ELSEVIER

Catalysis Today 75 (2002) 359–365

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Catalytic $DeNO_x$ activity of cobalt and copper ions in microporous MeALPO-34 and MeAPSO-34

A. Frache [a], B. Palella [b], M. Cadoni [a], R. Pirone [c], P. Ciambelli [d], H.O. Pastore [e], L. Marchese [a,f,*]

[a] *Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "A. Avogadro", C.so Borsalino 54, 15100 Alessandria, Italy*

[b] *Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, P.le V. Tecchio 80, 80125 Napoli, Italy*

[c] *Istituto di Ricerche sulla Combustione, CNR, P.le V. Tecchio 80, 80125 Napoli, Italy*

[d] *Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, 84084 Fisciano (SA), Italy*

[e] *Instituto de Química, Universidade Estadual de Campinas, 13083-970 Campinas, SP, Brazil*

[f] *Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy*

Abstract

A combined spectroscopic and catalytic study of the NO reactivity on microporous aluminophosphates, with chabasite-related structure, CoAPO-34, CuAPO-34 and CuAPSO-34, is reported. NO and CO adsorption were monitored by FTIR spectroscopy, and revealed that Co^{2+}/Co^{3+} and Cu^{+}/Cu^{2+} redox couples, the sites responsible for the catalytic activity, are present in these catalysts. CoAPO-34 catalysts showed exceptionally high performances in the oxidation of NO to NO_2, and poor activity in other $DeNO_x$ reactions. Copper-based aluminophosphates and silico-aluminophosphates, besides good performances in the NO oxidation to NO_2, showed good activity in the N_2O decomposition even in the presence of oxygen or water in the feed. The presence of silicon has beneficial effects both on the thermal and hydrothermal stability of the zeolitic structure, as well as on the catalytic performances of the metal-aluminophosphates.

Keywords: $DeNO_x$ reaction; Cobalt and copper ions; FTIR spectroscopy

1. Introduction

NO_x abatement in gas emissions from both fixed and mobile sources is a relevant environmental issue, which may be tackled by means of catalytic processes [1]. Thus, an expanding amount of new materials are nowadays continuously prepared and studied as possible catalysts for $DeNO_x$ reactions. Among these, zeolite-based systems are of growing interest for their high performances under clean laboratory conditions, although their lack of stability under real operating conditions seems to be an unavoidable limitation [1–3]. In this context, metal-containing aluminophosphates and silicon-aluminophosphates with redox properties [4,5], appear attractive for their potentially higher resistance to the presence of water vapour, although they have not been extensively studied for $DeNO_x$ reactions. Good catalytic performances of Cu-SAPO-34 in selective reduction (SCR) of NO with propene [6], Cu–Me-AlPO-11 (Me = Mg^{2+} and Zn^{2+}) in NO decomposition [7] and CoAPO-34 in NO oxidation to NO_2 [8], were reported. Although spectroscopic studies of NO and CO adsorption on

* Corresponding author. Present address: Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "A. Avogadro", C.so Borsalino 54, 15100 Alessandria, Italy.
E-mail address: leonardo.marchese@mfn.unipmn.it (L. Marchese).

0920-5861/02/$ – see front matter
PII: S0920-5861(02)00065-2

these catalysts [8,9] enlightened their potential applications, the examples of catalytic studies concerning the use of new metal-aluminophosphate molecular sieves in NO_x reactions are limited.

In our previous work [8], we found that the activity of CoAPO-34 systems in the oxidation of NO is related to the presence of redox Co^{3+}/Co^{2+} couples involving the metal inserted into the chabasite framework. However, when probed in NO and N_2O decomposition, as well as in NO reduction by CO, these catalysts revealed a surprisingly poor activity, and this prompted us to focus our attention to Cu-containing aluminophosphates and silico-aluminophosphates.

In this study we report on a comparison between catalytic and spectroscopic properties of CoAPO-34, CuAPO-34 and CuAPSO-34 catalysts. Whilst copper-containing aluminophosphates monitored so far in NO_x reactions were prepared via ion-exchange procedure [6,7], in the present work CuAPO-34 and CuAPSO-34 were prepared via one-pot synthesis in which copper salts were added directly in the synthesis gels of the materials. We have found that this methodology is more convenient and leads to very interesting catalysts.

2. Experimental

2.1. Materials syntheses

CoAPO-34 catalyst was prepared by using morpholine and following the procedure reported in Ref. [8]. CuAPO-34 and CuAPSO-34 were synthesised by adding CuO at a diluted solution of orthophosphoric acid and, after stirring at 80 °C to a complete dissolution, $Al(OH)_3$ was added at room temperature with vigorous stirring until a homogeneous gel was obtained. Subsequently, SiO_2 (only for CuAPSO-34), morpholine and HF (only for CuAPO-34) were added always under stirring. The resulting gels, with composition of xCu:$(1.0 - x)$Al:0.90P:0.25Si:0.35HF:1.25 morpholine:50H_2O ($x = 0.04$–0.08) molar ratio, were crystallised in a Teflon-lined autoclave under autogeneous pressure at 190 °C for 7–10 days. The crystalline products were filtered, washed with water and dried in open air. Pure, and highly crystalline, phases of CuAPO-34 with ALPO-34-type structure [10] and CuAPSO-34 with SAPO-34-type structure [10,11] were obtained. Cu-ZSM-5 was prepared by previously reported ion-exchange procedure [12] with commercial powders of the parent zeolite (zeolyst Si/Al = 25, Cu/Al = 0.29). The metal loading in the final products was determined by ICP-AE yielding 1.84 wt.% for CoAPO-34, 2.06 wt.% for CuAPO-34, 1.1 wt.% for CuZSM-5 and for two CuAPSO-34 samples, named as CuAPSO-34(1.23) and CuAPSO-34(2.14), the values found were 1.23 and 2.14 wt.%, respectively.

2.2. Materials characterisation and catalysis

XRD measurements, both at room and higher temperatures were collected using a Shimadzu XRD 6000, with Cu Kα radiation. Diffractograms were obtained at 2° 2θ/min. The experiments at high temperatures were conducted with the aid of a Shimadzu heating accessory model HA1001, at a heating rate of 10 °C/min. FTIR spectra of adsorbed CO and NO on template-free, pelletised samples were recorded at room temperature with a Bruker IFS88 spectrometer. The pre-treatments to activate the catalysts were: (a) heating at 5 °C/min under vacuum up to 550 °C; (b) heating at 550 °C for 1–2 h; (c) heating at 550 °C for 20–25 h under oxygen (100 Torr), and by changing the gas phase two to three times; (d) outgassing at 550 °C for 1–2 h. These treatments led to cobalt-containing catalysts where both Co^{2+} and Co^{3+} ions were simultaneously present within the zeolite framework [13–15]; hereafter named *oxidised catalysts*. However, it is known that by outgassing copper-containing zeolites at high temperatures, a significant fraction of copper ions can be reduced to monovalent, Cu^+ state, whereas heating at 400–500 °C in hydrogen was needed to reduce to divalent state all cobalt ions in CoAPOs. The Co-containing samples treated by that procedure are hereafter named *reduced catalysts*.

Catalytic activity measurements were carried out in a flow apparatus by using a quartz fixed bed micro-reactor. The standard conditions adopted for the feed of the NO oxidation were: NO (2000 ppm); O_2 (5 vol.%) and balance He; weight/feed ratio $(W/F) = 0.042\,\mathrm{g\,s\,Ncm^{-3}}$. N_2O decomposition dry tests were carried out as follows: N_2O (600 ppm) and balance He, $W/F = 0.11\,\mathrm{g\,s\,Ncm^{-3}}$. Wet gas feeds were obtained by saturating helium stream at

room temperature. The overall water concentration of the feed in N_2O decomposition tests was 2.0 vol.%. The concentration of NO, NO_2, N_2O, and O_2 were monitored by using Hartmann and Braunn continuous analysers for NO and N_2O (URAS 10E), O_2 (MAGNOS 6G) and a catalytic converter (CGO-K) for NO_2. After template removal, as described in Ref. [8], the cobalt-containing catalysts were treated at 600 °C under H_2 flow for 12 h, whereas the copper-containing catalysts at 600 °C under He flow for 2 h. Finally, CuZSM-5 and CuAPSO-34(1.23) were treated 60–80 h at 550-600 °C in helium streams saturated with H_2O.

3. Results and discussion

Fig. 1 shows the XRD patterns of SAPO-34, CoAPSO-34 and CuAPSO-34 recorded at 900 °C, and suggests that in all cases the chabasite structure was essentially retained at this temperature [16]. However, only the sample which does not contain transition metal ions keeps a nearly pure chabasite phase. Additionally, there are significant differences between the spectra of cobalt and copper-containing MeAPSO-34 samples. In fact, CuAPSO-34 showed a behaviour similar to SAPO-34, indicating a high thermal resistance of the framework, only a small fraction of the material is transformed to tridimite dense phase (reflection at $2\theta = 21.3$ value). CoAPSO-34 instead, showed a higher loss of the initial crystallinity and the appearance of a higher fraction of tridimite phase. As a consequence, Cu-containing systems seem to be more stable than the corresponding Co-containing ones.

A similar trend of stability was found when the catalysts were treated under hydrothermal conditions, e.g. CuAPSO-34 samples are more stable in the presence of H_2O at 600 °C, and for this reason the efforts were focused over copper–silico-aluminophosphates as potential catalysts in $DeNO_x$ reactions [6,17].

FTIR spectra of CO adsorbed on copper-based systems, CuAPO-34 and CuAPSO-34, are shown in Fig. 2A. CO adsorption at room temperature on CuAPO-34 produced two sharp bands at 2175 and 2147 cm^{-1} (lower curves, spectrum 1) which gradually decreased in intensity with the CO pressure until, after evacuating the sample at RT (spectrum 2), a new sharp band at 2152 cm^{-1} was formed.

Similar results were obtained for Cu-ZSM-5 and suggested that $Cu^+(CO)_2$ dicarbonyl species were formed at higher CO dosages [18,19], and that the dicarbonyls transformed into monocarbonyl $Cu^+(CO)$

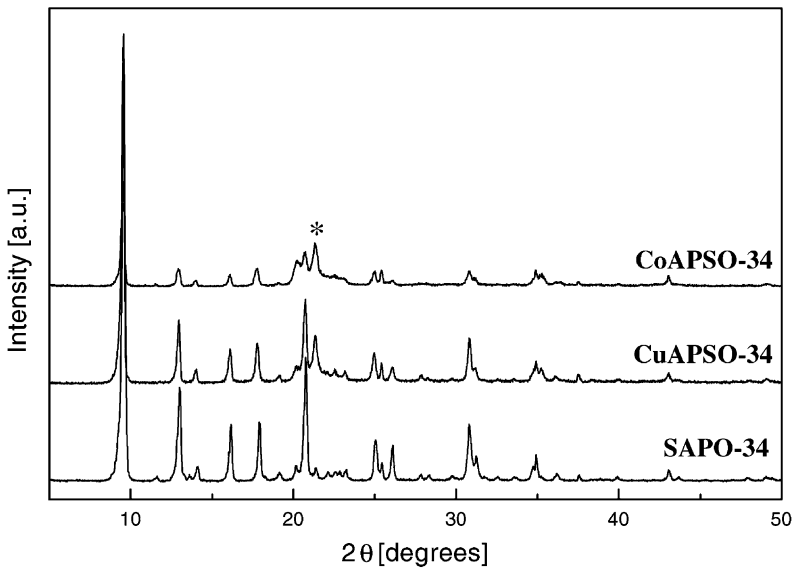

Fig. 1. XRD patterns of SAPO-34, CuAPSO-34 and CoAPSO-34 at 900 °C after template removal. (∗) reflection due to tridimite dense phase.

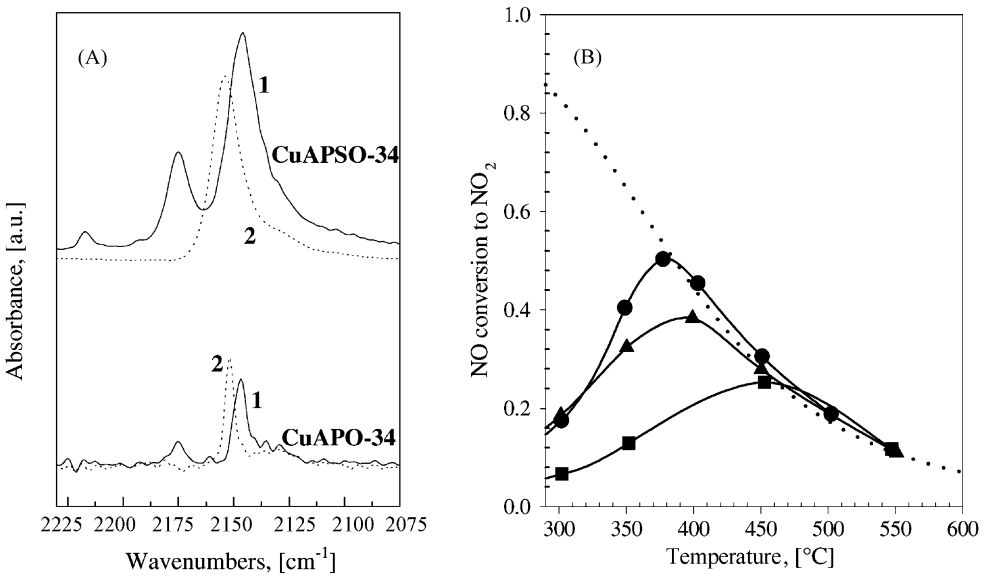

Fig. 2. (A) CO adsorbed at RT on CuAPO-34 and CuAPSO-34. Spectrum 1 was recorded under 100 Torr CO. Spectrum 2 was recorded after evacuation at RT for 20 min. (B) NO conversion to NO_2 as a function of temperature over different Me-aluminophosphates (Me = Co, Cu) and CuAPSO-34 at similar metal content. (●) CoAPO-34 (Co = 1.84 wt.%), (▲) CuAPSO-34 (Cu = 2.14 wt.%), (■) CuAPO-34 (Co = 2.07 wt.%). Feed: NO (2000 ppm), O_2 (5 vol.%) and balance He. $W/F = 0.042\,\mathrm{g\,s\,Ncm^{-3}}$. Dotted line represents the equilibrium conversion.

complexes at lower CO dosages [18–20]. When compared to the Co^{2+}(CO) complexes formed on cobalt-containing aluminophosphates [8,13,14], the Cu^{+}(CO) species are much more stable upon evacuation at RT, since in these latter complexes π back-donation should be more significant.

CO adsorption on CuAPSO-34 led to similar complexes (Fig. 2A, top curves), however, significant differences were observed between the two samples. Bands of dicarbonyls and monocarbonyls are much broader and more intense in case of CuAPSO-34 (the integrated intensity being around four times larger). This implies that in CuAPSO-34 samples there is a higher concentration of accessible Cu^{+} centres, which are likely to be located in a larger variety of sites [21]. This is to be expected, as the presence of silicon in the SAPO-34-type structure led to negative charges in the framework [10,22] which could be compensated by copper ions introduced during the molecular sieve synthesis or that have moved to these sites after the template removal. The catalysts prepared in this way should have some sites similar to those obtained by ion-exchange procedure [6,22,23].

By considering that the copper loading is similar in CuAPO-34 and CuAPSO-34(2.14), it may be additionally inferred from the spectroscopic results that in CuAPO-34 a significant fraction of copper ions is not accessible to CO adsorption. This is an indirect evidence of the larger amount of Cu^{2+} ions buried in the zeolite framework.

Fig. 2B shows the results of catalytic tests in NO oxidation with O_2 over pre-reduced MeAPO-34 (Me = Co and Cu) and CuAPSO-34 catalysts. It is evident that both copper- and cobalt-based aluminophosphates are active in NO oxidation to NO_2, although CoAPO-34 catalyst is more active than the Cu-containing ones with similar metal loading. However, CuAPSO-34 was found more active than CuAPO-34 as revealed by the higher values of NO conversion to NO_2 measured in the region of kinetically controlled regime, and this accounts for the higher fraction of accessible copper sites in CuAPSO-34. As a consequence, NO conversion reaches the thermodynamic limit at temperatures approximately 50 °C lower in CuAPSO-34 than in CuAPO-34. In analogy to the results found on

CoAPOs systems [8,17], the catalytic behaviour of CuAPO-34 and CuAPSO-34 could be connected to the presence of the Cu^{+}/Cu^{2+} redox couple, as evidenced by FTIR of adsorbed CO (Fig. 2A), as well as adsorbed NO (vide infra). However, the activity of these catalysts in NO oxidation is not interesting enough to develop novel processes of $DeNO_x$ abatement, if not accompanied by a good activity in NO SCR, which generally occurs on similar systems through the reaction between the reducing agent (hydrocarbons, CO or NH_3) and NO_2.

Thus, a more detailed FTIR study of adsorbed NO has been carried out over the most promising CuAPSO-34 sample (Fig. 3), in dependence of NO partial pressure and exposure time. The NO adsorption on CuAPSO-34 led to mono-nitrosyls on Cu^{+} which absorb at 1805 cm^{-1}, whose intensity decreased slightly upon increasing NO pressure (curves 1–8) [11,20,21,24]. Mono-nitrosyls adsorbed on different Cu^{2+} sites in the region 1850–1950 cm^{-1} were also found, and their band intensities increased upon increasing NO dosages. Some of these bands could be assigned on the basis of the data reported for Cu-ZSM-5 catalysts: particularly the bands at 1913 and 1895 cm^{-1} were assigned, respectively, to Cu^{2+}(NO) and $Cu^{2+}(O^{-})$ NO [11,20,21,24]. Additionally, in Cu-Y zeolite with high copper loadings [25] bands at 1920 and 1950 cm^{-1} due to Cu^{2+}–NO complexes were found. Therefore, the CuAPSO-34 catalyst presents spectroscopic features very similar to those detected on both Cu-ZSM-5 and Cu-Y. Moreover, spectra recorded upon prolonged time of contact with higher NO dosages (curves 8 and 9), showed that the band at 1805 cm^{-1} decreased with simultaneous increase of the band at 1895 cm^{-1}, confirming that a fraction of Cu^{+} ions was transformed into Cu^{2+}, as generally found on Cu-ZSM-5. This redox behaviour has been frequently correlated to the catalytic properties of Cu-ZSM-5 in both NO and N_2O decomposition reactions [26,27]. Other bands which depended on both NO pressure and time of contact, were found. Bands in the region 2200–2100 cm^{-1}, due to linearly adsorbed NO_2 species [21], increased constantly whereas the band at 2244 cm^{-1}, due to adsorbed N_2O

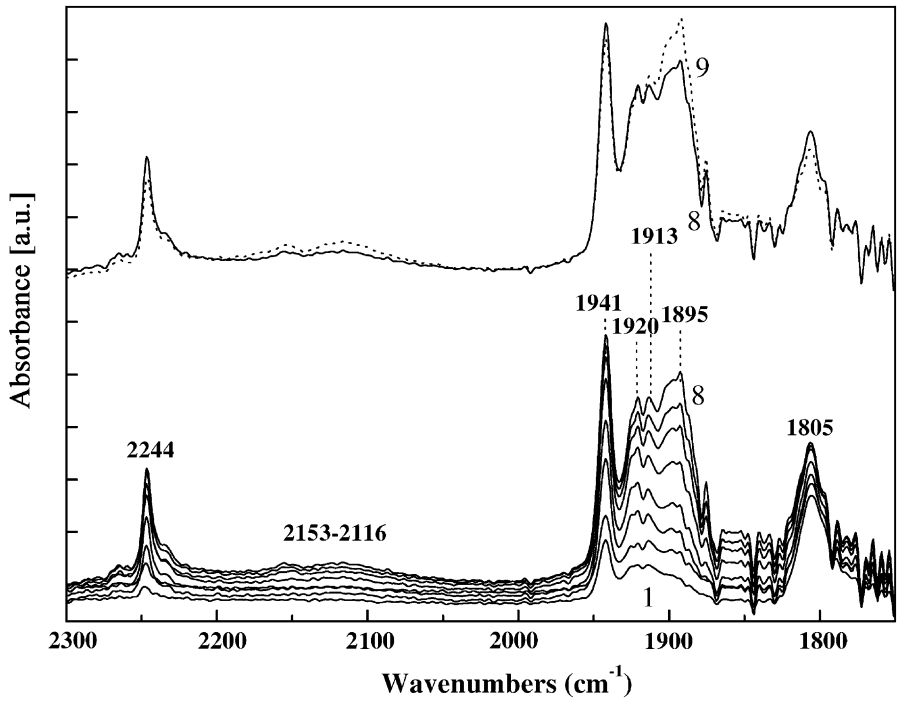

Fig. 3. IR spectra of NO adsorbed at RT on CuAPSO-34. Spectra 1–8 were recorder after increasing gradually the pressure from 0.5 to 50 Torr. Spectrum 9 (dotted line) was recorded after 30 min of contact with 50 Torr of NO.

[21,28], increased with NO doses (Fig. 3, curves 1–8) and decreased with prolonged time of contact (Fig. 3, curves 8 and 9). This behaviour supports the proposal that both these species are intermediates of the NO decomposition to N_2 and O_2 [21,28]. Finally, it was noted that the band at 1805 cm^{-1} of the mono-nitrosyl complexes, Cu^+(NO), is more intense and broader for the CuAPSO-34 catalyst in comparison with CuAPO-34 and this is a further evidence that Cu^+ sites in Si-containing samples are more abundant and more heterogeneously distributed.

Preliminary tests of catalytic activity have been performed on N_2O decomposition both in the presence and in the absence of O_2 and water vapour in the feed, with the aim of investigating not only activity properties of the different systems but also the stability of the most promising catalysts. Fig. 4 shows the results of such tests carried out on CuAPSO-34(1.23), CuAPO-34 and Cu-ZSM5 samples, the last one being selected as reference catalyst. It is evident that under dry conditions (closed symbols), Cu-ZSM5 is the most active catalysts for N_2O decomposition. CuAPSO-34(1.23) also exhibits good activity in the range of temperatures from 400 to 600 °C, even in excess of oxygen (1 vol.%, as compared with N_2O feed content of 600 ppm), which resulted in a very weak depressing effect on N_2O conversion (dotted line).

CuAPO-34 catalyst is much less active than both Cu-ZSM5 and CuAPSO-34(1.23), even though its copper content is nearly twice the one of the two other catalysts. This behaviour is in agreement with the spectroscopic results which show that the number of catalytic Cu^+ sites is less abundant in CuAPO-34. Although CuAPSO-34 has a lower catalytic activity than Cu-ZSM5, its activity level is sustained both in the presence of water (data not shown) and after a long treatment (80 h) at 600 °C under water vapour (Fig. 4, open squares). On the contrary, Cu-ZSM-5 was unable to withstand an even milder treatment (60 h at 550 °C), as a nearly complete loss of catalytic activity was observed (Fig 4, open circles). This very low hydrothermal resistance of Cu-ZSM-5 was already known and represents the main limitation to its application. Additionally, the presence of water in the feed reduces the performances of the CuAPSO-34 catalyst (not shown in the figure), but this is a reversible phenomenon in that the activity in dry conditions can be recovered. Further catalytic investigation in more severe exhaust conditions (presence of larger amounts of water in the feed), accompanied by systematic spectroscopic and

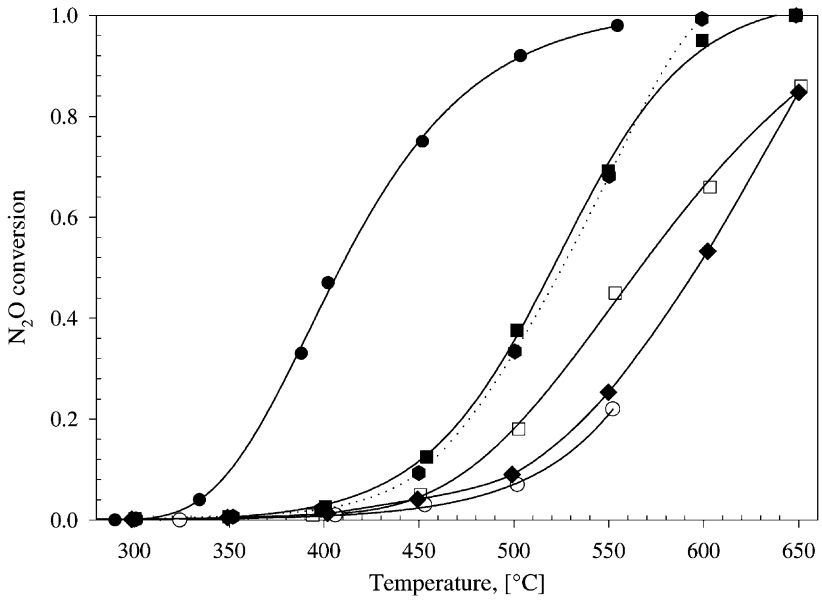

Fig. 4. N_2O conversion as a function of temperature over CuZSM-5 (● and ○), CuAPSO-34(1.23) (●, ⬢, and □) and CuAPO-34 (◆). Feed: N_2O (600 ppm), O_2 (1 vol.%) only for (⬢) and balance He. $W/F = 0.1\ g\,s\,Ncm^{-3}$. Open symbols represent catalytic test after ageing treatment.

diffraction studies of chemical and physical transformation of the catalysts are in progress.

4. Conclusions

The study of the catalytic properties of Co- and Cu-containing MeAPO-34 and MeAPSO-34 catalysts revealed that only the copper-containing ones behave similarly to Cu-ZSM5 in NO and N_2O decomposition. The catalytic activity in N_2O decomposition of CuAPSO-34 is much higher than those of CuAPO-34, likely due to the presence of a larger fraction of monovalent copper ions, as suggested by FTIR of adsorbed NO and CO. The former catalyst is even more active and stable than Cu-ZSM-5 when the reaction tests are performed in the presence of water vapour. Finally, the CuAPSO-34 catalysts showed a high thermal and hydrothermal resistance, being still active even after treatments at 900 °C in dry conditions and in the presence of water at 600 °C.

Acknowledgements

This work has been supported by "Ministero dell'Università e della Ricerca Scientifica e Tecnologica" (Progetti di Rilevante Interesse Nazionale, Cofinanziamento 2000). Authors wish to thank Prof. S. Coluccia (University of Turin) and G. Russo (University of Naples "Federico II") for fruitful discussions.

References

[1] V.I. Pârvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[2] J.N. Armor, Microporous Mesoporous Mater. 22 (1998) 451.
[3] Y. Traa, B. Burger, J. Weitkamp, Microporous Mesoporous Mater. 30 (1999) 3.
[4] M. Hartman, L. Kevan, Chem. Rev. 99 (1999) 635.
[5] J.M. Thomas, Angew. Chem. Int. Ed. Engl. 38 (1999) 3588.
[6] T. Ishihara, M. Kagawa, F. Hadama, Y. Takita, J. Catal. 169 (1997) 93.
[7] J. Dedecek, J. CejKa, B. Wichterlová, Appl. Catal. B 15 (1998) 233.
[8] L. Marchese, E. Gianotti, G. Martra, S. Coluccia, B. Palella, R. Pirone, P. Ciambelli, Stud. Surf. Sci. Catal. 130C (2000) 3005.
[9] D.B. Akolekar, S.K. Bhargava, Appl. Catal. A 207 (2001) 355.
[10] L. Marchese, A. Frache, E. Gianotti, G. Martra, M. Causà, S. Coluccia, Microporous Mesoporous Mater. 30 (1999) 145.
[11] M. Ito, Y. Shimoyama, Y. Saito, Y. Tsurita, M. Otake, Acta Cryst. C 41 (1985) 1698.
[12] P. Ciambelli, P. Corbo, M. Gambino, G. Minelli, G. Moretti, P. Porta, G. Moretti, G. Russo, Appl. Catal. B 8 (1996) 197.
[13] E. Gianotti, L. Marchese, G. Martra, S. Coluccia, Catal. Today 54 (1999) 495.
[14] L. Marchese, G. Martra, N. Damilano, S. Coluccia, J.M. Thomas, Stud. Surf. Sci. Catal. 101 (1996) 861.
[15] 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.
[16] Y. Watanabe, A. Koiwai, H. Takeuchi, S. Hyodo, S. Noda, J. Catal. 143 (1993) 430.
[17] A. Frache, L. Marchese, M. Cadoni, S. Coluccia, B. Palella, R. Pirone, P. Ciambelli, Stud. Surf. Sci. Catal. 140 (2001) 269.
[18] G. Spoto, A. Zecchina, S. Bordiga, G. Ricchiardi, G. Martra, G. Leofanti, G. Petrini, Appl. Catal. B 3 (1994) 151.
[19] A. Zecchina, D. Scarano, G. Spoto, S. Bordiga, C. Lamberti, G. Bellussi, Stud. Surf. Sci. Catal. 117 (1998) 343.
[20] Y. Kuroda, R. Kumashiro, T. Yoshimoto, M. Nagao, Chem. Phys. 1 (1999) 649.
[21] J. Dedecek, B. Wichterlová, P. Kubát, Microporous Mesoporous Mater. 32 (1999) 63.
[22] S. Coluccia, L. Marchese, G. Martra, Microporous Mesoporous Mater. 30 (1999) 43.
[23] D.B. Akolekar, S.K. Bhargava, K. Foger, J. Chem. Soc., Faraday Trans. 94 (1998) 155.
[24] M.V. Konduru, S.S.C. Chuang, J. Phys. Chem. B 103 (1999) 5802.
[25] Y. Li, J.N. Armor, J. Catal. 150 (1994) 376.
[26] P. Ciambelli, G. Moretti, G. Russo, Catal. Lett. 43 (1997) 255.
[27] P. Ciambelli, A. Di Benedetto, E. Garufi, R. Pirone, G. Russo, J. Catal. 175 (1998) 161.
[28] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura, M. Anpo, J. Catal. 136 (1992) 510.