ELSEVIER

Catalysis Today 54 (1999) 547–552

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The interaction of NO with Co^{2+}/Co^{3+} redox centres in CoAPOs catalysts: FTIR and UV–VIS investigations

E. Gianotti [a], L. Marchese [b,*], G. Martra [a], S. Coluccia [a]

[a] *Dipartimento di Chimica IFM, Università di Torino V. P. Giuria 7, I-10125 Torino, Italy*

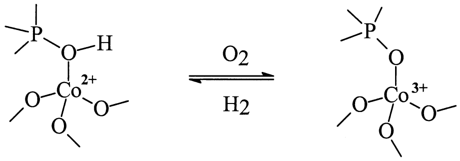
[b] *Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale 'A. Avogadro', c.so Borsalino 54, I-15100 Alessandria, Italy*

Abstract

The interaction of NO with Co^{2+}/Co^{3+} redox sites in CoAPO-18 and CoAPO-5 catalysts was studied by means of FTIR and diffuse reflectance UV–Vis spectroscopy both at 298 and 85 K. Two families of Co^{2+} sites were found in the CoAPO-18 structure. (A) *Ions in framework* [Co^{2+}(OH)P], associated with Brønsted acid sites which adsorb NO to produce dinitrosyls absorbing at 1903 and 1834 cm^{-1}; these dinitrosyl complexes are reactive, in that Co^{2+} is oxidized to Co^{3+} and N_2O is formed. (B) S*tructural defects* Co^{2+} (Lewis acid sites) which stabilize dinitrosyls absorbing at 1900 and 1813 cm^{-1}. The NO adsorption both on reduced and, more significantly, on oxidised CoAPO-18 also leads to the formation of $NO_2^{\delta+}$ adsorbed species. It was found that the two kinds of dinitrosyl complexes have different reactivity in presence of oxygen. Both families of sites are also present in CoAPO-5 catalysts on which, however, the redox reaction upon NO adsorption does not occur significantly. ©1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Metal-aluminophosphates molecular sieves (MeAPOs) are of growing interest because of their potential use as catalysts for organic reactions [1]. Among these, CoAPOs, in which cobalt ions substitute for some Al^{3+} ions into the aluminophosphate framework, appear very attractive for their catalytic properties [2]. CoAPO-18, for instance, is a microporous acid catalyst for the conversion of methanol to light olefins which occurs on Brønsted hydroxyl groups (OH bridged between Co^{2+} and P^{5+} of the AEI framework) [3,4]. XANES and EXAFS [4], FTIR [4–6] and DR UV–Vis [6] studies revealed that the Brønsted acidity is associated with Co^{2+}/Co^{3+} redox couples: in fact, when Co^{2+} framework ions are oxidized to Co^{3+} (in oxygen at 823 K), the Brønsted acidity disappears (Scheme 1). Such behavior also reveals the potential redox properties of the catalyst which may have some bearings on the use in selective catalytic reduction (SCR) of NO_x with hydrocarbons [7–11].



Scheme 1.

Though NO has been frequently used as molecular probe of transition metal ions in zeolites [12–13], studies of NO dissociation on metal ion-exchanged ZSM-5 have opened more attractive prospective. It

---

* Corresponding author. Fax: +39-11-6707855.
E-mail address: marchese@ch.unito.it (L. Marchese)

PII: S0920-5861(99)00216-3

was found, in fact, that Cu/ZSM-5 has high activity towards the decomposition of NO directly to N_2 and O_2, and this property was attributed to the presence of redox Cu^+/Cu^{2+} couples [14–16]. More recently, many efforts have also been focused on cobalt ion-exchanged zeolites (CoZSM-5, Co-mordenite, Co-Y, Co-X, Co-ferrierite) as they revealed an high activity in the selective catalytic reduction of NO_x by ethene and methane in oxidising atmosphere [8,9,11,12,17,18].

In view of the importance of such reaction in environmental chemistry, it is interesting to extend this kind of studies to other cobalt-containing molecular sieves, and, in such a context, CoAPO-18 catalyst is very promising. In fact, besides bi-functional centers (framework Co^{2+} ions [Co(OH)P] in tetrahedral coordination may have both Brønsted acidity and redox behavior), CoAPO-18 has coordinatively-unsaturated Co^{2+} Lewis acid centres [6] and it is here shown that these two families of cobalt ions behave differently towards NO adsorption/decomposition. However, because of the complexity of this system, it was useful to compare with another Co-aluminophosphate, CoAPO-5 (AFI structure), in which acid, redox and Lewis centres are also present [19]. The main scope of this work is to clarify the nature of the interaction of NO with the various cobalt ions in CoAPO-18 and CoAPO-5 catalysts. Catalytic tests of NO decomposition in different conditions are in progress.

2. Experimental

Details of the synthesis of CoAPO-18 catalysts are reported in Ref. [5]. *N,N*-diiso-propylethylamine (DIPE) was used as organic template and a gel with a composition of $0.08CoO : Al_2O_3 : P_2O_5 : 0.16Hac : 1.7DIPE : 50H_2O$ was crystallised in a teflon-lined autoclave at 453 K for 10 days. CoAPO-5 was synthesised by using Triethylamine (TEA) as templating agent and a gel with a composition of $0.04CoO:0.48Al_2O_3:0.75P_2O_5:0.08Hac:0.8TEA:35H_2O$ was crystallised at 463 K for 24 h.

The organic templates were removed from the as-synthesised catalysts prior to the spectroscopic analysis with the following in situ procedure: (a) heating in vacuo with a slow increase of temperature (5–10 K/min) up to 823 K; (b) admitting 80–100 Torr O_2 and calcining 3–4 h at 823 K (the oxygen was changed three times) and (c) evacuating at 823 K for 30 min (final pressure $\leq 10^{-5}$ Torr). After these treatments the CoAPO-18 catalyst had green colour, whereas the CoAPO-5 was greenish-blue. The samples were finally reduced in H_2 (80–100 Torr) at 623 K and subsequently evacuated at 823 K for 30 min. Both catalysts had, in this case, blue colour. NO adsorption experiments were run on the catalysts both after calcination and reduction.

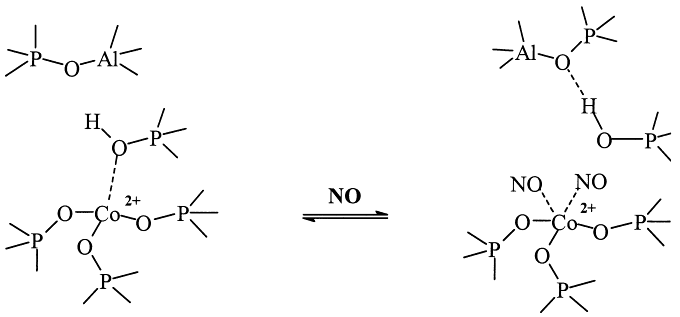
The FTIR spectra (resolution of 4 cm^{-1}) were collected on pelletised samples using a Bruker IFS88 spectrometer. The IR spectra of adsorbed NO are shown in absorbance scale, having subtracted the background due to the bare sample. Diffuse reflectance (DR) UV–Vis experiments were performed on powdered samples by using a Perkin–Elmer (Lambda 19) spectrometer equipped with an integrating sphere attachment.

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 1 shows the FTIR spectra of NO adsorbed at 85 K on reduced CoAPO-18 catalyst. *At low* NO *dosages* ($p \leq 0.02$ mbar, Fig. 1(A), curves 1–3), two bands at 1903 and 1834 cm^{-1}, whose intensity grows up by increasing the NO pressure, are present. These bands are assigned to the symmetric and asymmetric stretching modes of dinitrosyl species adsorbed on Co^{2+} ions [9,11–13,20]. A very sharp peak at 1869 cm^{-1} due to liquid-like NO [21] is also observed.

The formation of the dinitrosyls has a deep effect on the band of the OH-stretching vibration of the Brønsted [Co–O(H)–P] groups which absorb at 3571 cm^{-1} [4–6]. It was observed, in fact, that the band was completely depleted, whereas a new much broader band at 3104 cm^{-1} was formed, and from this result it was argued that H-bonding effects occur by NO adsorption [22]. The overall phenomenon and the size of the shift ($\Delta\nu = 467\ cm^{-1}$) resembles that observed upon CO adsorption [6] and explained by a ligand displacement forcing the OH groups to H-bond with structural oxygens of the aluminophos-



Scheme 2.

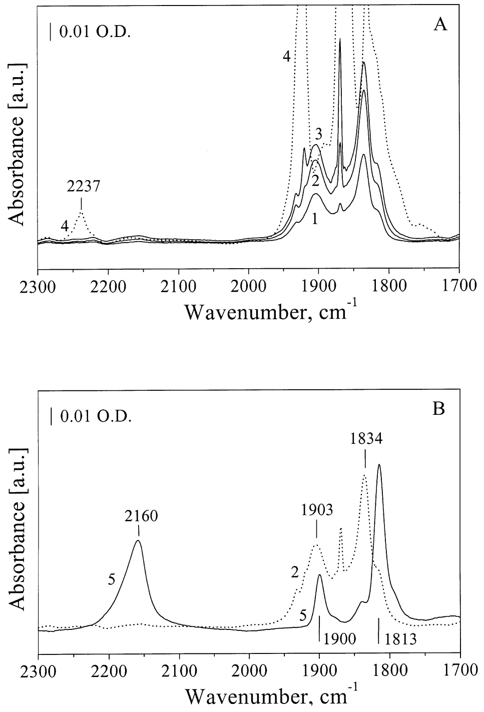


Fig. 1. FTIR spectra of NO adsorbed at 85 K on reduced CoAPO-18 catalyst. Sect A: (1–3) spectra under increasing NO pressure ($p_{\max}$ = 0.02 mbar); (4) 1 mbar NO. Sect B: (2) is the same as in Sect A, 5) after warming up to 153 K (in vacuo).

phate framework. We propose that nitric oxide modifies the Brønsted acid centres by a similar displacement process (see Scheme 2). All Brønsted sites are involved in this process.

At higher NO *dosages* (Fig. 1(A), curve 4; p = 1 mbar), new very intense bands appear in the 2000–1750 cm^{-1} region, due to $(NO)_x$ clusters [21], together with a much weaker band at 2237 cm^{-1}, which is due to N_2O species [21] adsorbed on Co^{2+} ions. The latter species were identified by adsorbing directly N_2O on the CoAPO-18. *By evacuating and warming up* (from 85 to 153 K) the sample (Fig. 1(B), curve 5), new bands were observed: a doublet at 1900 and 1813 cm^{-1} also attributable to dinitrosyls on Co^{2+} ions and a band at 2160 cm^{-1} due to $NO_2{}^{\delta+}$ adsorbed species [9,20]. All these species are therefore formed through activated processes. In particular, the presence of surface $NO_2{}^{\delta+}$ complexes suggests that NO oxidation is occurring.

While the dynitrosyl complexes at 1903–1834 cm^{-1} are observed immediately after the admission of small doses of NO, and yield to N_2O, those at 1900–1813 cm^{-1} are produced slowly, either at temperature higher than 153 K or in presence of an high NO coverages. The two types of dinitrosyls have, therefore, a different origin and this confirms our previous suggestions that two families of Co^{2+} ions are present in CoAPO-18 [5,6]. It is proposed that the dinitrosyls at 1900–1813 cm^{-1} are formed on defect Lewis acid Co^{2+} sites (those which are not related to [Co–O(H)–P] groups) through an activated mechanism which may involve the breaking of some framework Co–O bonds. These dinitrosyls are adsorbed irreversibly even at 298 K (*vide infra*).

Fig. 2 shows the IR spectra of NO adsorbed at 298 K on both CoAPO-18 and CoAPO-5 catalysts. In presence of NO gas (15 mbar), and after prolonged time of contact (30 min), two couples of bands at 1910–1837 and 1898–1813 cm^{-1} for CoAPO-18 (curve a — the 1910 cm^{-1} band being a shoulder of the 1898 cm^{-1} one) and at 1914–1844, 1895–1813 cm^{-1} for CoAPO-5 (curve a′) are observed. It is therefore inferred that two families of dinitrosyls, although in

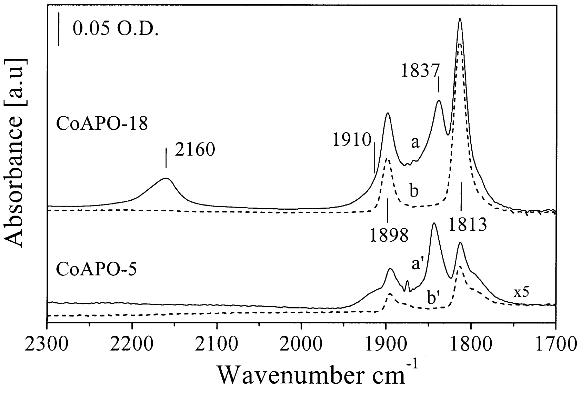


Fig. 2. FTIR spectra of NO adsorbed at 298 K on reduced CoAPOs: a and a′) after 30 min of contact with 15 mbar NO; b and b′) after evacuation for 30 min. The absorbance scale for the CoAPO-5 is expanded five times.

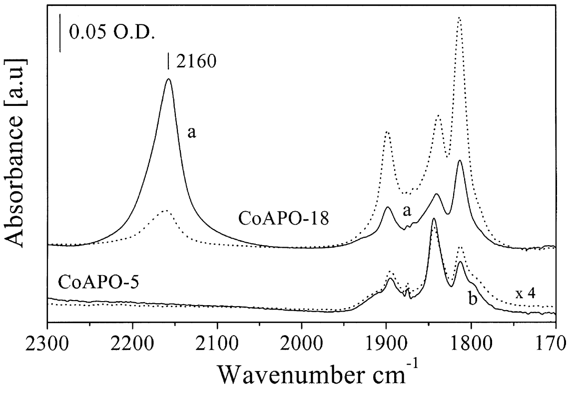


Fig. 3. FTIR spectra of NO (15 mbar) in contact for 30 min with oxidised CoAPOs (curves a and b) compared to the spectra of 15 mbar NO in contact for the same time with reduced samples (dotted lines). The absorbance scale for the CoAPO-5 is expanded four times.

different concentration, are present, also at 298 K, on both catalysts. It is worth to note that $NO_2^{\delta+}$ species (band at 2160 cm^{-1}) are only formed, after prolonged time of contact, on CoAPO-18. As in the experiment at 85 K, the band at 3571 cm^{-1} of the bridged OH shifts to 3104 cm^{-1}, and this is particularly evident in the case of CoAPO-18 [23]. The NO adsorption mechanism represented in Scheme 2 is therefore valid also at 298 K.

The evolution of all these species as a function of NO pressure and time of contact was followed in a series of systematic experiments and will be presented in a separate contribution. We only notice here that, in the case of CoAPO-18, the bands at 1898–1813 and 2160 cm^{-1} increase in intensity as the time of contact with NO (15 mbar) increases, whereas those at 1910–1834 cm^{-1} decrease. The two couples of bands at 1914–1844 and 1895–1813 cm^{-1} for the CoAPO-5 behave similarly, although, in this case, the variations are less significant.

Upon subsequent evacuation of CoAPO-18 for 30 min at 298 K, the couple of bands at 1910–1837 cm^{-1} and the band at 2160 cm^{-1} completely disappear whereas the couple at 1898–1813 cm^{-1} remains (Fig. 2, curve b). At the same time, the band at 3751 cm^{-1} of the bridged OH is restored but with lower intensity, suggesting that some of the [Co(OH)P] centres are transformed.

The bands at 1898–1813 cm^{-1}, which are irreversibly formed on CoAPO-18 (curve b), and those at 1895–1813 cm^{-1}, for the CoAPO-5 (curve b′), are assigned to dinitrosyls which are more tightly bonded to Co^{2+} Lewis acid centres. These complexes are not reactive in presence of O_2. Conversely, their oxidation to NO_2 occurs rapidly, as demonstrated both spectroscopically and by catalytic tests, in an excess of NO and in presence of O_2 [24].

When NO is adsorbed on oxidized CoAPO-18 catalysts (Fig. 3, curve a), the bands due to dinitrosyls on Co^{2+} are three times less intense than on the reduced samples (Fig. 3, dotted line). This is due to the fact that during the oxidation treatment a fraction of Co^{2+} is transformed into Co^{3+}, the ions more involved in such process being those responsible of the presence of bridged OH groups [6]. In contrast, the band at 2160 cm^{-1}, due to $NO_2^{\delta+}$ adsorbed species, is five times more intense on oxidised CoAPO-18, and this is a clear cut evidence that Co^{3+} ions promote the oxidation of NO to NO_2. This result suggests that the activated processes which lead to the formation of $NO_2^{\delta+}$ on the reduced CoAPO-18 catalysts (Figs. 1 and 2), also produce some Co^{3+} ions.

The absence of $NO_2^{\delta+}$ species upon NO adsorption on CoAPO-5 catalysts (Fig. 2), even on the sample treated in oxygen at 823 K (Fig. 3, curve b), demonstrates that these systems do not show a redox behavior. Accordingly, it was proposed that only a minor fraction of Co^{2+} ions transforms into Co^{3+} in CoAPO-5 catalysts [19].

3.2. Diffuse reflectance UV–Vis spectroscopy

While the IR spectroscopy gives information on the molecular complexes formed at the surface of the catalysts, and suggests that Co^{2+}(OH)P centres in CoAPO-18 are modified upon NO adsorption, DR UV–Vis spectroscopy may provide direct evidences on the oxidation state and coordination of the cobalt ions.

As synthesised CoAPOs catalysts have bright blue colour which is typical of Co^{2+} ions in tetrahedral coordination. Their electronic spectra were taken as a proof that cobalt divalent ions substitute for some Al^{3+} ions of the aluminophosphate framework [6,25,26]. Upon calcination in O_2 at 823 K the colour of the samples changes to green, from which fact the presence of Co^{3+} sites was inferred [6,25–28]. By reduction in H_2 at 623 K the blue colour reappears indicating that cobalt ions are now again in a bivalent state and in tetrahedral coordination.

DR UV–Vis spectroscopy (Fig. 4(A)) was used to obtain direct information on the oxidation state of cobalt ions before (curve a) and after (curve b) NO adsorption at 298 K on reduced CoAPO-18. The absorptions (triplet bands) in the visible (20 000–15 000 cm^{-1}) and in the near IR (10 000–4000 cm^{-1}) were assigned respectively to $^4T_1(P) \leftarrow {}^4A_2(F)$ and $^4T_1(F) \leftarrow {}^4A_2(F)$ ligand field transitions of tetrahedral Co^{2+} ions [6,29]. The triplet bands somewhat decrease in intensity after NO admission and new absorptions in the 45 000–20 000 cm^{-1} appear; in this region a very intense band at ca. 38 700 cm^{-1} dominates the spectrum. This band may be assigned to ligand to metal charge transfer (LMCT) transitions of NO complexes adsorbed on Co^{3+} (*vide infra*). When the excess of NO is removed by evacuating the CoAPO-18 catalyst (Fig. 4(A), curve c), the 38 700 cm^{-1} band decreases and, at the same time, a doublet at 30 500 and 24 500 cm^{-1} increases.

These results suggest that a fraction of Co^{2+} ions are irreversibly oxidised to Co^{3+} in presence of NO at 298 K. In fact, thermally oxidised catalysts (Fig. 4(B), curve a), have electronic transitions at 30 500 and 24 500 cm^{-1} (charge transfers) and at around 9000 cm^{-1} ($^5T_2 \leftarrow {}^5E$) associated with tetrahedral Co^{3+} centres [6]. All these bands decrease in intensity upon NO adsorption (curve b), whereas a new band at 38 500 cm^{-1} is formed. Such an effect is not completely reversible. After evacuation at 298 K the doublet at 30 500 and 24 500 and the band at 9000 cm^{-1} are not completely restored. These facts confirm our proposal based on the IR data presented above as they demonstrate that after NO adsorption some Co^{3+} can be reduced.

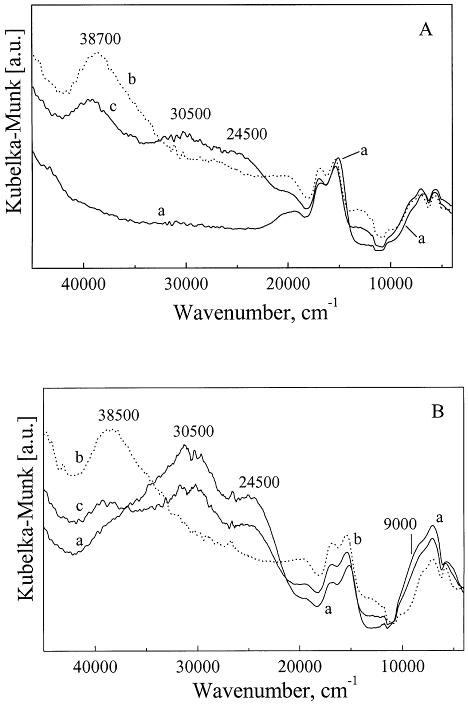


Fig. 4. Diffuse reflectance UV–VIS spectra of reduced (Sect. A) and oxidised (Sect. B) CoAPO-18 before (curves a) and after (curves b) NO adsorption at 298 K; (c) were obtained by evacuating the samples for 2 h at 298 K.

4. Conclusion

FTIR and diffuse reflectance UV–Vis studies suggest that, upon NO adsorption on reduced CoAPO-18 catalysts, a redox reaction occurs which yields to N_2O formation and to the oxidation of a fraction of Co^{2+} ions to Co^{3+}. A small amount of $NO_2^{\delta+}$ is also slowly formed during such process. However, $NO_2^{\delta+}$ species are more abundantly formed when NO is adsorbed directly on oxidized CoAPO-18, and at the same time a fraction of Co^{3+} is reduced. The redox mechanism is not effective on CoAPO-5 catalysts, which show a low propensity to be oxidized. We propose that the Co^{2+} ions that are oxidized in presence of NO are those responsible for Brønsted acid sites [Co^{2+}(OH)P], which are more abundant in CoAPO-18.

Acknowledgements

Support by the ‘Ministero dell’Universita’ e della Ricerca Scientifica e Tecnologica’ (MURST), Confinan ziamento 1998, is acknowledged.

References

[1] I.W.C.E. Arens, R.A. Sheldon, M. Wallau, U. Schuchard, Angew. Chem. Int. Ed. Engl. 36 (1997) 1144.
[2] J.M. Thomas, Angew. Chem. Int. Ed. Engl. 33 (1994) 913.
[3] J. Chen, J.M. Thomas, J. Chem. Soc. Chem. Commun. (1994) 603.
[4] J.M. Thomas, G.N. Greaves, G. Sankar, P.A. Wright, J. Chen, A.J. Dent, L. Marchese, Angew. Chem. Int. Ed. Engl. 33 (1994) 1871.
[5] L. Marchese, J. Chen, J.M. Thomas, S. Coluccia, A. Zecchina, J. Phys. Chem. 98 (1994) 13350.
[6] L. Marchese, G. Martra, N. Damilano, S. Coluccia, J.M. Thomas, Stud. Surf. Sci. Catal. 101 (1996) 861.
[7] F. Witzel, G.A. Sill, W.K. Hall, J. Catal. 149 (1994) 229.
[8] Y. Li, J.N. Armor, J. Catal. 150 (1994) 376.
[9] Y. Li, T.L. Slager, J.N. Armor, J. Catal. 150 (1994) 388.
[10] D.B. Lukyanov, G. Sill, J.L. d’Itri, W.K. Cant, J. Catal. 153 (1995) 265.
[11] B.J. Adelman, T. Beutel, G.D. Lei, W.H.M. Sachtler, J. Catal. 158 (1996) 327.
[12] K.A. Windhorst, J.H. Lunsford, J. Am. Chem. Soc. Farady Trans. 97 (1975) 1407.
[13] T. Izuka, J.H. Lunsford, J. Mol. Catal. 8 (1980) 391.
[14] W.-X. Zhang, H. Yahiro, N. Mizuno, J. Izumi, M. Iwamoto, Chem. Lett. (1992) 851.
[15] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shiona, T. Namura, M. Anpo, J. Catal. 136 (1992) 510.
[16] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa, S. Kagawa, J. Phys. Chem. 96 (1992) 9360.
[17] W.X. Zhang, H. Yahiro, M. Iwamoto, J. Chem. Soc. Faraday Trans. 91 (1995) 767.
[18] D.B. Lukyanov, E.A. Lombardo, G.A. Sill, J.L. d’Itri, W.K. Hall, J. Catal. 163 (1996) 447.
[19] P.A. Barret, G. Sankar, C.R.A. Catlow, J.M. Thomas, J. Phys. Chem. 100 (1996) 8977.
[20] A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell, Stud. Surf. Sci. Catal. 101 (1996) 661.
[21] J. Lanee, J.R. Ohlsen, Progress Inorg. Chem. 27 (1980) 465.
[22] E. Gianotti, L. Marchese, G. Martra, S. Coluccia, Proc. 12th Int. Zeolite Conference, Baltimore, 5-10 July 1998.
[23] E. Gianotti, L. Marchese, G. Martra, S. Coluccia, unpublished results.
[24] L. Marchese, E. Gianotti, G. Martra, S. Coluccia, B. Palella, R. Pirone, P. Ciambelli, submitted to the 12th International Congress on Catalysis, 9–14 July, 2000, Granada, Spain.
[25] R.A. Schoonheydt, R. De Vos, J. Pelgrims, H. Leeman, Stud. Surf. Sci. Catal. 49 (1989) 559.
[26] K.Y. Lee, M. Chon, J. Catal. 126 (1990) 667.
[27] B. Kraushaar-Czarnetszki, W.G. Hoogervorst, R.R. Andrea, C.A. Emeis, W.H.J. Stork, J. Chem. Soc. Faraday Trans. 87 (1991) 891.
[28] K. Nakashiro, Y. Ono, Bull. Chem. Soc. Jpn. 66 (1993) 9.
[29] B.N. Figgis, Introduction to Ligand Field, Wiley-Interscience, New York, 1966.