Catalysis Letters 37 (1996) 107–111

Assessing the Brønsted acidity of CoAPO-18 catalysts by using N_2 as molecular probe

L. Marchese, E. Gianotti, N. Damilano, S. Coluccia
Dipartimento di Chimica IFM, Universitàt di Torino, v. P. Giuria 7, 10125 Turin, Italy

and

J.M. Thomas
Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

Received 15 September 1995; accepted 7 November 1995

Whilst there is merit in using NH_3 or CO as probes to determine the surface acidity of solid catalysts by thermal and/or spectroscopic means, we show that, following Wakabayashi et al., quantitative spectroscopic changes accompanying the adsorption of dinitrogen offer more reliable assessments. Subtle differences arising from the use of N_2 as between CoALPO and zeolitic (aluminosilicate) catalysts are also discussed.

Keywords: N_2 adsorption; FTIR; microporous acid catalysts; CoAPO-18; Brønsted hydroxyls

1. Introduction

SAPO-18 and MeAPO-18 (Me = Mg, Zn, Co) are good microporous catalysts for the conversion of methanol to light olefins (mainly ethene and propene) because of the presence of Brønsted acid sites that are strong enough to promote the reaction [1,2]. It is widely accepted that the Brønsted active centres in SAPOs, such as in SAPO-18 [2], are OH groups bridged to Si and Al similar to those present in zeolites. Isomorphous substitution of Al^{3+} with bivalent metal ions Me^{2+} can, in principle, generate bridging hydroxyl groups joined to both metal and phosphorus in MeAPOs (the structure A in scheme 1 represents the case of CoAPOs). Among MeAPO catalysts, CoAPOs are unusual in that they exhibit Brønsted acidity which is intimately associated with Co(II)/Co(III) redox couples: such, for instance, is the case with CoAPO-18 catalysts [3,4].

Temperature programmed desorption (TPD) of NH_3 [1,2,5], as well as infrared studies of CO adsorbed at 77 K [6], is widely used to evaluate the strength of the Brønsted OH in these acidic materials. However, NH_3 and CO cannot be reliably used to study the acidity of CoAPOs because cobalt may act as an adsorptive centre for the probe molecules and, in this case, the Co–O(H) bond can be broken and the locus of the Brønsted acidity thereby modified [5,7]. In fact, the equilibrium between bridging OH (structure A) and coordinatively-unsaturated cobalt paired to POH (structure B), represented in scheme 1, is the best way to depict the Brønsted catalytic centres in CoAPO catalysts [5]. It is of note that the presence of Lewis acid sites, such as the unsaturated cobalt represented in the structure B of the scheme, is revealed by adsorbing water [4] or ammonia [5] or carbon monoxide [5,7].

Scheme 1.

To overcome the difficulty in revealing the Brønsted acidity of CoAPO catalysts by means of the adsorption of CO or NH_3, we propose the use of N_2 as molecular probe because it is a weaker base and unlikely to affect the catalytic centres. Recent experimental [8–10] and theoretical [11] studies have, in fact, revealed that N_2 is a very effective probe of the Brønsted acidity of zeolites and, as described below, it may be used with success to assess the Brønsted acidity of Co-containing aluminophosphates.

2. Experimental

CoAPO-18 catalysts were synthesized hydrothermally by heating cobalt aluminophosphate gel in the presence of N,N-diisopropylethylamine (DIPE) at 150–180°C for 10 days [1,4,12]. The empirical composition of the gels was typically $0.08CoO : Al_2O_3 : P_2O_5 : 0.16HAc : 1.70DIPE : 50H_2O$. FTIR experiments on a pelletized sample were performed using a Bruker IFS88

© J.C. Baltzer AG, Science Publishers

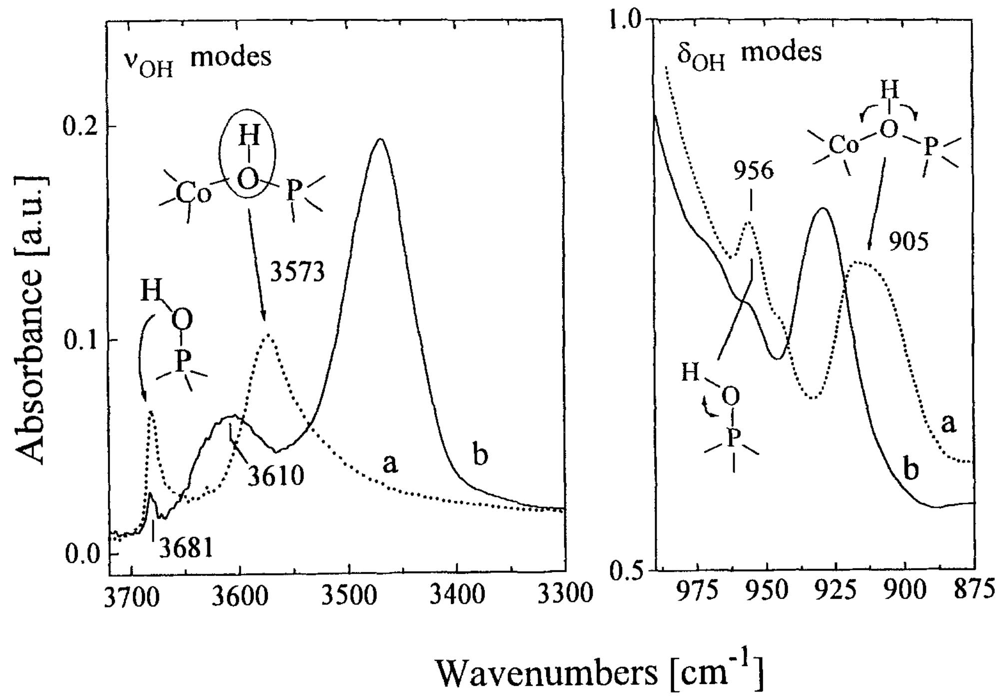


Fig. 1. IR spectra in the OH stretching and bending modes regions of CoAPO-18 catalyst (Co/Co + Al + P = 0.02). (a) Background; (b) in the presence of N_2 (10 Torr) at 77 K.

spectrometer at a resolution of 4 cm^{-1}. The spectrometer was equipped with a high vacuum variable temperature infrared cell (LB-100 of the Infraspac of Novosibirsk, Russia) which was permanently connected to a vacuum line (ultimate pressure $\leq 10^{-5}$ Torr). The cell permits to activate in situ the catalyst and to make adsorption–desorption experiments at 77 K. The organic template was removed from the as-synthesized catalyst with the procedure reported in ref. [4].

3. Results and discussion

Two broad and complex bands centred at ca. 3573

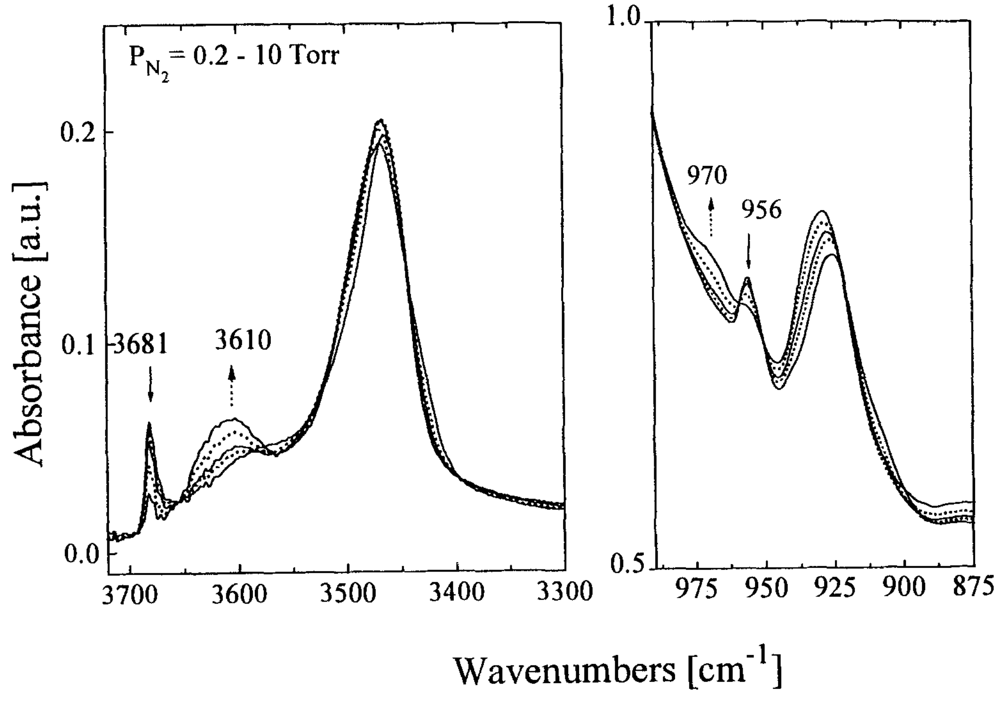


Fig. 2. N_2 adsorption on OH groups in CoAPO-18 catalyst: high coverages (up to an equilibrium pressure of 10 Torr).

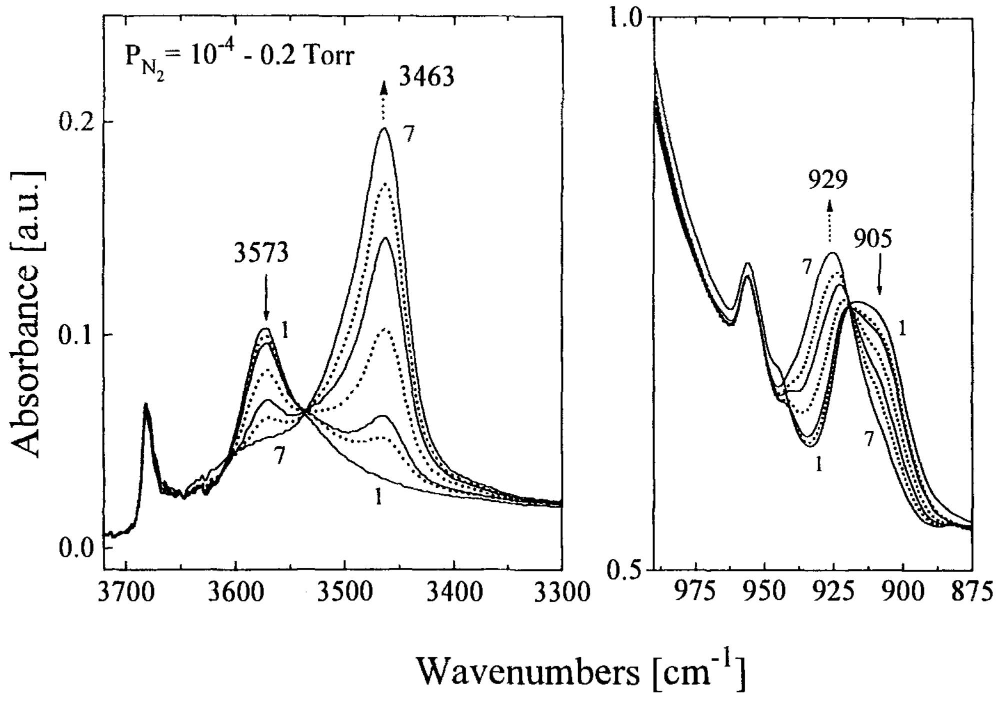


Fig. 3. N_2 adsorption on OH groups in CoAPO-18 catalyst: low coverages (up to an equilibrium pressure of 0.2 Torr).

and ca. 905 cm^{-1}, assignable to stretching and bending vibrations respectively of hydroxyls bridged between Co and P [4], are always present in the IR spectra of reduced CoAPO-18 catalysts (see dotted line in fig. 1). The composite nature of these absorptions was also revealed, but not discussed in detail, in ref. [4]. We note that the stretching absorption is composed of two bands at 3575–3565 and 3550–3500 cm^{-1} and the bending absorption of two bands at 905 and ca. 915 cm^{-1}; this suggests that two families of OH groups, probably located in two structurally different sites, exist in CoAPO-18. We also assigned the bands at 3681 and 956 cm^{-1} to stretching and bending vibrations respectively of P-OH present as framework defects.

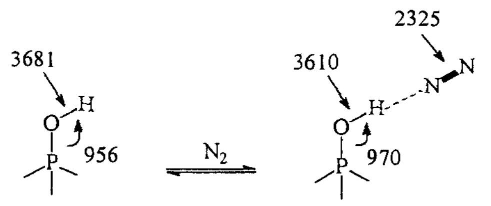
Finally, but not less importantly, we found that a band at ca. 945 cm^{-1} (in the sample of fig. 1 present as a shoulder of the 956 cm^{-1} band) is always detectable in CoAPO-18 catalysts [4], and because its intensity is related to the concentration of cobalt ions [13] it can be considered as a finger-print of the presence of Co ions in the ALPO-18 framework. The nature of this band is not discussed in detail: it is only important to recall that a Ti-sensitive mode at 960 cm^{-1}, attributed to stretching modes of $[SiO_4]$ units perturbed by the presence of Ti(IV), has been found in Ti-silicalites (ref. [14], and references therein). Similarly, the band at 945 cm^{-1} in CoAPO-18 can be assigned to a local mode produced by the stretching vibrations of $[TO_4]$ groups (T = P and Al) perturbed by the presence of Co(II) ions.

The bands at 3573 and 3681 cm^{-1}, as well as the related ones at 905 and 956 cm^{-1}, strongly decrease and, contemporaneously, two absorptions at 3468 and ca. 3610 cm^{-1} and two at 929 and ca. 970 cm^{-1} appear by adsorbing N_2 at 77 K ($p = 10$ Torr).

The spectra at different levels of dosing of N_2 reported in fig. 2 (N_2 pressure ranging from 10 to 0.2 Torr) reveal clearly that the stretching vibration of the P-OH at 3681 cm^{-1} shifts downward to 3610 cm^{-1} ($\Delta\nu_{OH} = -71$ cm^{-1}) and the bending at 956 cm^{-1} shifts upward to 970 cm^{-1} ($\Delta\delta_{OH} = +14$ cm^{-1}) upon the adsorption of N_2. In the pressure range 10 to 0.2 Torr of N_2 the bands at 3468 and 929 cm^{-1} are not significantly modified: the former shifts to 3463 cm^{-1} and becomes sharper, with a shoulder at higher frequency. The shape of the 3463 cm^{-1} band can be better evaluated from fig. 3.

The downward shift of the stretching and the upward shift of the bending of the P-OH groups upon the adsorption of N_2 is clear-cut evidence of the formation of H-bond complexes between N_2 and OH (see scheme 2). It is well established that, when hydroxyls are H-bonded to bases, the bending vibration shifts to the opposite direction than the stretching one [15].

The spectra corresponding to lower doses of N_2 (0.2



Scheme 2.

Table 1
Frequencies (cm^{-1}) of the Brønsted sites in CoAPO-18 and HZSM5 catalysts before and after the interaction with dinitrogen

	Before interaction	After interaction	$\Delta\nu_{OH}$	Before interaction	After interaction	$\Delta\delta_{OH}$	$\nu_{N\equiv N}$
P-OH[a]	3681	3610	−71	956	970	+14	2325
Co-O(H)-P[a]	3573	3463	−110	905	929	+24	2334
Si-OH[b]	3747	3710	−37	–	–	–	2325
Si-O(H)-Al[c]	3619	3499	−120	–	–	–	2334

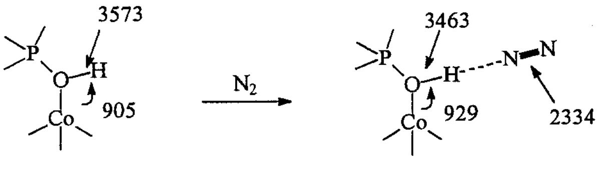
[a] This work. [b] Ref. [10]. [c] Ref. [9].

to 10^{-4} Torr, fig. 3) reveal that the band at 3573 cm^{-1} shifts to 3463 cm^{-1} ($\Delta\nu_{OH} = -110$ cm^{-1}) and that at 905 cm^{-1} shifts to 929 cm^{-1} ($\Delta\delta_{OH} = +24$ cm^{-1}) upon adsorption of N_2. As for the P-OH groups, also in the case of OH bridged between Co and P, the downward shift of the stretching and the upward shift of the bending upon N_2 dosage is clear-cut evidence of the formation of H-bonded dinitrogen complexes. Both experimental [10] and theoretical [11] studies demonstrate that the more stable complexes are in linear configuration (e.g. the end-on interaction in the OH/N_2 complexes, such as those represented in schemes 2 and 3, is preferred to the side-on). The H-bond in the complexes is composite in nature [11] and a review of the interactions occurring between adsorbates and surface sites is reported in ref. [16].

Another spectroscopic feature of the H-bond formation is the increase in the bandwidth and the band intensity of the hydroxyl vibrations [15]. Makarova et al. [17] revealed that a linear correlation exists between the shift ($\Delta\nu_{OH}$) produced by adsorbing molecules of increasing basicity and the variation of the intensity ($\Delta A/A_0$) of the stretching of the bridged OH in HZSM5. The values $\Delta A/A_0$ and $\Delta\nu_{OH}$ of the N_2 species adsorbed on CoAPO-18 fit very well the curve of Makarova's diagram, and this confirms that the band at 3573 cm^{-1} in CoAPO-18 is attributable to a bridging OH.

Assessing the OH acidic strength

The shift produced by H-bond formation ($\Delta\nu_{OH}$) upon introducing N_2 can be considered as a measure of the strength of the OH acidity. In fact, when N_2 interacts with hydroxyls of low intrinsic acidity, such as Si-OH or P-OH values of 37 and 71 cm^{-1} respectively (table 1) are obtained. These shifts are smaller than those produced by N_2 interacting with the more acidic bridging OH in HZSM5 [9] and CoAPO-18 (respectively 120 and 110 cm^{-1}). However, from the $\Delta\nu_{OH}$ values it is inferred that CoAPO-18 has a lower (or nearly the same) acidity as HZSM5 contrary to what we found by means of TPD of NH_3 [1]. This suggests that great care has to be exercised when data obtained by employing probe molecules of very different basicity are compared.



Scheme 3.

The adsorption of NH_3 on CoAPO-44, according to Lohse et al. [5], can affect greatly the Co–O bond in the [≡Co−O(H)−P≡] groups in that the equilibrium represented in scheme 1 should be in favour of the structure B, in which case the cobalt ions could act as Lewis centres on which the NH_3 is adsorbed. A similar mechanism is thought to operate when CO is adsorbed on CoAPO-18 [7]. These facts suggest that N_2 is an admirable probe for assessing the Brønsted acidity of acidic microporous catalysts, especially of those containing cobalt.

IR modes of the adsorbed N_2

Fig. 4 shows the spectra in the 2350–2300 cm^{-1} range of different doses of N_2 on CoAPO-18. Two distinct bands at 2334 and 2325 cm^{-1} are present at the maximum dosage of N_2 ($p = 10$ Torr). The band at 2325 cm^{-1} gradually disappears, following the same trend shown by those at 3610 and 970 cm^{-1} of the P-OH groups H-bonded to N_2 (fig. 2), when the pressure is gradually decreased to 0.2 Torr (fig. 4A) indicating that this vibration belongs to the complex P-OH/N_2 represented in scheme 2. Moreover, the band at 2334 cm^{-1} decreases when the pressure of N_2 is decreased to 10^{-4} Torr (fig. 4B) and, in this case, the behaviour is similar to the OH vibrations (bands at 3463 and 929 cm^{-1}) of bridging hydroxyls in the complex represented in scheme 3.

The N≡N stretching vibrations of the molecule adsorbed on Lewis and Brønsted acid centres [8–11] fall in the region 2350–2300 cm^{-1}. Whereas N_2 in the gas phase has only a Raman-active mode, the positive electric field associated to cations (such as alkali metal ions or protons in zeolites) induces a polarization, and a dipole moment, on the adsorbed molecule and the stretching vibration becomes IR-active. On the basis of their evolution upon N_2 dosage, the bands at 2325 and 2334 cm^{-1} can be assigned to the N≡N vibration of the dinitrogen H-bonded to P-OH and bridging OH respectively.

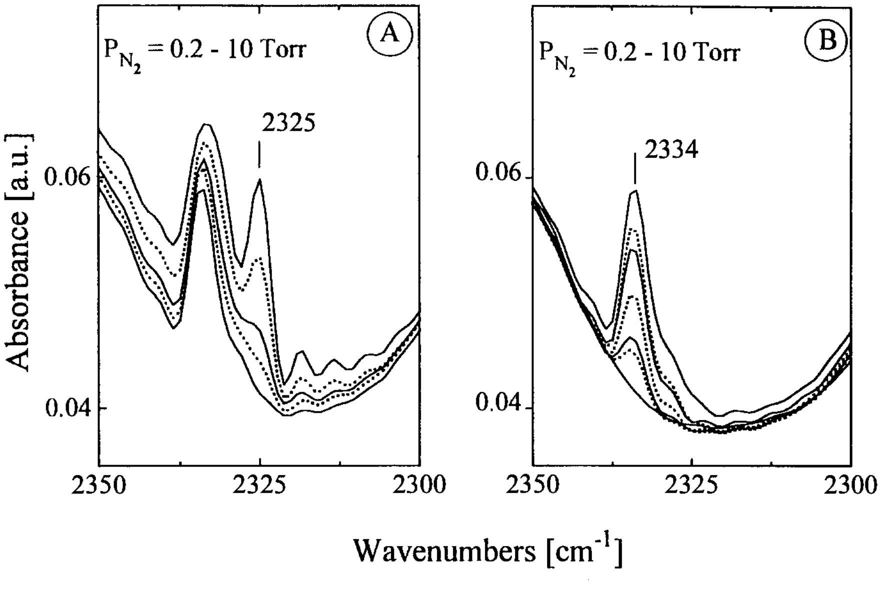


Fig. 4. N≡N stretching modes upon N_2 adsorption on CoAPO-18 catalyst. (A) High coverages (maximum equilibrium pressure = 10 Torr);(B) low coverages (maximum equilibrium pressure = 0.2 Torr).

Positive frequency shifts for the N≡N stretching vibration of adsorbed N_2 were found by using, as a reference, the Raman frequency of the N_2 physically adsorbed in zeolites (2324 cm^{-1} [18]) rather than that of the molecule in gas phase (2330.7 cm^{-1}). A good correlation exists [10] between frequency shifts and electric field of the cations in alkali-exchanged zeolites.

Similarly, taking as reference the value of the dinitrogen physically adsorbed in zeolites, the frequency shift of the bridging OH is larger than that of the less acidic P-OH. The frequency shift of the N≡N vibration should therefore also be considered as a tool for assessing the acidity of hydroxyl groups. However, the stretching frequencies of dinitrogen adsorbed on HZSM5 and CoAPO-18, which, as revealed by the $\Delta\nu_{OH}$ values, have different acidity, are similar (table 1). This is probably because the frequency shift of the N≡N vibration ($\Delta\nu_{N\equiv N}$) is very small compared to the OH frequency shift ($\Delta\nu_{OH}$) in the OH/N_2 complex, and it is not sufficiently sensitive to small variation of the proton acidity. It cannot be excluded that because the polarity of the aluminosilicates is probably different from that of the aluminophoshates, more appropriate reference values have to be used in the two cases. It would be sensible if the vibration of N_2 physically adsorbed in pure ALPO structures were used as reference for the CoAPO-18 catalysts.

Acknowledgement

Italian MURST and ASP and British EPSRC are acknowledged for grants and financial support.

References

[1] J. Chen and J.M. Thomas, J. Chem. Soc. Chem. Commun. (1994) 603.

[2] J. Chen, P.A. Wright, J.M. Thomas, S. Natarajan, L. Marchese, S.M. Bradley, G. Sankar, C.R.A. Catlow and P.L. Gai-Boyes, J. Phys. Chem. 98 (1994) 10216.

[3] J.M. Thomas, G.N. Greaves, G.Sankar, P.A. Wright, J. Chen, A.J. Dent and L. Marchese, Angew. Chem. Int. Ed. Engl. 33 (1994) 1871.

[4] L. Marchese, J. Chen, J.M. Thomas, S. Coluccia and A. Zecchina, J. Phys. Chem. 98 (1994) 13350.

[5] U. Lohse, R. Bertram, K. Jancke, I. Kurzawski, B. Parlitz, E. Löffler and E. Schreier, J. Chem. Soc. Faraday Trans. 91 (1995) 1163.

[6] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Petrini, G. Leofanti, M. Padovan and C. Otero Areàn, J. Chem. Soc. Faraday Trans. 88 (1992) 2959.

[7] L. Marchese, G. Martra, N. Damilano, S. Coluccia and J.M. Thomas, submitted to 11th ICC.

[8] F. Wakabayashi, J. Kondo, A. Wada, K. Domen and C. Hirose, J. Phys. Chem. 97 (1993) 10761.

[9] F. Wakabayashi, J. Kondo, K. Domen and C. Hirose, Catal. Lett. 21 (1993) 257.

[10] F. Geobaldo, C. Lamberti. G. Ricchiardi, S. Bordiga, A. Zecchina, G. Turnes Palomino and C. Otero Arean, J. Phys. Chem., in press.

[11] K.M. Neyman, P. Strodel, S.P. Ruzankin, N. Schlensog, H. Knözinger and N. Rösch, Catal. Lett. 31 (1995) 273.

[12] J. Chen, J.M. Thomas, R.P. Townsend and C.M. Lok, UK Patent Application 93186443 (1993).

[13] L. Marchese et al., unpublished results.

[14] D. Scarano, A. Zecchina, S. Bordiga, F. Geolbaldo, G. Spoto, G. Petrini, G. Leofanti, M. Padovan and G. Tozzola, J. Chem. Soc. Faraday Trans. 89 (1993) 4123.

[15] G.C. Pimentel and A.L. Mc Clellan, in: *The Hydrogen Bond* (Freeman, San Francisco, 1960).

[16] J. Sauer, P. Ugliengo, E. Garrone and V.R. Saunders, Chem. Rev. 94 (1994) 2095.

[17] M.A. Makarova, A.F. Ojo, K. Karim, M. Hunger and J. Dwyer, J. Phys. Chem. 98 (1994) 3623.

[18] D.D. Saperstein and A.J. Rein, J. Phys. Chem. 81 (1977) 2134.