can polarize the CH bond with similar spectroscopic effects.

In order to clarify this point, we have studied the effect of CO dosage (which is known to give strong surface carbonyls with chromium centres) [7,8] on preadsorbed methane. The results are shown in figure 3.

It can be readily observed that: (i) CO displaces all adsorbed methane with subsequent formation of the usual peaks of CO adsorbed on Cr^{3+} centres on $(01\bar{1}2)$ (2167 cm^{-1}) and on $(11\bar{2}0)$ (2160 cm^{-1}) faces [7,8]; (ii) only the spectrum of gaseous methane is observed in presence of CO. It is evident that this experiment reinforces the hypothesis advanced before that methane is adsorbed on metallic centres. Furthermore this result definitely indicates that, unlike observed for MgO, the surface chemistry of α-chromia is dominated by the properties of metallic centres and that the most plausible structure formed upon methane adsorption is

$$\equiv C\text{–}H \cdots Cr^{3+}$$

which is characterized by a C–H bond polarization opposite to that found on MgO and similar to that observed for n-heptane adsorbed on α-chromia at RT [8]. Notice that the agostic type $C\text{–}H \cdots Cr^{3+}$ interaction can well explain the downward shift of the ν(CH) stretching frequencies and the upward shift of the bending modes. In conclusion, from ours and Knözinger's results [4,5] it is inferred that the CH group of methane can be used to probe both Lewis acid and basic sites.

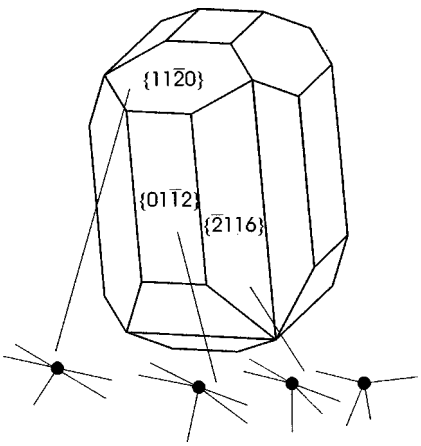

Figure 2. Preferential morphology of sintered α-Cr_2O_3 microcrystal as observed in [8]. Chromium coordination on different faces is shown.

So far we have discussed the effect of CO on adsorbed methane which is causing the complete displacement of adsorbed CH_4. Now we briefly describe the opposite experiment, i.e., the adsorption of methane on preadsorbed CO. Because of the large difference in stability of the CO and methane complexes, this experiment has been performed by dosing CH_4 on a small dose of adsorbed CO (approximately 1/10 of the monolayer capacity).

The results concerning the effect of methane coadsorption on the ν(CO) of preadsorbed CO (which is not displaced at all by the weak methane adsorbate) are illustrated in figure 4.

The spectra of adsorbed methane in the stretching and bending regions are omitted because they do not substantially differ from those illustrated in figure 1. The following can be commented:

(i) The intensity of the ν(CO) peak of CO adsorbed on the $(01\bar{1}2)$ faces (dotted curve) does not change upon methane dosage (as expected because the latter one is a much weaker adsorbate);

(ii) The ν(CO) frequency moves downwards gradually because of the building up of methane–CO lateral interactions in the adsorbed phase, the total shift being -10 cm^{-1}. A similar shift has been observed upon dosage of n-heptane on preadsorbed CO [8]. The shift is not fully continuous because the frequency of CO depends upon the number of methane molecules adsorbed in adjacent position (which is changing with coverage in a discrete way). Unlike other cases [7,13,14] the discrete components corresponding to the different variants are not resolved (only the component corresponding to one CO sourronded by four methane molecules in adjacent position can easily be distinguished at 2167 cm^{-1}).

The gradual shift caused by methane on ν(CO) is the typical response of lateral interactions on extended faces or terraces: hence, the conclusion that the stretching and bending bands illustrated in figure 1 correspond to methane adsorbed on extended faces is reinforced. At the same time the similarity with the effect caused by n-heptane (where

Table 1
Comparison of CH_4 vibrational frequencies: normal modes, gas phase frequencies, CH_4 adsorbed on MgO [4,6] and CH_4 adsorbed on α-Cr_2O_3 faces: A species $(01\bar{1}2)$ and B species $(11\bar{2}0)$.

Vibrational mode	Gas phase (cm^{-1})	CH_4/MgO[a] (cm^{-1})	CH_4/α-Cr_2O_3[a] (cm^{-1})	
			A	B
ν_1 (a_1) sym. stret.	2914	2897 (-17)	2888 (-26)	$\sim$2900 (-14)
ν_2 (e) def.	1526	–	1540 ($+14$)	1536 ($+10$)
ν_3 (t_2) antisym. stret.	3020	3002 (-18)	2979 (-41)	3005 (-15)
$\nu_4 + \nu_2$	2834	–	–	–
ν_4 (t_2) def.	1302	1302 (0)	1320–14 ($+18$–$+12$)	1304 ($+2$)

[a] In parentheses the shifts relative to the gas phase frequency.

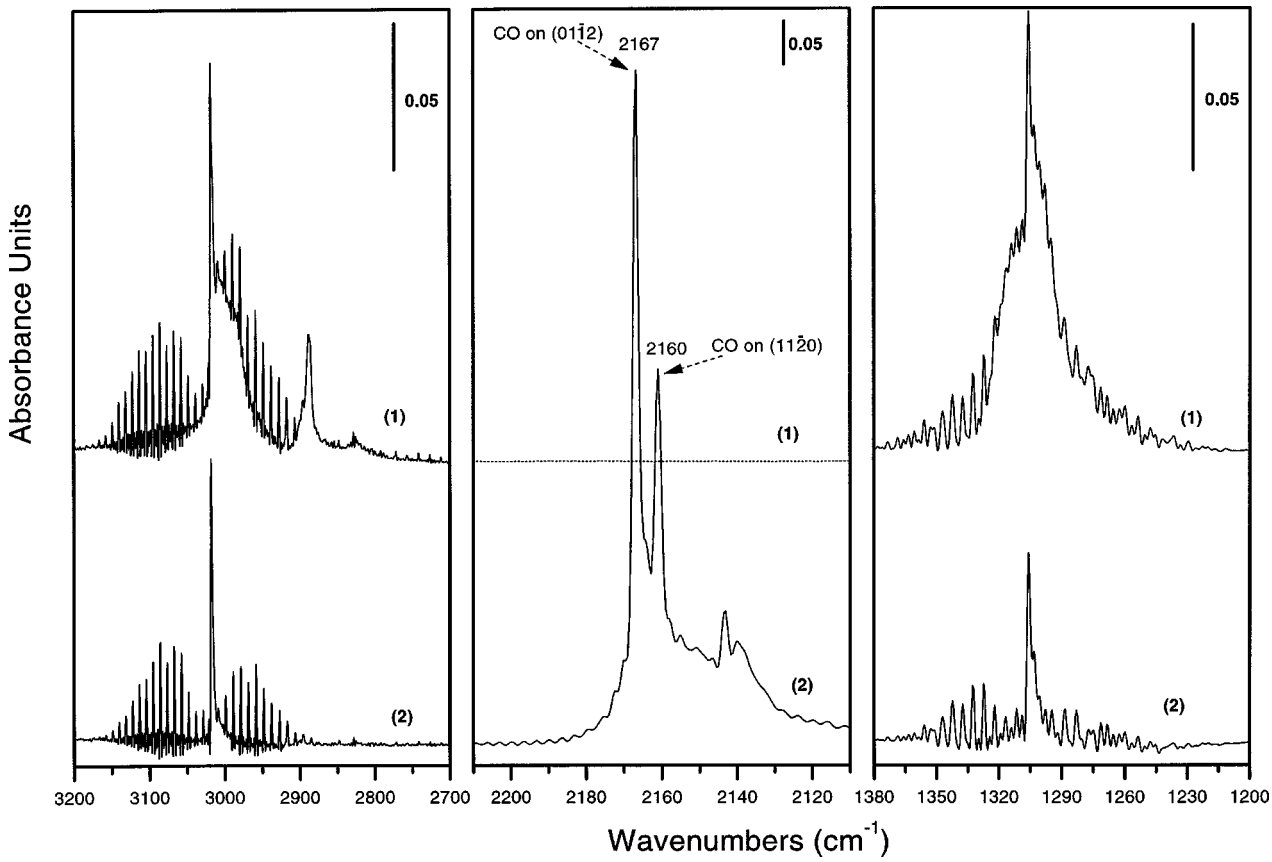

Figure 3. Effect of CO dosage (p_{CO} = 266 Pa) on preadsorbed methane (p = 930 Pa): nominal temperature 77 K. The three parts of the figure correspond to the CH_4 stretching, to the CO stretching and to the CH_4 bending regions, respectively.

the presence of C–H $\cdots$ Cr^{3+} interactions has been demonstrated beyond any doubt) is in favour of a similar interaction mechanism.

3.3. Hydrogen and hydrogen/CO coadsorption

The spectra of increasing doses of hydrogen adsorbed on α-chromia are illustrated in figure 5.

We can immediately notice that at the nominal 77 K temperature, one peak (likely composite) centred at 3935 cm^{-1} is showing up upon H_2 dosage. This peak is due to reversibly adsorbed molecular hydrogen because it disappears upon outgassing at 77 K. As this peak is absent when the surface is precovered by CO, it is assigned to the ν(H–H) of hydrogen adsorbed on Cr^{3+} centres located on the most reactive (01$\bar{2}$0) face. This peak is downward shifted with respect to a free molecule: $\Delta\nu = -225$ cm^{-1}. A similar negative shift of the H–H stretching frequency has been observed for hydrogen adsorbed on positive ions in zeolites and zeolitic materials [15 and references therein] and has been explained in terms of polarization of the H–H bond caused by the positive electric field centred at the cationic sites. We think that this interpretation is also valid in the present case and that the absence of a relevant band due to hydrogen adsorbed on the (11$\bar{2}$0) face (where the electric field is lower, because the Cr^{3+} ions are partially shielded [14]) finds a simple explanation on this ground. In fact the strength of the electric field associated with these centres is not large enough to make the the ν(H–H) appreciably IR active. From all the considerations presented before a clear analogy between the behaviour of dihydrogen (H–H) and of the C–H group is emerging. This similarity has been already stressed [16]. As a final remark let us underline that on the basis of the presented results it is difficult to exclude the presence of a small contribution of overlap forces between d orbitals of the metallic centre and the σ orbitals of the H–H and C–H bonds to the stabilization of the surface/CH_4 and surface/H_2 interactions.

4. Conclusions

Methane and hydrogen are both adsorbed on Cr^{3+} centres of microcrystalline α-chromia. The metallic centres located on (01$\bar{1}$2) facelets are more active than those located on (11$\bar{2}$0) ones. The adsorption on metallic centres is accompanied by a downward shift of the stretching frequencies (CH_4, H_2) and by an upward shift of the bending frequencies (CH_4). These effects are explained in terms of perturbation caused by the electrostatic field centred at the positive ions. Unlike observed on the more basic MgO, the surface oxygen ions present on extended faces do not seem to play a direct role in methane and hydrogen adsorption.

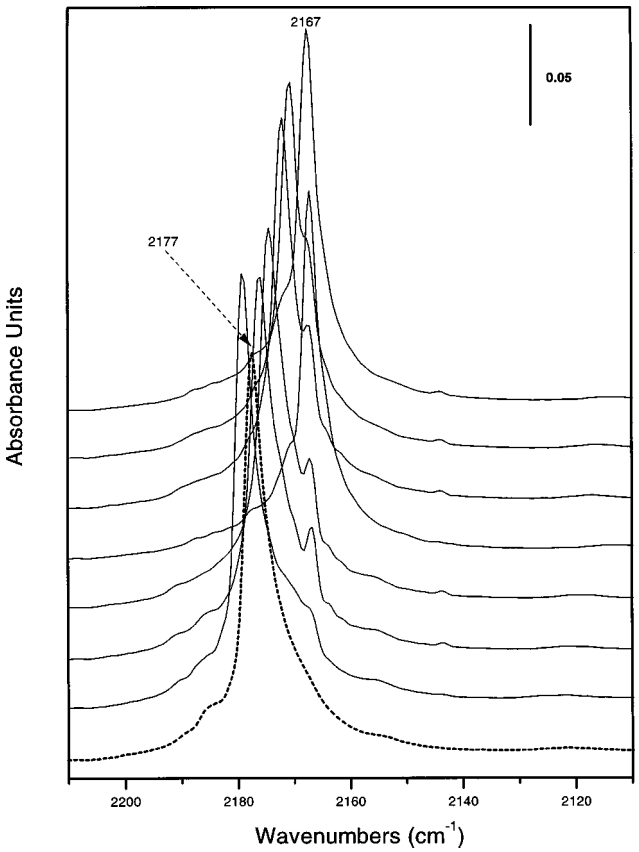

Figure 4. Effect of CH_4 dosage at 77 K (nominal temperature) on the stretching mode of adsorbed CO (starting coverage ∼0.1, peak at 2177 cm^{-1}). The different spectra correspond to increasing pressures of methane. The last spectrum (peak at 2167 cm^{-1}) corresponds to $p_{CH_4} = 2.66$ kPa.

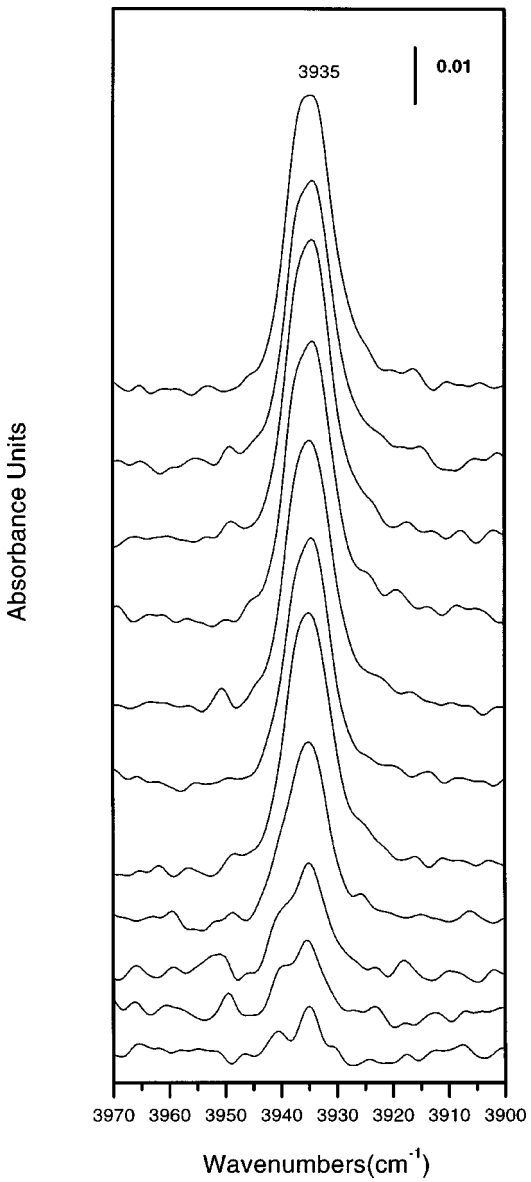

Figure 5. The IR spectra of increasing doses of hydrogen adsorbed on α-chromia at 77 K (nominal temperature). The upper spectrum corresponds to $p = 5.3$ kPa.

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References

[1] J. Chengguo, P. Donguo, O. Juzo, L. Wanjim, K. Tsugio and F. Yuzo, Science 287 (1992) 2000.
[2] H. Chen, S. Sehlecht, T.C. Semple and J.F. Hartwig, Science 287 (1995) 2000.
[3] J.M. Thomas and W.J. Thomas, *Principles and Practice of Heterogeneous Catalysis* (VCH, New York, 1997).
[4] H. Knözinger, in: *Handbook of Heterogeneous Catalysis*, Vol. 2, eds. G. Ertl, H. Knözinger and J. Weitkamp (Wiley/VCH, Weinheim, 1997) p. 207.
[5] H. Knözinger, Science 287 (2000) 1407.
[6] A.M. Ferrari, S. Huber, H. Knözinger, K.M. Neyman and N. Rosch, J. Phys. Chem. B 102 (1998) 4548.
[7] D. Scarano, A. Zecchina, S. Bordiga, G. Ricchiardi and G. Spoto, Chem. Phys. 177 (1993) 547.
[8] D. Scarano, G. Spoto, S. Bordiga, L. Carnelli, G. Ricchiardi and A. Zecchina, Langmuir 10 (1994) 3094.
[9] B.M. Weckhuysen, I.E. Wachs and R.A. Schoonheydt, Chem. Rev. 96 (1996) 3327.
[10] R.H. Crabtree and D.G. Hamilton, Adv. Organomet. Chem. 28 (1988) 299.
[11] A. Zecchina et al., unpublished results.
[12] D. Scarano, A. Zecchina and A. Reller, Surf. Sci. 198 (1988) 11.
[13] D. Scarano, G. Ricchiardi, S. Bordiga, P. Galletto, C. Lamberti, G. Spoto and A. Zecchina, Faraday Discuss. 105 (1996) 119.
[14] D. Scarano, G. Spoto, S. Bordiga, A. Zecchina and C. Lamberti, Surf. Sci. 276 (1992) 281.
[15] A. Zecchina, C. Otero Arean, G. Turnes Palomino, F. Geobaldo, C. Lamberti, G. Spoto and S. Bordiga, Phys. Chem. Chem. Phys. 1 (1999) 1649.
[16] J.Y. Saillard and R. Hoffman, J. Am. Chem. Soc. 106 (1984) 2006.