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Vibrational spectroscopy of carbon monoxide and dinitrogen adsorbed on magnesium-exchanged ETS-10 molecular sieve

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Carbon monoxide and dinitrogen adsorbed, at nominally liquid-nitrogen temperature, on Mg^{2+}-exchanged ETS-10 were found to form $Mg^{2+}\cdots CO$ and $Mg^{2+}\cdots N_2$ adducts involving cations located in the main channels (12-membered rings) of the titanosilicate molecular sieve. These adducts gave main IR absorption bands at 2190 and 2203 cm^{-1} for CO, and at 2336 and 2339 cm^{-1} for N_2, which were assigned to the fundamental stretching mode of the diatomic molecules polarized by the electric field created by Mg^{2+} ions. Corresponding adducts with Na^+ and K^+ ions, not exchanged with Mg^{2+}, were also present. The results, which are relevant to the potential use of ETS-10 as a catalyst, lend support to previous structural studies suggesting the existence of two different cation sites along the main channel of ETS-10.

Keywords: carbon monoxide adsorption, ETS-10, heterogeneous catalysis, IR spectroscopy, molecular sieves, nitrogen adsorption

1. Introduction

ETS-10 (Engelhard titanosilicate structure 10) is a molecular sieve having a crystal structure topologically related to that of zeolite β [1]. The framework of ETS-10 is formed by orthogonal chains of corner-sharing TiO_6 octahedra which are linked by corner-sharing SiO_4 tetrahedra [2], as shown in figure 1(a). This arrangement of structural units generates 12- and 7-membered ring channels. Only the channels formed by 12-membered rings (hereafter called main channels), which show a free entrance of about 0.8×0.5 nm, are permeable to CO and dinitrogen molecules. Those formed by 7-membered rings, having a diameter of about 0.55×0.15 nm, are not accessible.

Each TiO_6 octahedron in the framework carries a 2– negative charge, and the electrical neutrality of the system is preserved by extra-framework charge-balancing cations which are exchangeable; in the as-synthesized material [3], which has the chemical formula $(Na,K)_2TiSi_5O_{13}$, two alkali metal cations are incorporated for every titanium atom. Recent structural studies [4,5], using 2D multiple-quantum NMR spectroscopy and lattice energy minimisation calculations, gave strong evidence that ETS-10 contains five types of extra-framework cation sites, which are distributed as shown in figure 1(b). Sites I and II, which are crystallographically non-equivalent, are tucked away on either side of the main channel and close to 5-ring apices. Site IV lies inside the 7-ring, midway between two orthogonal titanium–oxygen chains. Sites III and V are located within the main channel, close to a titanium–oxygen chain (site III) and more loosely bound along the channel (site V); the distance between these sites, which are both accessible to adsorbed molecules, is about 0.55 nm.

Alkali- and alkaline-earth-exchanged molecular sieves, including ETS-10, can act as heterogeneous catalysts for a variety of chemical processes, including alcohol dehydration, alkane dehydrocyclisation and aldol-type condensation reactions [6–9]. Understanding of these catalytic processes requires detailed knowledge about the behaviour of extra-framework cations. A powerful technique for elucidating such a behaviour is infrared spectrometry of adsorbed probe molecules [10–15]. Frequently, weakly interacting diatomic molecules (such as CO, N_2 or H_2) are used as IR-spectroscopic probes. When adsorbed on zeolites, the vibrational frequency of these molecules is affected by polarization in the electric field created by extra-framework metal ions and their environment, and the corresponding frequency shift (related to the free molecule) gives precise information on the adsorbing centre [13,16,17].

The aim of this work was a detailed study of the infrared spectra of CO and N_2 adsorbed (at liquid-nitrogen temperature) on magnesium-exchanged ETS-10, so as to gain knowledge on the behaviour of extra-framework cations. Parallel studies on Na^+- and K^+-exchanged ETS-10 were reported elsewhere [18]. However, to the best of our knowledge, alkaline-earth-exchanged ETS-10 was not studied before.

2. Experimental

The original ETS-10 sample used in this study was supplied by Engelhard (Iselin, NJ, USA). Chemical analysis showed a $Na^+ : K^+$ ratio of 2.64, and powder X-ray diffraction showed good crystallinity and confirmed the expected

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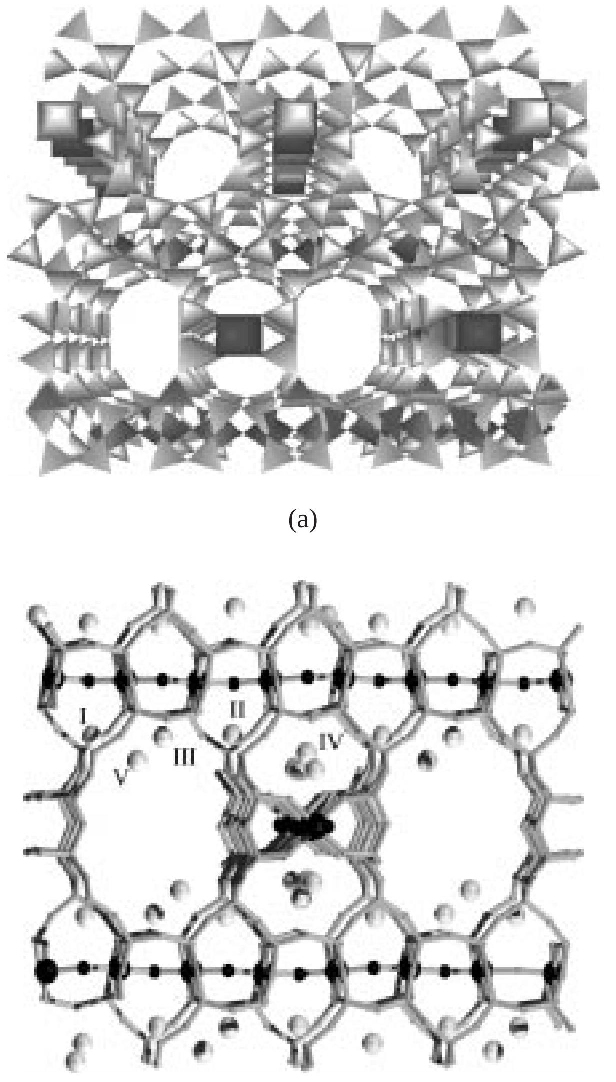

(a)

(b)

Figure 1. The ETS-10 structure: (a) layout of TiO_6 octahedra and SiO_4 tetrahedra forming the framework of the molecular sieve, and (b) distribution of extra-framework cations (shown as isolated spheres) among sites I–V.

structure type. No additional diffraction lines were found. A portion of this sample was repeatedly exchanged with a 1 M aqueous solution of magnesium nitrate (analytical grade) for a total of 7 days.

For infrared studies, portions of the ion-exchanged sample were made into self-supporting wafers and outgassed in a dynamic vacuum (residual pressure $<10^{-4}$ Torr) at 550 K for 3 h inside an IR [19] cell which allowed *in situ* high-temperature treatments, gas dosage, and low-temperature measurements to be carried out. The infrared spectra were recorded at 3 cm^{-1} resolution on a Bruker IFS66 FTIR spectrometer. Although the IR cell was permanently cooled with liquid nitrogen during acquisition of the spectra, the actual sample temperature (under the IR beam) was likely to be about 100–110 K. The wafer spectrum taken before dosing with either CO or dinitrogen was used as a blank. All spectra shown in this paper are blank subtracted.

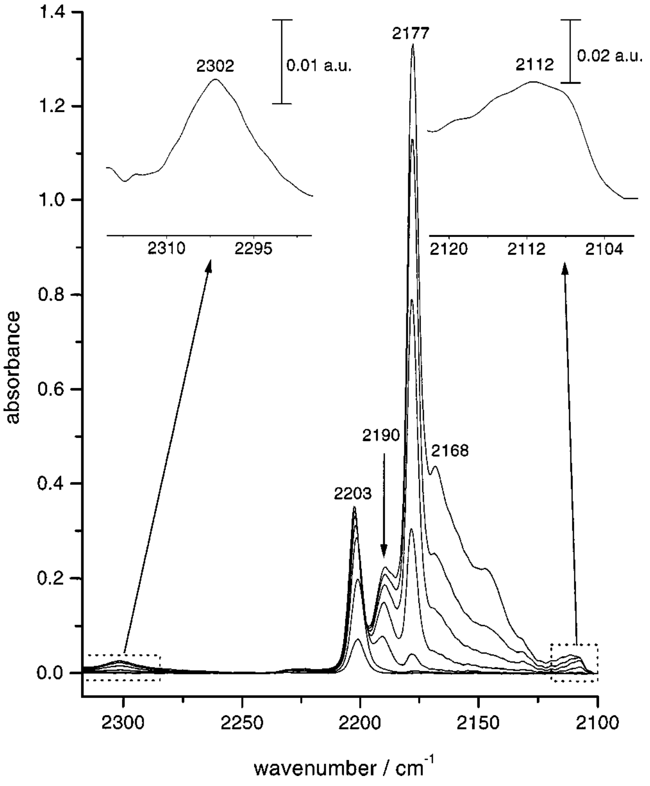

Figure 2. FTIR spectra of CO adsorbed at increasing equilibrium pressure (about 10^{-2}–2 Torr) and liquid-nitrogen temperature on magnesium-exchanged ETS-10.

3. Results and discussion

3.1. Spectra of adsorbed carbon monoxide

The IR spectra of CO adsorbed at nominal liquid-nitrogen temperature and increasing equilibrium pressure on Mg^{2+}-exchanged ETS-10 are shown in figure 2. For the lowest CO equilibrium pressure a single IR absorption band is seen at 2203 cm^{-1}. Upon increasing the equilibrium pressure new bands develop: at 2190, 2177, 2168 (shoulder) and ca. 2143 cm^{-1} (shoulder). Minor (and complex) bands are also seen at 2302 and at 2112 cm^{-1}; for better definition see the insets in figure 2.

On Na^{+}-exchanged ETS-10 the main IR absorption band of adsorbed CO was found [18] at 2176 cm^{-1} (with a tail on the low-frequency side), while for K^{+}-ETS-10 two bands were reported at 2168 and at 2162 cm^{-1}. These bands were assigned [18] to the fundamental C–O stretching vibration of $Na^{+}\cdots CO$ and $K^{+}\cdots CO$ adducts, for Na^{+}-ETS-10 and K^{+}-ETS-10, respectively. Referring to figure 2, it should therefore be clear that bands at 2177 and 2168 cm^{-1} correspond, respectively, to CO interacting (via the carbon atom) with Na^{+} and K^{+} ions not exchanged by Mg^{2+} in the original (Na^{+}/K^{+})-ETS-10 sample. Note the broad tail on the low-frequency side of the band at 2168 cm^{-1}, which should correspond to the 2162 cm^{-1} band observed for CO adsorbed on K^{+}-ETS-10. Once these bands are assigned, it should be clear that those at 2203 and 2190 cm^{-1} correspond to the C–O stretching mode of $Mg^{2+}\cdots CO$ adducts formed on two different Mg^{2+} sites. Note that bands at these wavenumber values were not observed for CO adsorbed on either Na^+-ETS-10 or K^+-ETS-10. Since only sites III and V (figure 1(b)) are accessible to adsorbed CO, we tentatively assign the band at 2203 cm^{-1} to $Mg^{2+}\cdots CO$ adducts formed at site V, and that at 2190 cm^{-1} to similar adducts at site III. Note that site III is closer to framework oxygen anions which should attenuate the positive electric field created by the Mg^{2+} ion.

The hypsochromic frequency shift of adsorbed CO with respect to the free-molecule value (2143 cm^{-1}) gives a measure of the (positive) electric field in the neighbourhood of extra-framework cations [13,20,21]. For a weak (ion–dipole) interaction, the frequency shift ($\Delta\nu$) can be considered to arise (mainly) from the vibrational Stark effect, and the corresponding electric field strength, E, can be obtained [22] from the expression: $\Delta\nu = k_{\mathrm{ST}}E$, where k_{ST} is the vibrational Stark constant for CO, which according to Lambert [23], takes the value $k_{\mathrm{ST}} = 4.29 \times 10^{-9}\ \mathrm{m\,cm^{-1}\,V^{-1}}$. For the band at 2203 cm^{-1} (figure 2), $\Delta\nu = 60\ \mathrm{cm^{-1}}$, which leads to $E = 14\ \mathrm{V\,nm^{-1}}$. A smaller value, $E = 11\ \mathrm{V\,nm^{-1}}$, is obtained for the band at 2190 cm^{-1}. However, both of these values represent quite strong electric fields which can significantly affect the electron distribution of adsorbed molecules, and hence reactivity. For comparison, the electric field corresponding to Na^+ and K^+ ions in ETS-10 and alkali-metal-exchanged zeolites is of the order of 5–8 $\mathrm{V\,nm^{-1}}$ [18,24,25].

It remains to comment on the minor bands in figure 2. The band (shoulder) at about 2143 cm^{-1}, which gains intensity only at a relatively high CO equilibrium pressure can readily be assigned to free (or physisorbed) CO. The small band at 2302 cm^{-1} is assigned to the combination mode of the C–O and $Na^+{-}C$ stretching vibrations of $Na^+\cdots CO$ adducts. This assignment, which leads to a value of 125 cm^{-1} for the metal–carbon stretching vibration, is in agreement with previous reports on CO adsorbed on Na^+-ETS-10 and Na^+-ZSM-5 [18,26]. It should also be pointed out that, by using intense IR radiation from a synchrotron source, a band at 139 cm^{-1} was clearly observed [27] for CO adsorbed on the zeolite Na-Y. This observation gave direct evidence for the metal–carbon vibration mode which usually is not possible to obtain in standard IR spectroscopy measurements, where the far IR region is not accessible because of both instrumental limitations and the small transparency of zeolite wafers in that spectral region. It should be noted that the metal–carbon vibration is very sensitive not only to the specific cation involved but also to its environment. This consideration explains the (small) differences found for the same $Na^+\cdots CO$ adduct in molecular sieves having different framework structure. For organometallics and for CO adsorbed on transition metals the metal–carbon stretching vibration is usually found [29,29] at about 450–380 cm^{-1}, but a smaller value is expected for $Na^+\cdots CO$ adducts where adsorbed CO is stabilized only by electrostatic interaction with the cation. The corresponding band for the combination mode $\nu_{\mathrm{CO}} + \nu_{\mathrm{MgC}}$ of $Mg^{2+}\cdots CO$ adducts was not observed in our spectra, presumably because the corresponding ν_{CO} bands (figure 2) are not intense enough. Note that, despite repeated ion exchange, Mg^{2+} ions have replaced only a small fraction of Na^+ (and K^+) ions, as shown by the intense band of $Na^+\cdots CO$ adducts (at 2177 cm^{-1}).

The complex band which peaks at about 2110–2112 cm^{-1} (figure 2) is assigned to $Na^+\cdots OC$ adducts (a contribution from $K^+\cdots OC$ species can also be present) in which the CO molecule interacts with the cation via the oxygen atom, thus leading to a bathochromic shift of the C–O stretching mode [21,30,31]. This complex band was fully discussed in a recent work devoted to CO adsorption on alkali-metal-exchanged ETS-10 [18], where $^{12}CO/^{13}CO$ mixtures were used to isolate possible components due to $Na^+\cdots{}^{13}CO$ species, therefore no further comments are made here. Note, however, that the corresponding band for $Mg^{2+}\cdots OC$ species should appear at about 2080–2095 cm^{-1}, i.e., with a bathochromic shift having a magnitude similar to that of the hypsochromic shift for the corresponding $Mg^{2+}\cdots CO$ species [25,32]. This band was not observed. Again, the explanation has to be found in the relatively small intensity of the $Mg^{2+}\cdots CO$ bands; note that C- and O-bonded adducts should be in a temperature-dependent equilibrium [32], where the proportion of the latter species is always very small [17,25,32].

3.2. Spectra of adsorbed dinitrogen

Figure 3 shows the IR spectra of N_2 adsorbed, at liquid-nitrogen temperature and increasing equilibrium pressure, on Mg^{2+}-exchanged ETS-10. Main IR absorption bands are seen at 2333 (with a shoulder at 2331) and at 2339 cm^{-1}. A weaker band appears (as a shoulder) at 2336 cm^{-1} (see inset to figure 3). Previous studies [18] have shown that the band at 2333 cm^{-1} should be assigned to the fundamental N–N stretching mode of $Na^+\cdots N_2$ adducts, where the dinitrogen molecule is axially polarized by the electric field created by the Na^+ ion. This polarization renders IR active the Raman active mode of free N_2 which appears at 2331 cm^{-1} in the gas phase, and at 2321($\pm$2) cm^{-1} for dinitrogen adsorbed on silicalite [13] which is a purely siliceous molecular sieve having no extra-framework cations. Note that interaction of N_2 with the Na^+ cation raises the N–N stretching frequency, as expected on the basis of theoretical calculations [33,34]. When reference is made to N_2 adsorbed on silicalite, a value $\Delta\nu = 12\ \mathrm{cm^{-1}}$ is found. The shoulder at 2331 cm^{-1} should be assigned to the N–N stretching mode of $K^+\cdots N_2$ adducts; for K^+-exchanged ETS-10 the corresponding band was found at 2331.5 cm^{-1} [18].

The band at 2339 cm^{-1} and its small component at 2336 cm^{-1} are assigned to the N–N stretching mode of $Mg^{2+}\cdots N_2$ adducts formed at cation sites V (2339 cm^{-1}) and III (2336 cm^{-1}). The higher electric field of Mg^{2+} (compared to that of Na^+) results, as expected, in a larger

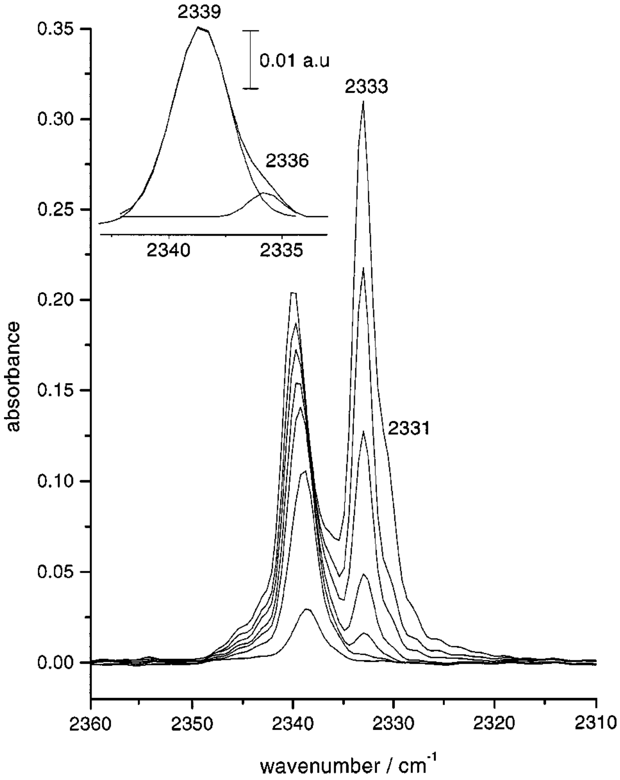

Figure 3. FTIR spectra of N_2 adsorbed at increasing equilibrium pressure (about 10^{-1}–5 Torr) and liquid-nitrogen temperature on magnesium-exchanged ETS-10. Inset shows magnification and computer resolution of the high-frequency band corresponding to the smallest equilibrium pressure.

hypsochromic shift of the N–N stretching frequency; referring to the $Mg^{2+}\cdots N_2$ adduct formed at site V, we have $\Delta\nu = 18$ cm^{-1}. For Mg^{2+}, the IR spectra of adsorbed dinitrogen confirm the presence of two different cation sites (III and V) within the main channel; one of them (site V) is less shielded by framework oxygens and therefore shows a stronger electric field. These results lend further support to the assignments already made for the spectra of adsorbed CO, and also to the structural studies quoted in section 1. Note that the small intensity of the band at 2336 cm^{-1} (as compared to that at 2339 cm^{-1}) can be explained on account of the fact that for the N_2 molecule (which has no permanent electric dipole) the intensity of the field-induced IR absorption should be proportional to the second power of the electric field [35], which at site III is smaller than at site V (section 3.1) because of the negative contribution from nearby oxygen atoms.

For $Na^{+}\cdots N_2$ and $K^{+}\cdots N_2$ adducts the presence of two different cation sites accessible to adsorbed dinitrogen appears to be less clear, as was also the case for adsorbed CO. This fact can be explained in terms of the larger size of the alkali metal cations (as compared to Mg^{2+}) which would render the electric field in their immediate neighbourhood less sensitive to nearby (framework) oxygens. However, it should also be considered that the broad (unresolved) band due to these adducts could actually contain more than two components.

4. Conclusions

By using carbon monoxide and dinitrogen as probe molecules, FTIR spectroscopy has confirmed the presence of two different extra-framework cation sites within the main channels of ETS-10, as previously suggested by NMR spectroscopy and lattice energy minimisation calculations. These two sites appear to differ from each other in the number, or proximity, of framework oxygen atoms, which results in a corresponding difference in the magnitude of the electric field in the vicinity of the cation. For Mg^{2+} this electric field amounts to 11–14 V nm^{-1}. Such a strong field gives rise to a considerable polarization of the adsorbed molecules, CO and N_2, which is reflected in the hypsochromic shift of their fundamental stretching mode. Strong electric fields could similarly modify the electron distribution, and hence reactivity patterns, of other molecules entering the ETS-10 main channels, which would be relevant to the potential use of the molecular sieve as a catalyst.

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References

[1] W.M. Meier and D.H. Olson, *Atlas of Zeolite Structure Types* (Butterworth/Heinemann, London, 1992).
[2] M.W. Anderson, O. Terasaki, T. Ohsuna, P.J. O'Malley, A. Philippou, S.P. MacKay, A. Ferreira, J. Rocha and S. Lidin, Philos. Mag. B 71 (1995) 813.
[3] S.M. Kuznicki, US Patent 4853202 (1989).
[4] M.E. Grillo and J. Carrazza, J. Phys. Chem. 100 (1996) 12261.
[5] M.W. Anderson, J.R. Agger, D.P. Luigi, A.K. Baggaley and J. Rocha, Phys. Chem. Chem. Phys. 1 (1999) 2287.
[6] R.J. Davis and E.G. Derouane, Nature 349 (1991) 313.
[7] G.S. Lane, F.S. Modica and J.T. Miller, J. Catal. 129 (1991) 145.
[8] E.J. Rode, P.E. Gee, L.N. Marquez, T. Uemura and M. Bazargani, Catal. Lett. 9 (1991) 103.
[9] A. Philippou and M.W. Anderson, J. Catal. 189 (2000) 395.
[10] K.M. Neyman, P. Strodel, S.Ph. Ruzankin, N. Schlensog, H. Knözinger and N. Rösch, Catal. Lett. 31 (1995) 273.
[11] J.C. Lavalley, Catal. Today 27 (1996) 377.
[12] J.A. Lercher, C. Gründling and G. Eder-Mirth, Catal. Today 27 (1996) 353.
[13] A. Zecchina and C. Otero Areán, Chem. Soc. Rev. 25 (1996) 187.
[14] L.M. Kustov, Topics Catal. 4 (1997) 131.
[15] H. Knözinger and S. Huber, J. Chem. Soc. Faraday Trans. 94 (1998) 2047.
[16] G. Turnes Palomino, C. Otero Areán, F. Geobaldo, G. Ricchiardi, S. Bordiga and A. Zecchina, J. Chem. Soc. Faraday Trans. 93 (1997) 189.
[17] E. Garrone, B. Fubini, B. Bonelli, B. Onida and C. Otero Areán, Phys. Chem. Chem. Phys. 1 (1999) 513.
[18] A. Zecchina, C. Otero Areán, G. Turnes Palomino, F. Geobaldo, C. Lamberti, G. Spoto and S. Bordiga, Phys. Chem. Chem. Phys. 1 (1999) 1649.

[19] L. Marchese, S. Bordiga, S. Coluccia, G. Martra and A. Zecchina, J. Chem. Soc. Faraday Trans. I 89 (1993) 3483.

[20] C. Lamberti, S. Bordiga, F. Geobaldo, A. Zecchina and C. Otero Areán, J. Chem. Phys. 103 (1995) 3158.

[21] N.S. Hush and M.L. Williams, J. Mol. Spectrosc. 50 (1974) 349.

[22] Yu.A. Tsyganenko, A.A. Tsyganenko and K.S. Smirnov, Vib. Spectrosc. 6 (1993) 15.

[23] D.K. Lambert, Solid State Commun. 51 (1984) 297.

[24] A. Zecchina, S. Bordiga, C. Lamberti, G. Spoto, L. Carnelli and C. Otero Areán, J. Phys. Chem. 98 (1994) 9577.

[25] A.A. Tsyganenko, E. Escalona Platero, C. Otero Areán, E. Garrone and A. Zecchina, Catal. Lett. 61 (1999) 187.

[26] S. Bordiga, E. Escalona Platero, C. Otero Areán, C. Lamberti and A. Zecchina, J. Catal. 137 (1992) 179.

[27] C. Otero Areán, G. Turnes Palomino, A. Zecchina, G. Spoto, S. Bordiga and P. Roy, Phys. Chem. Chem. Phys. 1 (1999) 4139.

[28] P.S. Braterman, *Metal Carbonyl Spectra* (Academic Press, London, 1975).

[29] L.H. Little, *Infrared Spectra of Adsorbed Species* (Academic Press, London, 1966).

[30] A.M. Ferrari, K.M. Neyman and N. Rösch, J. Phys. Chem. B 101 (1997) 9292.

[31] P. Ugliengo, E. Garrone, A.M. Ferrari, A. Zecchina and C. Otero Areán, J. Phys. Chem. B 103 (1999) 4839.

[32] C. Otero Areán, A.A. Tsyganenko, E. Escalona Platero, E. Garrone and A. Zecchina, Angew. Chem. Int. Ed. Engl. 37 (1998) 3161.

[33] V. Staemmler, Chem. Phys. 7 (1975) 17.

[34] L. Koubi, M. Blain, E. Cohen de Lara and J.M. Leclercq, Chem. Phys. Lett. 217 (1994) 544.

[35] E. Cohen de Lara and Y. Delaval, J. Chem. Soc. Faraday Trans. II 74 (1978) 790.