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Nature, distribution and reactivity of copper species in over-exchanged Cu-ZSM-5 catalysts: an XPS / XAES study

Efim S. Shpiro [1], Wolfgang Grünert [2], Richard W. Joyner
and Galina N. Baeva [3]

Leverhulme Centre for Innovative Catalysis, Department of Chemistry,
University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

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Cu-ZSM-5 catalysts prepared by "over-exchange" (degree of exchange = 130%) and by impregnation have been studied by X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger spectroscopy (XAES). In both preparations, the external surface region of the catalysts is highly enriched in copper. In the over-exchanged zeolite, the observation of high XPS binding energies and unexpectedly low Auger kinetic energies shows that copper is present as isolated ions or small clusters. In the impregnated material large aggregates of metallic copper at the external zeolite surface are produced by reduction in hydrogen, which are not dispersed by treatment in oxygen or NO. In the exchanged materials, the copper becomes more evenly distributed across the zeolite crystal as a result of calcination or reductive treatment. Changing the composition of the atmosphere to which the exchanged Cu-ZSM-5 is exposed shows that there is ready conversion between Cu(II) and Cu(I). Copper is predominantly in the +2 oxidation state under conditions relevant to selective catalytic reduction of NO in lean-burn engine exhaust gas purification.

Keywords: XPS; Cu-ZSM-5; surface enrichment; Auger shift; NO_x reactions; dispersed Cu species; Cu(I); Cu(II)

1. Introduction

The reports by Iwamoto et al. [1] and Held et al. [2] on the selective catalytic reduction (SCR) of nitrogen monoxide, NO, by hydrocarbons in an excess of oxygen, i.e., in an atmosphere close to that of lean-burn engine exhaust gases, have prompted a wide range of studies aimed at the development of new catalytic sys-

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[1] Permanent address: N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia.

[2] Permanent address: AG Katalyse i.T. KAI e.V., Permoserstrasse 15, O-7050 Leipzig, Germany.

[3] N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia.

tems, the elucidation of the reaction mechanism and the characterisation of the active sites. Among the catalysts reported so far (see, e.g. refs. [3,4]), copper-exchanged ZSM-5, in particular where the extent of exchange exceeds 100% [5], is one of the most promising systems. Because Cu-ZSM-5 is also active in other NO reactions, the catalysts and their interaction with NO have been extensively studied by various techniques including infrared spectroscopy [6–8], EPR [8–10], photoluminescence [11] and EXAFS [12]. There is also considerable interest in the reaction mechanism by which the catalyst operates [13–16].

Despite considerable progress in our understanding of these catalysts, several important questions remain open. Thus, the reduction of Cu(II) ions in ZSM-5 to Cu(I) appears to be facile [6–8,10,11] as is the reoxidation of the Cu(I) by NO [6–8]. On the other hand, some reports suggest a considerable stability of Cu(II) towards reduction in ZSM-5 [9], casting doubt on the relevance of redox mechanisms in the decomposition [17] and the SCR of NO [14–16]. In a recent mechanistic study, Ansell et al. [15] present good evidence for the importance of Cu(II) in the SCR of NO in lean-burn exhaust gas conditions, while a mechanism involving Cu(I) as the active site is favoured by Iwamoto et al. [18]. Moreover, the nature of the copper species produced by the over-exchange process is not well understood, although there are clear differences in redox properties compared to impregnated catalysts [19]. Enrichment of Cu near to the external surface may be anticipated from experience with other metal oxide–ZSM-5 systems (Ga [20], Cr [21], Mg [22]). The observation of Cu–Cu distances in an EXAFS study suggests that aggregated copper species can be formed [12]. In contrast, the correlation between NO conversion and the exchange level of copper has been claimed to show that all of the Cu ions in the zeolite are involved in the catalytic reaction [23].

The present paper reports a study of some of these questions by X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES). Cu-ZSM-5 samples prepared by "over-exchange" and, for comparison by impregnation, have been studied after treatments in different reducing and oxidising atmospheres, including a mixture containing the more relevant lean-burn engine exhaust gas components. We are particularly interested in the surface concentration and chemistry of the copper species in the over-exchanged ZSM-5 and on their reactivity. X-ray excited electron spectroscopy studies are particularly powerful for this class of materials, although some care is needed in the experiments to minimise reduction of Cu(II) species in the X-ray beam. A fuller account with particular emphasis on the diagnostic value of combined XPS and XAES studies is in preparation [24].

2. Experimental

The over-exchanged Cu-ZSM-5 was prepared from a Na-ZSM-5 zeolite (Si/Al ratio 22) made by a template-free synthesis, using the procedure described by

Iwamoto et al. [5]. The zeolite (10 g) was exchanged three times with 500 ml of a 0.01 molar solution of Cu(II) acetate [5]; a new solution was used for each exchange. After the third exchange the catalyst was washed in deionised water and dried at ambient temperature. A similar solution was used to impregnate Cu(II) onto the ZSM-5, and the solution was evaporated to dryness at 303 K. The copper content determined by X-ray fluorescence was 2.6 wt% for the exchanged sample, representing 130% "exchange"; and 2.9% for the impregnated sample. No sodium remained in the over-exchanged samples.

XP spectra were recorded with a VG ESCA 3 spectrometer (Mg Kα excitation, base pressure $<5 \times 10^{-8}$ mbar) in the fixed pass energy mode, analyser energy 50 eV. The samples were deposited onto a stainless steel plate from a pentane slurry, and maintained at 170–200 K to avoid X-ray induced reduction of Cu(II). For the same reason the X-ray power was limited to 200 W (10 keV/20 mA). Stability of Cu(II) species under these measurement conditions was established by repeated monitoring of the Cu $2p_{3/2}$ line shape in oxidised samples. Prior to analysis the samples were treated in the spectrometer preparation chamber under appropriate conditions, except for calcination which was performed ex situ. Samples were pretreated for 30 min as reactor studies had shown that the catalyst attained steady state in <15 min. Identical spectra were observed when the treatment time was increased to 1 h. Binding energies (BE) and Auger kinetic energies (KE) are referred to C 1s = 285.0 eV and are given with an accuracy of about ±0.2 eV (KE: ±0.3 eV). Pretreatment did not substantially affect the C 1s line shape, and the same binding energies were obtained when the Si 2p line (BE = 103.6 eV) was used as an internal standard [20,21]. The kinetic energy response of peak intensities, which includes both escape depth and analyser transmission effects, was measured using the 2p, 3p, and 3s peaks from a copper metal standard. This experimentally determined response value was used, together with ionisation cross sections due to Scofield [25], in the calculations of atomic concentrations, which are accurate to about ±20%.

3. Results and spectral assignments

Four types of sample have been studied, namely over-exchanged and impregnated samples before and after calcination at 773 K. Typical Cu $2p_{3/2}$ photoelectron spectra and Cu L_3VV Auger spectra are shown in figs. 1–3, and the relevant spectral information is listed in tables 1–3. In addition to silicon, oxygen and aluminium peaks, spectra of the as-received samples showed the presence of small calcium and nitrogen impurities. The catalysts have been subjected to different sequences of treatment, to study their reactivity in conditions likely to occur during SCR. Fig. 1 shows the spectra for the *uncalcined, ion exchanged* material. Fig. 2. shows an extended sequence of results for the *calcined exchanged* material. The catalyst was activated either by heating in nitrogen to 623 K, or by heating in vacuum

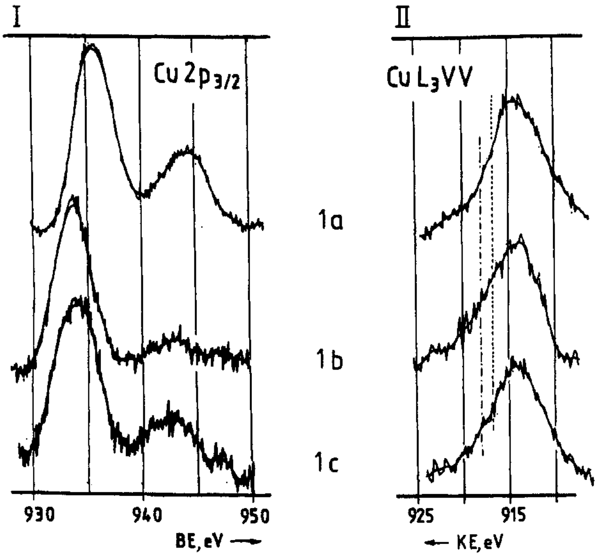

Fig. 1. (I) Cu $2p_{3/2}$ photoelectron spectra, and (II) Cu L_3VV Auger spectra of *uncalcined*, over-exchanged Cu-ZSM-5 catalysts. For treatment conditions see table 1. (- - -) Cu L_3VV KE measured for Cu_2O [26]; (– · –) Cu L_3VV KE measured for CuO [26].

to a similar temperature. The result of exposing the material to NO at room temperature, after heating in vacuum is shown in spectrum 2d. The sample was then reoxidised at 633 K and exposed either to NO/propene (fig. 2f) or to an NO/propene/oxygen mixture designed to simulate exhaust gas (fig. 2g). Fig. 3 shows results for *impregnated* samples. Where appropriate, nitrogen 1s spectra have also been recorded. They are, however weak and their interpretation is complicated by the presence of the impurity N 1s signal.

Oxidation states have been assigned using Cu $2p_{3/2}$ binding energies, the associated shake up satellites and the kinetic energy of the Cu $L_{III}VV$ Auger transition. The presence of a shake up satellite at higher apparent binding energy than the main core level is a characteristic feature of all Cu(II) compounds and is the best indicator of the presence of this oxidation state. The relative amount of Cu(II) present was estimated from the shake up satellite, using the ratio of the satellite to that of the main Cu $2p_{3/2}$ peak, I_S/I_P, as shown in fig. 1. The mean value of the ratio in fully oxidised samples was used for calibration. Curve-fitting techniques, in which a fixed ratio I_S/I_P was maintained for the Cu(II) component, yielded comparable results.

We have observed binding energies which are markedly higher than those reported for bulk copper compounds; for comparison the Cu $2p_{3/2}$ binding energy in CuO is 933.8 eV while that in Cu_2O is 932.3 eV [26]. An increase in the BE of metal ions in zeolites, compared to bulk oxides, has been widely reported [27–29]. The shifts are considered to reflect the presence of isolated metal ions and small

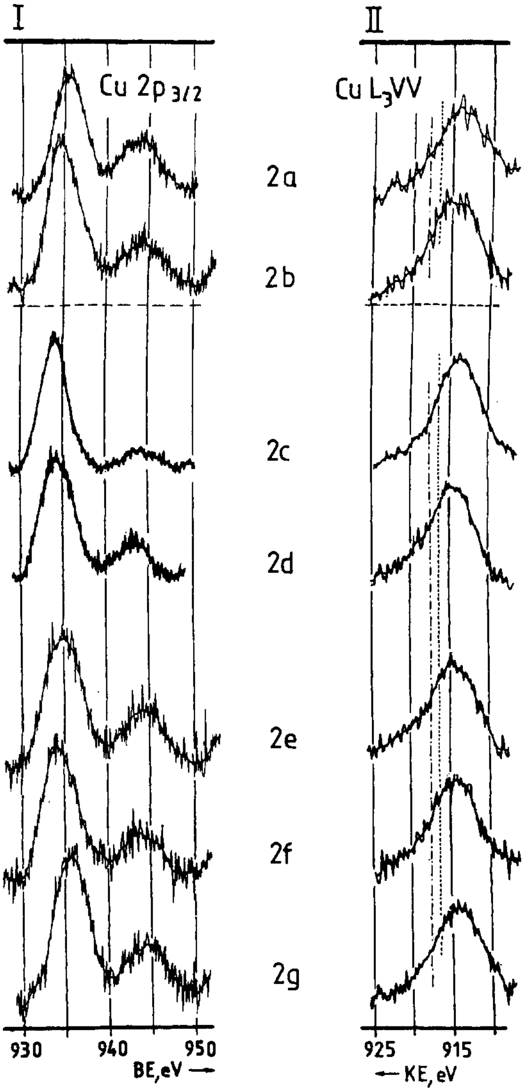

Fig. 2. (I) Cu $2p_{3/2}$ photoelectron spectra, and (II) Cu L_3VV Auger spectra of *calcined*, over-exchanged Cu-ZSM-5 catalysts. For treatment conditions see table 2. (- - -) Cu L_3VV KE measured for Cu_2O [26]; (–·–) Cu L_3VV KE measured for CuO [26].

clusters of ions dispersed in the zeolite matrix, although their origin is not unambiguously established. Possible factors contributing to the unusual spectral parameters observed include the Madelung potential of the zeolite and relaxation effects.

Usually, the Cu L_3VV Auger line can be used to discriminate between Cu(I) and Cu(0). The Auger kinetic energies for the most appropriate reference compounds, Cu_2O and Cu metal, have been reported to be 916.6 and 918.3 eV [26]. We

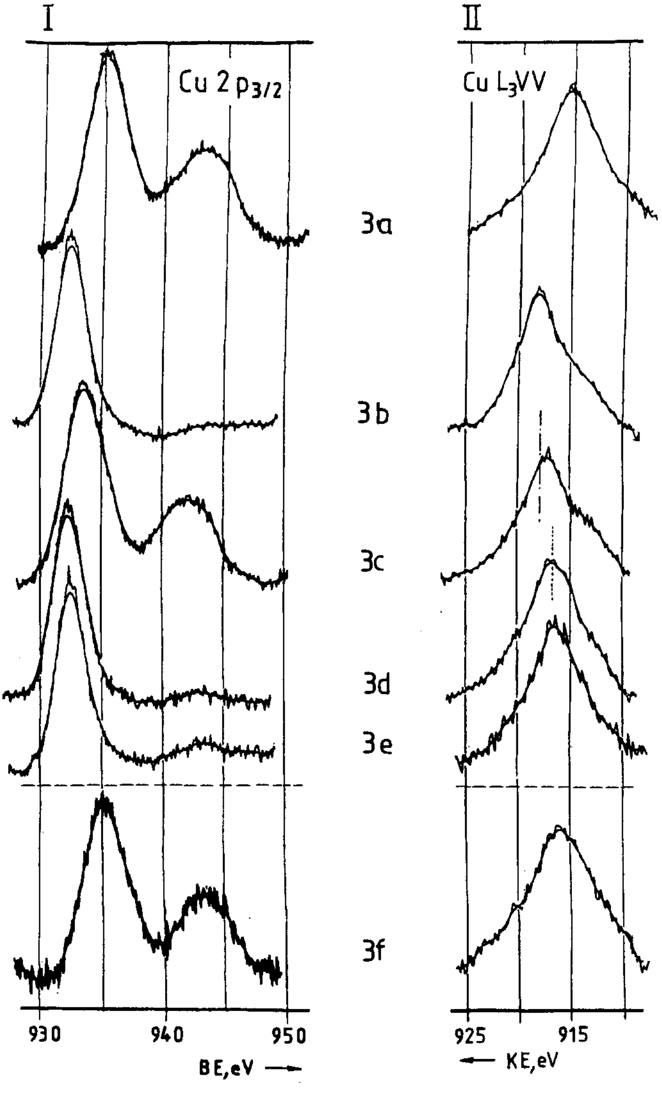

Fig. 3. (I) Cu $2p_{3/2}$ photoelectron spectra, and (II) Cu L_3VV Auger spectra of *impregnated* Cu-ZSM-5 catalysts. For treatment conditions see table 3. (- - -) Cu L_3VV KE measured for Cu_2O [26]; (– · –) Cu L_3VV KE measured for CuO [26].

have, however, observed values in this range only in experiments with an *impregnated* catalyst (table 3). In the *exchanged* catalysts, the kinetic energies are anomalously low, falling between 913 and 914 eV. These values are generally lower than the lowest Auger kinetic energy reported for bulk copper compounds, 914.2 eV for Cu(I) cyanide and 915.0 eV for copper(II) fluoride [30]. These low values of the Auger kinetic energy reflect the isolation of copper in the zeolite matrix and so parallel the high core level binding energies which we have observed. A low Cu L_3VV

Table 1
Characterization of *uncalcined ion-exchanged* Cu-ZSM-5 catalysts by XPS and XAES: parameters of spectra shown in fig. 1

Sample/ Treatment [a]	BE (eV) FWHM (eV)	I_S/I_P [b] % Cu reduced	Cu L_3VV, (eV)	Cu/Si atomic ratio [c]	Spectrum label (fig. 1)
as-received	935.1	0.51	914.1	0.21	(a)
	4.3	(0)			
N_2,	933.8	0.08	913.7	0.050	(b)
623 K, 1 bar	3.9	>90			
NO,	934.1 [d]	0.24	914.2	0.060	(c)
523 K, 50 mbar	4.5	60			

[a] Length of each successive treatment, 30 min; samples were cooled to ambient temperature in the treatment atmosphere.

[b] The ratio of the shake up satellite intensity to that of the main Cu $2p_{3/2}$ peak. There is contribution of ~ 0.05 to I_S/I_P due to the X-ray satellite of the Cu $2p_{1/2}$ component.

[c] The Cu/Si ratio for a uniform distribution would be 0.03.

[d] The peak position is due to a superposition of Cu(I) and Cu(II) contributions.

kinetic energy, 913.2 eV, has recently been reported by Jirka et al. [31] for Cu(I) exchanged into Y zeolite. As we discuss below, reactivity studies confirm the assignment of the reduced copper state in our samples to Cu(I). Hence, the Auger kinetic energy can be considered as a sensitive probe not only for the oxidation state of the metal ions, but also of their dispersion in zeolite materials. The deviation of the kinetic energy from the expected range is most probably due to changes in the extra-atomic relaxation energy [29]. The evaluation of the dispersion and the oxidation states of copper species from photoemission and Auger electron spectra will be discussed in more detail in a forthcoming paper [24].

4. Discussion

In the as-received, calcined and reoxidised states, the Cu 2p spectra of all of the Cu-ZSM-5 catalysts exhibit the high line width and the shake up satellite typical of Cu(II) (spectra 1a, 2a, 2e, 3a and 3f). For the *exchanged* catalysts the core level binding energies are considerably higher than that of CuO, and the Auger kinetic energies are low. As discussed above, these spectral parameters indicate that the Cu(II) ions are isolated from each other or present only in small clusters. The Cu/Si atomic ratios reported in tables 1 and 2 are much higher than the bulk value, showing that the surface regions of the fresh catalysts are highly enriched in copper, even though the copper is well dispersed. A decrease of the Cu/Si atomic ratio is found after calcination, but a more pronounced decline occurs when the ion-exchanged sample is subjected to reducing conditions.

Thermal treatment in vacuum or nitrogen has been reported to reduce Cu(II) in *ion-exchanged* Cu-ZSM-5 to Cu(I) [6–8,10,11]. When our catalysts were treated in

Table 2
Characterization of *calcined ion-exchanged* Cu-ZSM-5 catalysts by XPS and XAES: parameters of spectra shown in fig. 2

Sample/ Treatment [a]	BE (eV) FWHM (eV)	I_S/I_P [b] % Cu reduced	Cu L_3VV, (eV)	Cu/Si atomic ratio [c]	Spectrum label (fig. 2)
calcined	935.3	0.57	914.0	0.170	(a)
air, 773 K	4.5	0			
N_2,	934.9	0.44	913.9	0.056	(b)
623 K, 350 mbar	4.8	20			
Heating a fresh, calcined sample in:					
vacuum,	933.6	0.16	913.3	0.038	(c)
713 K	3.9	80			
NO,	934.3	0.31	914.1	0.047	(d)
298 K, 50 mbar	4.5	50			
O_2,	934.8	0.52	913.8	0.032	(e)
633 K, 350 mbar	4.8	0			
NO/propene [d]	934.2	0.3	913.3	0.031	(f)
633 K	4.6	50			
Oxygen, 350 mbar, 633 K followed by:					
Simulated	935.5	0.44	913.7	0.036	(g)
exhaust gas [e], 633 K	4.9	20			

[a] Length of each treatment, 30 min; samples were cooled to ambient temperature in the treatment atmosphere; treatments were successive if not stated otherwise.

[b] The ratio of the shake up satellite intensity to that of the main Cu $2p_{3/2}$ peak. A contribution of $I_S/I_P \approx 0.05$ is due to the X-ray satellite of the Cu $2p_{1/2}$ component.

[c] The Cu/Si ratio for a uniform distribution would be 0.03.

[d] NO and propene pressures both 0.4 mbar.

[e] NO and propene pressures both 0.4 mbar, oxygen pressure 2.5 mbar.

this way the core level satellites disappeared (spectra 1b and 2c) or decreased (spectrum 2b). The Cu $2p_{3/2}$ binding energy decreased by 1.3–1.7 eV (cp. spectra 1a and 1b, and 2a and 2c), the line became narrower and the kinetic energy of the Auger peak decreased by 0.4–0.7 eV. The binding energies were again higher than those of the bulk compounds copper(I) oxide or copper metal and the kinetic energies of the Auger peaks remained low. These spectral parameters show that the result of treatment in the absence of any oxidant is to reduce the Cu(II) ions. Because of the evidence from other techniques on the result of these treatments, in particular infrared spectroscopy [6–8], we expect reduction to the Cu(I) state and the spectra are entirely consistent with this. The extent of reduction caused by heating in nitrogen is considerably less when the catalyst has been calcined, as can be seen by comparing spectra 1b and 2b. On heating in nitrogen or vacuum the Cu/Si ratio fell significantly, and approached the expected bulk figure of 0.03. Taken together, the continued observation of anomalous spectral parameters and the decrease in surface copper content indicate migration of copper species into the bulk of the zeolite, rather than aggregation at the external surface.

Table 3
Characterization of *impregnated* Cu-ZSM-5 catalysts by XPS and XAES: parameters of spectra shown in fig. 3

Sample/ Treatment[a]	BE (eV) FWHM (eV)	I_S/I_P [b] % Cu reduced	Cu L_3VV, (eV)	Cu/Si atomic ratio[c]	Spectrum label (fig. 3)
as-received	935.2	0.60	915.2	0.53	a
dried	4.1	0			
Hydrogen	932.4	0.05	918.2	0.053	b
573 K, 50 mbar	2.9	100			
Oxygen	933.8	0.62	917.3	0.18	c
533 K, 50 mbar	4.0	0			
Vacuum,	932.3	0.10	916.2	0.11	d
713 K	3.2	90			
NO	932.6	0.12	916.2	0.083	e
373 K, 2.5 mbar	3.2	90			
A fresh sample was studied after calcination in air at 773 K:					
	935.0	0.55	915.9	0.19	f
	4.3	0			

[a] Length of each treatment, 30 min; samples were cooled to ambient temperature in the treatment atmosphere; treatments were successive if not stated otherwise.

[b] The ratio of the shake up satellite intensity to that of the main Cu $2p_{3/2}$ peak. A contribution of $I_S/I_P \approx 0.05$ is due to the X-ray satellite of the Cu $2p_{1/2}$ component.

[c] The Cu/Si ratio for a uniform distribution would be 0.033.

An *ion-exchanged* catalyst in which the copper had been subject to a reducing treatment, so that only Cu(I) was present, was exposed to NO at room temperature and the shake up satellite reappeared, indicating some reoxidation to Cu(II) (spectrum 2d). In contrast, when an oxidised sample containing only Cu(II) was heated in a 1 : 1 NO/propene mixture, partial reduction of the Cu(II) was observed, as shown in spectrum 2f. Addition of oxygen to this atmosphere, resulting in oxidising conditions, still gave a mixture of Cu(I) and Cu(II) species, but with a clear majority of the latter, ca. 80% (spectrum 2 g). These results in different gas mixtures confirm earlier observations that conversion between the two oxidation states of copper is facile in over-exchanged Cu-ZSM-5 catalysts [6–8,10,11]. The observation that the majority of copper is in the +2 state after heating in oxygen/NO/propene does not allow us to rule out any relevance of Cu(I) in selective catalytic reduction. However, it lends support to mechanisms involving Cu(II) as the active oxidation state for this reaction [15]. We also note that we used an oxygen concentration well below that expected in lean-burn exhaust gas catalysis, which might contain 5% oxygen and only 0.01% of NO and propene.

The Cu $2p_{3/2}$ peak for the as-received *impregnated* catalysts was in a similar position to that noted for the exchanged material, suggesting that relatively small copper containing clusters are again present. The Cu/Si ratio again indicated a very high concentration of copper in the surface region, consistent with the observation of an abnormally low Si/O intensity ratio, 0.12 ± 0.01, (compared to 0.16 in the parent zeolite) implying "shadowing" of the zeolite signal by copper acetate, hydroxide or oxide.

When the *impregnated* catalyst was reduced, the peak positions in the spectra became almost identical to those of the bulk compounds, as shown in fig. 3. Reduction in hydrogen gave spectral parameters indicative of metallic copper (spectrum 3b), oxidation resulted in spectra characteristic of CuO (spectrum 3c) while after heating in vacuo the spectra resembled bulk Cu_2O (spectrum 3d). These "normal" spectra and the high values of Cu/Si atomic ratios observed suggest that the copper compounds have formed three-dimensional aggregates at the external surface of the zeolite.

Only very small changes were observed when an impregnated catalyst containing Cu(I) aggregates was exposed to NO (cp. spectra 3d, 3e). The form, distribution and reactivity of copper species is clearly very different in impregnated and ion-exchanged catalysts, so it is surprising that their behaviour in the SCR reaction is reported to be so similar [1,19].

In summary, copper in *over-exchanged* ZSM-5 catalysts exists as isolated ions or in small clusters, adopting either the +1 or the +2 oxidation state according to the atmosphere present. Although initially concentrated at the external surface of the zeolite, copper in the *exchanged* samples becomes well dispersed throughout the bulk on exposure to reducing conditions or reactive atmospheres. Cu(II) is the major species present under conditions relevant to lean NO_x catalysis. The morphology and behaviour of *impregnated* catalysts is quite different, due to the presence of larger, aggregated copper species at the external surface of the zeolite.

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References

[1] M. Iwamoto, Stud. Surf. Sci. Catal. 54 (1990) 121.
[2] W. Held, A. König, T. Richter and L. Puppe, SAE Paper 900496 (1990).
[3] S. Sato, H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, Catal. Lett. 12 (1992) 193.
[4] G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, Appl. Catal. B 1 (1992) L15.
[5] M. Iwamoto, H. Yahiro, Y. Mine and S. Kagawa, Chem. Lett. (1989) 213.
[6] L. Li and W.K. Hall, J. Catal. 129 (1991) 202.
[7] J. Valyon and W.K. Hall, J. Phys. Chem. 97 (1993) 1204.
[8] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura and M. Anpo, J. Catal. 136 (1992) 510.

[9] A.V. Kucherov, A.A. Slinkin, D.A. Kondratiev, T.N. Bondarenko, A.M. Rubinstein and Kh.M. Minachev, Zeolites 5 (1985) 20; Kinet. Katal. 26 (1984) 409.
[10] C.E. Sass and L. Kevan, J. Phys. Chem. 93 (1989) 7856.
[11] G. Genti, S. Perathoner, Y. Shioya and M. Anpo, Res. Chem. Intermed. 17 (1992) 125.
[12] H. Hamada, N. Matsubayashi, H. Shimada, Y. Kintaichi, T. Ito and A. Nishijima, Catal. Lett. 5 (1990) 189.
[13] C.N. Montreuil and M. Shelef, Appl. Catal. B 1 (1992) L1.
[14] C. Bennett, P.S. Bennett, S.E. Golunski, J.W. Hayes and A.P. Walker, Appl. Catal. A 86 (1992) L1.
[15] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.M. Hayes, R.R. Rajaram and A.P. Walker, Appl. Catal. B 1 (1992).
[16] J.O. Petunchi and W.K. Hall, Appl. Catal. (1993) to be published;
J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal., to be published.
[17] M. Shelef, Catal. Lett. 15 (1992) 305.
[18] M. Iwamoto, paper presented at the ACS meeting 1993 (paper 23).
[19] J.L. D'Itri and W.M.H. Sachtler, Catal. Lett. 15 (1992) 289.
[20] E.S. Shpiro, D.P. Shevchenko, M.S. Kharson, A.A. Dergachev and Kh.M. Minachev, Zeolites 12 (1992) 670.
[21] E.S. Shpiro, G.J. Tuleuova, V.I. Zaikovski, O.P. Tkachenko, T.V. Vasina, O.V. Bragin and Kh.M. Minachev, Stud. Surf. Sci. Catal. 46 (1989) 143.
[22] Kh.M. Minachev, Ya.I. Isakov, E.S. Shpiro, T.I. Isakova and O.P. Tkachenko, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 2, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 461.
[23] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.
[24] E.S. Shpiro, W. Grünert, R.W. Joyner and G.N. Baeva, to be published.
[25] J.H. Scofield, J. Electron Spectry. Rel. Phenom. 8 (1976) 129.
[26] C.D. Wagner, in: *Practical Surface Analysis*, eds. D. Briggs and M. Seah (Wiley, Chichester, 1983) App. 4.
[27] Kh.M. Minachev and E.S. Shpiro, *Catalyst Surface: Physical Methods of Studying* (CRC Press, Boca Raton, 1990).
[28] Y. Okamoto, M. Ogawa, A. Maezawa and T. Imanaka, J. Catal. 112 (1988) 427.
[29] W. Grünert, U. Sauerlandt, R. Schlögl and H.G. Karge, J. Phys. Chem. 97 (1993) 1413.
[30] G. Moretti and P. Porta, Surf. Interf. Anal. 15 (1990) 47.
[31] I. Jirka, B. Wichterlova and M. Maryska, Stud. Surf. Sci. Catal. 65 (1991) 269.