SOLID ION EXCHANGE OF COPPER CHLORIDES WITH ZSM-5 ZEOLITE: NATURE OF COPPER SPECIES IN ZEOLITE MATRIX

H. TOUNSI *, S. MSEDDI **, S. DJEMEL *, J. F. LAMBERT ***

* Institut Préparatoire des Études d'Ingénieurs de Sfax, BP 805, 3003 Sfax, Tunisie
** Faculté des Sciences de Sfx, 3038 Sfax, Tunisie
*** Laboratoire de réactivité de surface et structure, UMR 7609-CNRS, UPMC,
4 place Jussieu, Tour 54-55, 2ᵉ étage, Casier 178, 75252 Paris Cedex 05, France

ABSTRACT : Copper exchanged ZSM-5 zeolites have been prepared between separate phases of copper chlorides (CuCl, $CuCl_2.2H_2O$) and NH_4^+-ZSM-5 by a solid ion exchange procedure. The ground mixture of the zeolite and the copper precursors has been heat-treated in a flow of dry air or in static conditions (without a flow of dry air). It has been shown that the solid ion exchange proceeds at high temperatures with consumption of the acidic OH groups and evolution of hydrochloric acid under the preservation of the zeolite structure. In contrast, in the case of samples prepared by static condition, we note the destruction of the zeolite structure and formation of amorphous materials when high loading of copper chlorides was used. Nature of copper species in the zeolite matrix has been also discussed.

Keywords: solid-state ion exchange; Cu-ZSM-5, zeolite structure destruction.

RESUME : Des zéolithes Cu-ZSM-5 ont été préparées par échange ionique en phase solide. Le mélange broyé NH_4^+-ZSM-5 – CuCl ($CuCl_2.2H_2O$) a été calciné sous flux d'air sec ou sous des conditions statiques (sans flux d'air). On a montré que l'échange se produit à haute température entre les protons des groupements hydroxyles de caractère acide et le cuivre avec émission de HCl sous préservation de la structure zéolithique. En revanche, pour les catalyseurs préparés sans flux d'air on a remarqué la destruction de la structure pour les pourcentages élevés en cuivre. La nature des espèces cuivriques à l'intérieur de la structure zéolithique a été aussi étudiée.

Mots clés : échange en phase solide, Cu-ZSM-5, destruction de la structure zéolithique.

I - INTRODUCTION

Air pollution due to the emissions of nitrogen oxides from various mobile and stationary sources has become a serious environmental problem in many countries. Several catalysts, including transition metal ion–exchanged zeolites have been suggested for industrial application [1-5]. Among zeolite catalysts group, the over exchanged Cu-ZSM-5 has proved to be the most promising in the low temperature catalytic decomposition of NO [6-9], and the selective reduction with hydrocarbons in excess oxygen (HC-SCR) [10-16]. Active Cu-ZSM-5 catalysts are usually prepared by conventional ion exchange of the zeolite with highly diluted solution of copper salts, preferably copper (II) acetate [6,7,14-16].

A new ion-exchange method, known as the solid- state ion exchange (SSIE), was developed to avoid the disadvantages of the conventional procedure [17]. Reported in 1973 by Rabo [18] and Clearfield [19], this method consists of heating in vacuum [20,21] or in a flow of inert gas [22-27] a mechanical mixture of the zeolite and a cation precursor. The highest exchange degrees were reached using copper chlorides [22,24-26] and the ammonium or protonic form of the zeolite [21-24]. In this case, hydrochloric acid (HCl) is released into the gas phase under preservation of the zeolite structure.

Many authors have proposed that Cu (I) sites in ZSM-5 zeolite are active for the decomposition [25,26,28-31] and reduction of NO_x [14,15,32,33]. The direct incorporation of Cu (I) ions by conventional ion exchange is practically impossible because of the low solubility of Cu (I) salts in water and the difficulties to avoid the oxidation of Cu (I) by the atmospheric oxygen during the exchange procedure. However, substantial exchange of protons for Cu (I) ions in ZSM-5 was achieved by solid state ion exchange using crystalline CuCl reactant [20,21,26].

The aim of the present work is to investigate and compare the high temperature interaction of CuCl and $CuCl_2.2H_2O$ with NH_4^+-ZSM-5 zeolite. Particular attention is paid to the mechanism of solid ion exchange and the nature of copper species in the zeolite matrix.

II - EXPERIMENTAL

II .1 – Preparation

NH_4^+-ZSM-5 with Si /Al atomic ratio of 15 and $S_{BET} = 400$ $m^2.g^{-1}$, supplied by Zeolyst (CBV-3024 E, Lot 1822- 560), was used as starting material. The procedure of solid ion exchange used in this work was as follows: In each case, an aliquot of copper chlorides (CuCl or $CuCl_2.2H_2O$) was intimately mixed with 2 g of NH_4^+-ZSM-5 in agate mortar for 15 minutes. This ground mixture was heated at 500 °C for 2 hours in dry air with a heating rate of 7.5 °C/min. The resulting samples were cooled to ambient temperature, washed chloride- free and finally dried overnight at 100 °C. For comparison, we have also prepared samples under static conditions (without dry air). This procedure was very simple and consisted of heating the mechanical mixture, transferred in ceramic crucible, in an oven at 500 °C for 2 hours. In table I were reported the code names and main characteristics of the samples prepared by the solid state exchange.

Table I : Samples prepared by the solid- state ion exchange.

Salt	Samples	% of Cu [a]	Gas	% of Cu [b]
	Cu1Za1	4.14	dry air	3.65
	Cu1Za2	8.27	"	5.64
CuCl	Cu1Za3	12.41	"	8.52
	Cu1Zsa1	4.14	without	3.51
	Cu1Zsa2	8.27	"	6.02
	Cu1Zsa3	12.41	"	7.43
	Cu2Za1	4.14	dry air	3.32
	Cu2Za2	8.27	"	6.16
	Cu2Za3	12.41	"	9.12
$CuCl_2. 2H_2O$	Cu2Zsa1	4.14	without	3.21
	Cu2Zsa2	8.27	"	5.84
	Cu2Zsa3	12.41	"	8.46

[a] Theoretical Cu percent per gram of a dry zeolite.
[b] Experimental Cu percent per gram of a dry zeolite.

II.2 - Characterization

The X-ray powder diffraction patterns were recorded using a Siemens D 500 diffractometer operating with a Cu- Kα radiation in the $4°<2\theta<50°$ range at room temperature. Infrared spectra were obtained with a Brucker IFS 66V Spectrometer at a resolution of 4 cm^{-1}. The pellet technique was used by pressing an identical amount of powdered sample diluted with KBr in an evacuable die to produce a transparent disk. Thermal analyses of the untreated and treated samples were conducted in TG/TDA 220 SEIKO microbalance. In all cases, 15 mg of the specimens were placed in a plate made from Pt and heated at the rate of 7.5 °C/ min in a 100 ml/ min air stream from room temperature to 1000 °C. Gaseous products that evolved during heating of 200 mg of the mixture in dry air were detected by a Hiden Analytical MASsoft V 3.5 mass spectrometer. The masses monitored were 36 and 37 for HCl, 18 and 17 for H_2O and 17 and 16 for NH_3. Specific surface area and pore volume distribution were measured by the nitrogen method in Accursorb 2100 E Micrometrics Adsorption Analyzer. Samples were degassed for 12 hours at 300 °C before adsorption. The BET method was used to determine the specific area at 77 k. The UV-Vis-NIR diffuse reflectance spectra were recorded in the 190- 2500 nm range using Cary 5 E Varian spectrometer. Crystallite morphology and size of the different samples were examined in a Philips XL 30 scanning electron microscope (SEM). The Chemical analyses were obtained by atomic absorption at the center of the CNRS in Vernaison. Temperature programmed reduction was carried out in a 5% H_2/Ar stream (25 ml/min) by heating from room temperature to 700 °C at the rate of 7.5 °C min^{-1}. A thermal conductivity cell was used to monitor H_2 consumption.

III - RESULTS AND DISCUSSION:

The solid ion exchange procedure was controlled for each sample by means of mass spectrometry (MS). The HCl evolution was confirmed by monitoring the m/e = 36 and 37. The curve obtained from the temperature – programmed evolution of HCl from CuCl- NH_4^+-ZSM-5 is shown in Figure 1. It exhibits a maximum at 494 °C. The HCl evolution starts at 430 °C which is the temperature of the beginning of CuCl melting (Figure 2). We note also the release of NH_3 (m/e = 16) at 345 °C which corresponds to the deammoniation of the NH_4^+-ZSM-5 zeolite:

$$NH_4^+\text{-ZSM-5} \longrightarrow H^+\text{-ZSM-5} + NH_3.$$
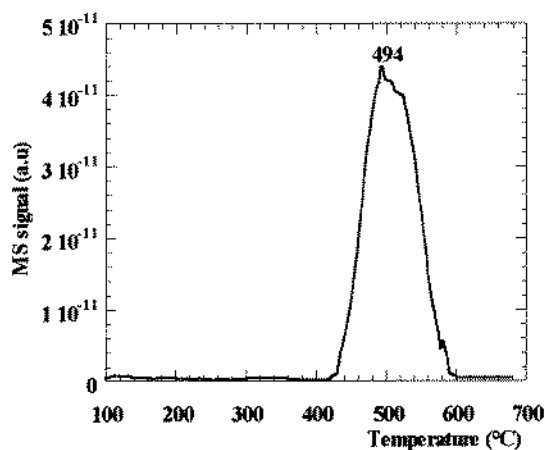
Figure1: T.P.E of HCl, m/e=36, from CuCl- NH_4^+-ZSM-5 mixture.

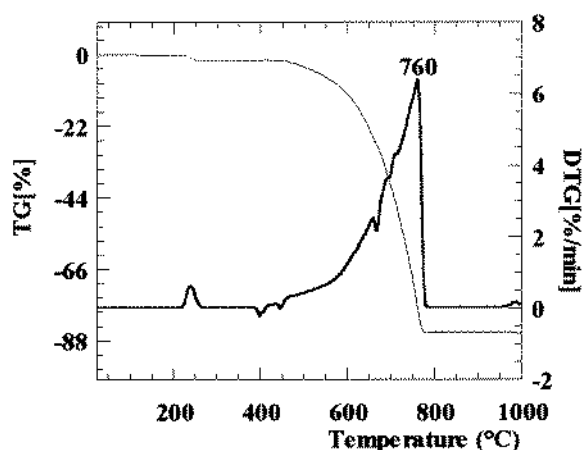**Figure 2:** Thermogravimetric profile of CuCl- NH_4^+-ZSM-5 mixture.

The HCl evolution is assumed to be due to the exchange of the copper chlorides with the strongly acidic protons bridging OH group already formed upon the deammoniation [20,34]. Figure 3 depicts spectra of NH_4^+-ZSM-5 and Cu2Za1 in the range of OH vibrations. The spectrum of NH_4^+-ZSM-5 contains three bands. The first at 3611 cm^{-1} characteristic of bridging hydroxy with Bronsted acid character (Si-OH-Al),the second at 3663 cm^{-1} attributed to –Al-OH groups in defective (internal or external) positions and the third at 3748 cm^{-1} corresponding to the lattice termination silanols SiOH groups [35]. After the solid exchange the intensity of the acidic band at 3611 cm^{-1} is reduced .The change in intensity of this band suggests that liquid CuCl entered the pore system and reacted with the protons of (Si-OH-Al) groups and gaseous HCl is evolved according to the equation:

$$Z\text{-}OH \ + \ CuCl \ \longrightarrow \ Z\text{-}O\text{-}Cu \ + \ HCl \ (I)$$
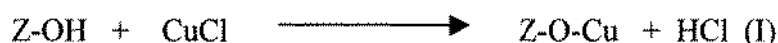
when stoichiometric mixture was used (without residual salt) [17]. It is of interest to mention the slight dehydroxylation of the bridging hydroxyls at 454 °C [21]. This effect is discovered by MS experiment when the m/e = 18, 17 were monitored.
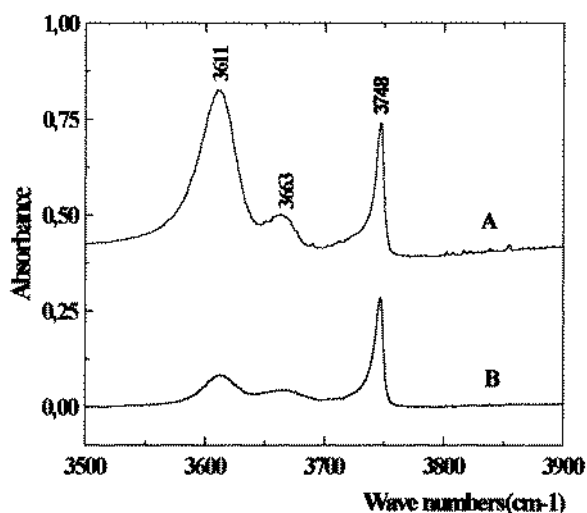

**Figure 3**: IR spectra of OH groups, **(A)** NH_4^+-ZSM-5, **(B)** Cu2Za1.

Taking into account the experimental findings reported above, the mechanism of the solid ion exchange of CuCl respectively $CuCl_2$. $2H_2O$ and ZSM-5 zeolite can be explained as follows: on the one hand, and for CuCl which has low solubility in water, it appears that upon the contact of the zeolite and the salt, a spontaneous   dispersion of the latter may occur and may be facilitated by heating the mixture. This dispersion takes place at the external surfaces of the zeolite crystal and at the pores mouths [17,36,37]. Then the transport of CuCl into the interior pore system may be proceeded by a slow surface diffusion of the salt molecules. As there is no deaggregation of the salt before 425 °C (Figure 2) and no HCl evolution (Figure 1) , the transport of the precursor should happen in the form of whole molecules, so CuCl may be first melt and is then transported to the solid channels [38]. Finally, CuCl molecules react with the protons of (-Si-(OH)-Al-) groups to yield copper occupying cationic positions with simultaneous evolution of HCl. The evolved gas will be continuously removed by the air stream which shifts the equilibrium (I) to the right hand side .

On the other   hand, the mixture of $CuCl_2$. $2H_2O$ with the zeolite leads to its   partial dissolution into the zeolitic water and Cu^{2+} cation can then freely penetrate the internal pore

system of ZSM-5. The remainder of the salt that has not been dissolved will react with the acidic OH groups. But the Si/Al ratio in our zeolite is 15 and the distance separating each two Z-OH groups seems too big for bridging with Cu^{2+} ions. Therefore, it is reasonable to assume that $CuCl_2$ may be reduced to $[CuCl]^+$ and spread out over the zeolite pores at significantly higher temperature [36,37]. After that, Cl⁻ ligands of $[CuCl]^+$ will be replaced by O⁻ or OH⁻ in the course of reaction when enough quantities of oxygen and water are present as this reaction shows [37]:

$$[CuCl]^+ + HOH \longrightarrow [CuOH]^+ + HCl \quad (II).$$

The HCl evolution did not affect the integrity of the zeolite structure. It seems that the use of the flow of dry air avoids framework collapse resulting from the production of HCl during the thermal treatment . As shown in Figure 4, the XRD patterns of Cu- exchanged samples are identical to that of NH_4^+-ZSM-5 [39]. Hence, It is of interest to note that the characteristic reflections assigned respectively to CuCl and $CuCl_2.2H_2O$ crystals disappear completely when the mixtures were heat-treated at 500°C for 2 hours. The disappearance of the precursors peaks might explain the high spreading of the copper chlorides in the channel of the NH_4^+-ZSM-5 zeolite. The diffractograms of samples prepared in a flow of dry air show no evidence of copper oxide phase. Whereas the ones prepared in static conditions show CuO peaks at 35.7 ° and 38.55 ° 2 θ, with particles sizes superior to 40 Å. For samples Cu1Zsa1 and Cu2Zsa1, there's no obvious destruction of the zeolite structure. It is probable that the preservation of the ZSM-5 structure comes from the low Al contents of the zeolite (Si/Al = 15) and, as a consequence, from the limited production of HCl. The diffractograms of samples with higher loading show a substantial increase of the background intensities in the region of 12 – 40 ° (Figure5). This indicated the formation of amorphous material in these samples. The amorphisation of the zeolitic structure is due to the high quantities of the non evacuated HCl and to the local destruction of the pores mouths by the sintering of the CuO crystallites.
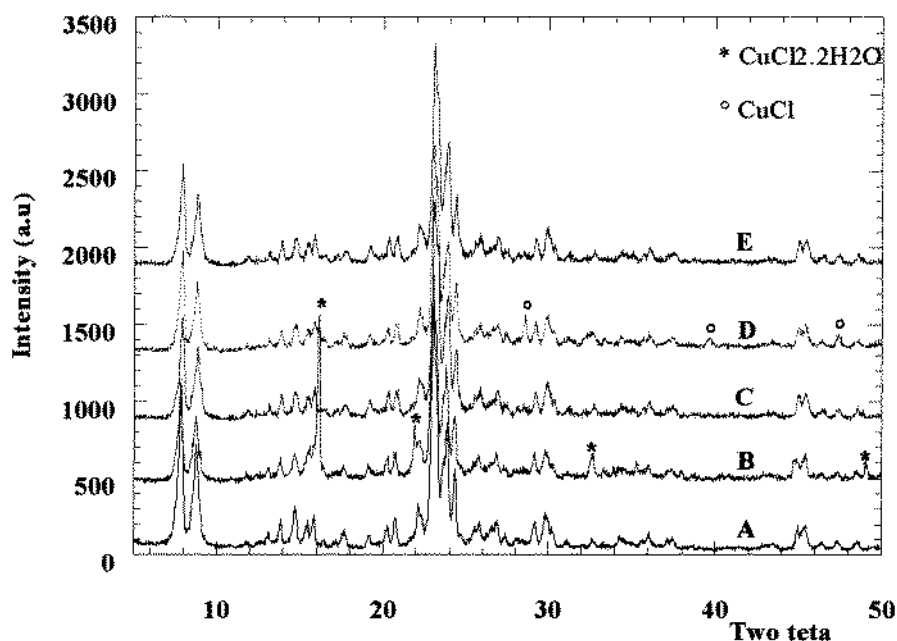
Figure 4 : XRD patterns of : (**A**) NH_4^+-ZSM-5; (**B**) $CuCl_2.2H_2O$ - NH_4^+-ZSM- 5 mixture before heat treatment; (**C**) after heat treatment in dry air (Cu2Za2); (**D**) CuCl-NH_4^+-ZSM- 5 before heat treatment, (**E**) after heat treatment in dry air (Cu1Za1) .
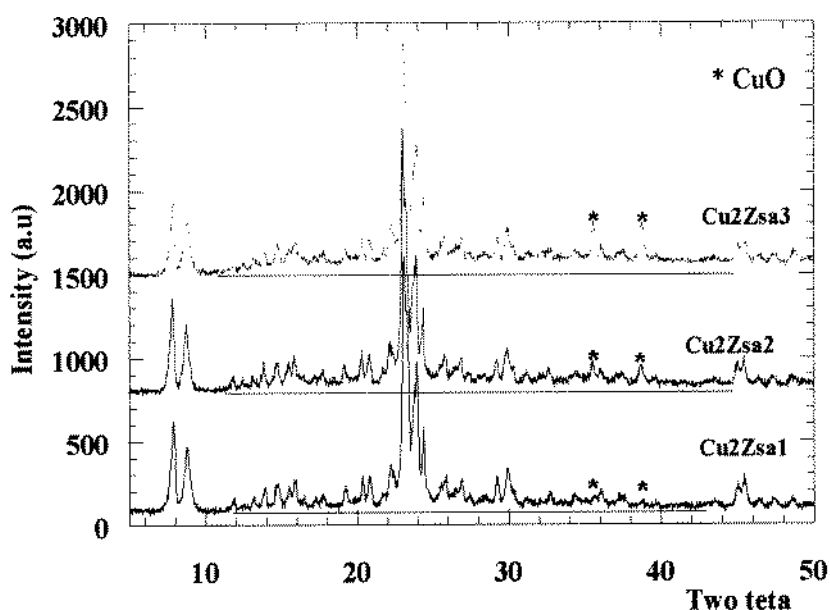
Figure 5 : XRD patterns of $CuCl_2.2H_2O$ - NH_4^+-ZSM- 5 mixtures heated under static conditions.

The results of surface area, micropore volume confirm the earlier finding with XRD. The BET measurements revealed that samples prepared in the flow of dry air have very similar specific areas. It follows that no destruction of the pore system occurred in consequence of the solid ion exchange. In contrast, the other samples show a decrease in BET surface area which is caused by the CuO particles that fill the micropore of the zeolite.

**Table II** : BET surface area, micropore volume of some samples.

Samples	S_{BET} (m^2/g)	μV (cm^3/g)
NH_4^+-ZSM-5	422.58	0.100
Cu1Za2	425.66	0.111
Cu2Za1	421.65	0.102
Cu1Zsa1	403.32	0.091
Cu2Zsa2	375.07	0.062

The morphology of the crystallites of Cu-ZSM-5 samples prepared via the solid ion exchange method is similar to the starting material when observed in SEM. Figure 6 presents the micrographs obtained during the solid state treatment of the mechanical mixture of CuCl and NH_4^+-ZSM-5. After only grinding, the micrograph of the sample shows numerous zeolitic crystals (spherical aggregates) with some rectangular particles. The EDS analysis indicates that they contain Cu and Cl. After calcination at 500 °C and washing, the non-zeolitic particles disappear and the aspect of the micrograph is identical to the initial NH_4^+-ZSM-5. Therefore the crystal morphology was not affected by the solid ion exchange.
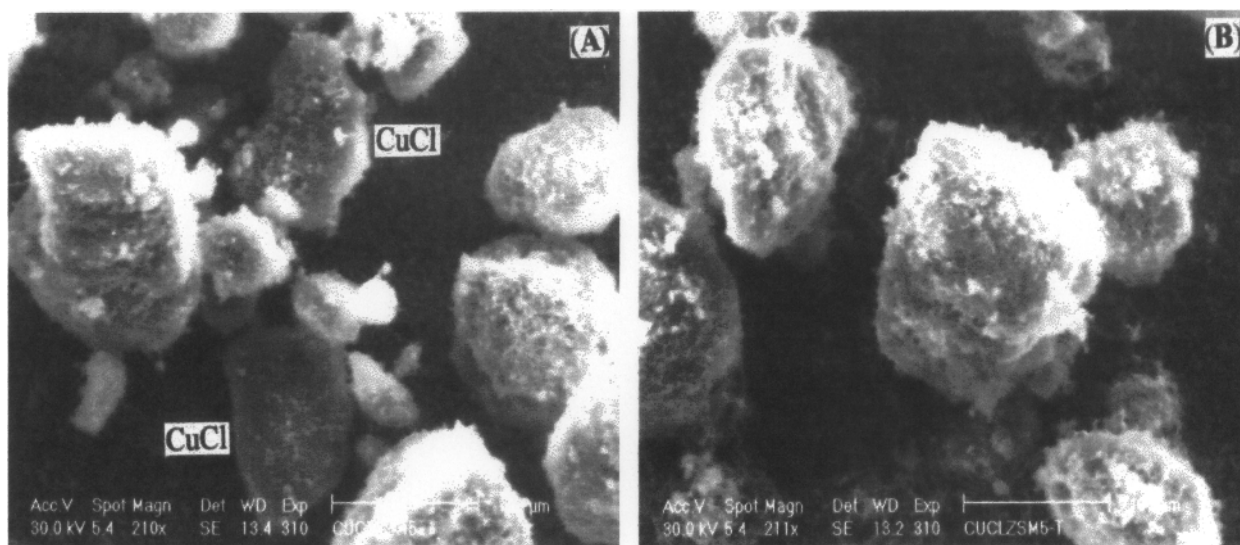
Figure 6: Scanning electron micrographs of (**A**) CuCl- NH_4^+-ZSM-5 mixture before heat treatment; (**B**) after heat treatment in dry air (Cu1Za2).

The UV-Vis- NIR diffuse reflectance (UVN-DR) spectra of Cu1Za1 and Cu2Za1 is shown in figure 7. The bands at 217 and 256 nm for Cu2Za1 can be attributed to low energy charge transfer (LCT) $Cu^{2+} \leftarrow O^{2-}$ of copper ions in octahedral environment. The presence of isolated octahedral Cu^{2+} ($3d^9$) sites is confirmed by a broad, but low intensity band centered near 827 nm, due to *d-d* transitions [40,41]. In addition to these bands, a shoulder centered at 330 nm is also clearly visible. This band was attributed according to Centi et al [40] to electron hopping in polynuclear copper–oxide species inside the zeolitic channels . The amount of this species increase with the increasing of copper loading. The sample Cu1Za3 spectrum (Figure 8) shows, besides the bands cited in the others samples, a new band about 450 nm .This band is attributed to the presence of some Cu^+ three dimensional clusters in CuO matrix [41].
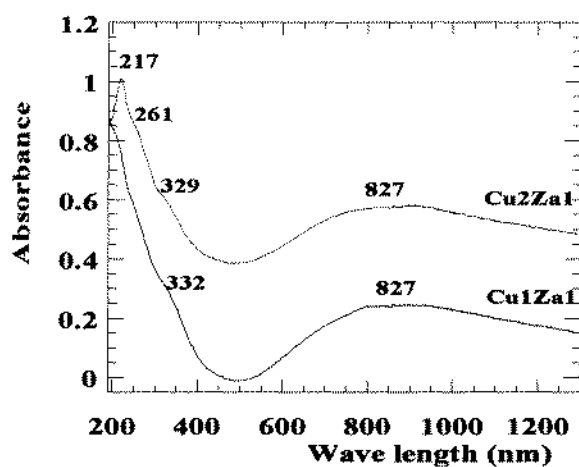
Figure 7: UVN-DR spectra of Cu1Za1 and Cu1Za2.
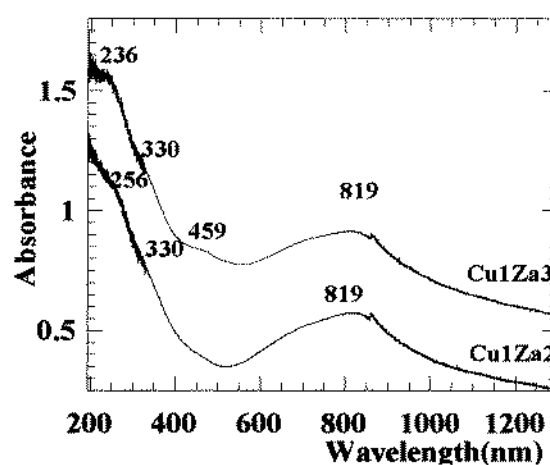
Figure 8: UVN-DR spectra of Cu1Za2 and Cu1Za3.

The UVN-DR spectra for samples prepared without dry air are presented in figure 9. The Cu1Zsa2 sample shows an absorption edge between 700 and 900 nm due to the energy gap of large particules of CuO, in agreement with XRD, besides the isolated Cu^{2+} and the copper polynuclear species. The formation of CuO particules is more pronounced in samples with higher copper loading.
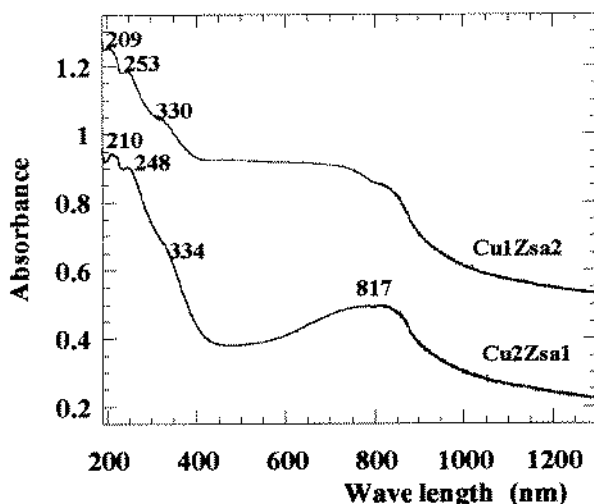

Figure 9: UVN-DR spectra of Cu1Zsa2 and Cu2Zsa1.

TPR has been used to identify the copper species in the exchanged zeolites and characterize their reducibility. According to previous works [42-44], the reactions involved in the reduction process are the following :
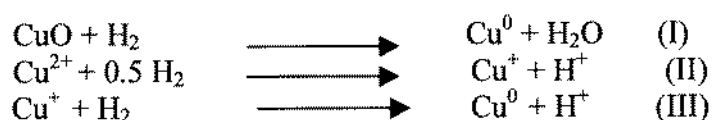
$$CuO + H_2 \longrightarrow Cu^0 + H_2O \quad (I)$$
$$Cu^{2+} + 0.5\ H_2 \longrightarrow Cu^+ + H^+ \quad (II)$$
$$Cu^+ + H_2 \longrightarrow Cu^0 + H^+ \quad (III)$$

Figure 10 shows the TPR profiles for samples Cu1Za2 and Cu2Za1. There were three H_2-consumption peaks centered at about 227, 277, 320 °C for Cu2Za1 and 217, 278, 340 °C for Cu1Za2. The first, is ascribed to the reduction of Cu^{2+} ions to Cu^+ with formation of H^+ (reaction I), the second represents the reduction of CuO clusters to Cu^0 (reaction II) and the third to Cu^+ to Cu^0 (reaction III).The relative quantities of the different copper species in the two samples are listed in table III.

Table III : The relative quantities of the different copper species.

| Samples	First peak (%)	Second peak (%)	Third peak (%)
Cu1Za1	18	52	30
Cu2Za1	51	41	9
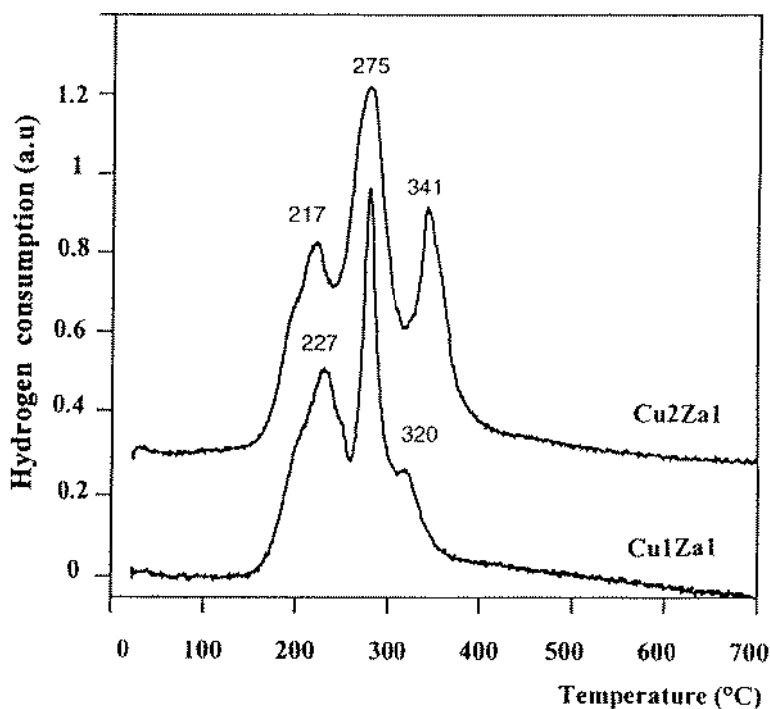
Figure 10: Temperature programmed reduction by H_2 of Cu1Za1 and Cu2Za1

The red–purple color of the reduced samples suggest the presence of copper metal particules. This result is confirmed by the XRD pattern of the reduced Cu2Za2 sample (Figure 11). It showed a new peak ($2\theta = 43.55$ °) which reveals the presence of metallic copper particles with sizes superior to 40 Å. The XRD diffractogram shows a little loss of crystallinity. The structure disruption is caused by the growth of the copper metal particules inside the zeolitic micropores which provoke the local destruction of the mouths of the channels.
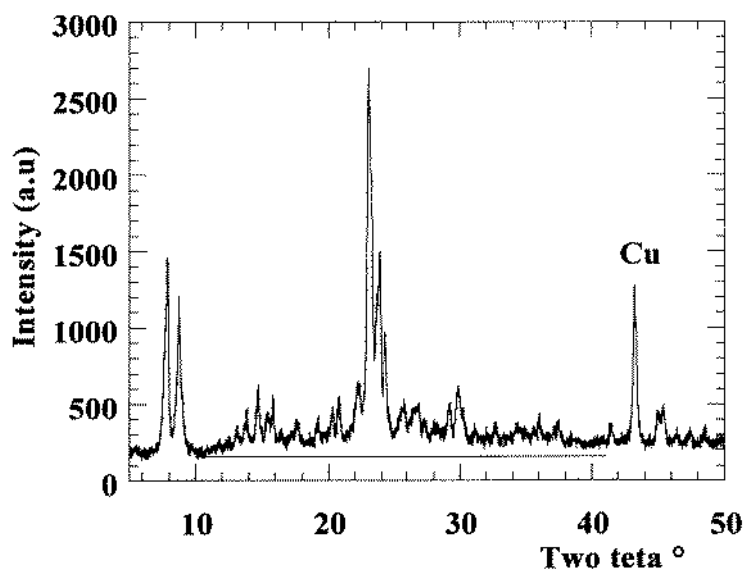
Figure 11: XRD pattern of Cu2Za2 after temperature programmed reduction by H_2.

The presence of Cu^+, Cu^{2+} and the oxygen – bridged copper species such $[Cu-O-Cu]^{2+}$ have been confirmed by TPR and UVN-DR techniques. The possible formation of the last species has been noted by several authors in ZSM-5 zeolite [40,42,43]. According to Halasz et al [37] it is possible, in ZSM-5 zeolite, that Z-O-Cu-O-Cu-O-Z bridges will be formed between two opposite Al-O sites in the double rings formed by 2×10 oxygen- bridged metal (Si or Al). The probability of such bridges is higher in those ZSM-5 samples which have Si/Al ratio inferior to 24, because some of their double rings necessarily contain two or more Al-O units.

BIBLIOGRAPHY

[1] M. Xin, I.C. Hwang, H. Kim, S.I. Cho, S.I. Woo, *App. Catal.B.*, **1999**, *21*, 183.

[2] C. Yokoyama, M. Misono, *Catal. Lett.*, **1994**,*1*, 29.

[3] X. Zhou, T. Zhang, Z. Xu, L. Lin, *Catal. Lett.*,**1996**,*40*, 35.

[4] Y. Li, J.N. Armor, *J. Catal.,***1994**,*1*,145.

[5] Y. Li, J.N. Armor, *Appl. Catal. B.,* **1993**, *3,* L1.

[6] M. Iwamoto, H. Yahiro, Y. Mine, S. Kagawa, *Chem. Lett.*,**1989**, 213.

[7] M. Iwamoto, H. Yahiro, Y. Torikai, T. Yoshioka, N. Mizuno, *Chem. Lett.*, **1991**, 1967.

[8] M. Shelef, *Catal. Lett.*, **1992**, *15*, 305.

[9] J. Vaylon, W.K. Hall, *Catal. Lett.*, **1993**, *19*, 109.

[10] M. Iwamoto, H. Hamada, *Catal. Today*, **1991**, *10*, 57.

[11] W. Held, A. Konig, T. Richter, L. Puppe, *SAE Paper N° 900496*, **1990**.

[12] G. Moretti, G. Minelli, P. Porta, P. Ciambelli, P. Corbo, M. Gambino, F. Migliardini, S. I coponi, *Stud. Surf. Sci. Catal.*, **1997**, *105*, 1525.

[13] R. Burch, P.J. Millington, *Appl. Catal. B.*, **1993**, *2*, 101.

[14] S. Sato, Y. Yu- u, H. Yahiro, N. Mizuno, M. Iwamoto, *Appl. Catal.*, **1991**, *70*, L1.

[15] F. Witzel, G.A. Sill, W. K. Hall, *J. Catal.*, **1994**, *149*, 229.

[16] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, *Appl. Catal.*, **1991**, *69*, L15.

[17] H. G. Karge, *Stud. Surf. Sci. Catal.*,**1997**, *105*, 1901.

[18] J. A. Rabo, M. L. Poutsma, G. W. Seels, Proceedings of the Fifth International Conference on Catalysis, North – Holland, pp. 1353, in J. W. Hightower Ed. New York, **1972**.

[19] A. Clearfield, C. H. Saldarriaga, R.C. Buckley, Third International Conference in Molecular Sieves, Paper N° 130, pp. 241, University of Leuwen Press, Leuwen, in J. B. Uytterhoeven Ed., **1973**.

[20] W. Grunert, T. Liese, C. Schobel, *Stud. Surf. Sci. Catal.*,**1997**, *105*, 1517.

[21] H. G. Karge, B. Wicherlova, H.K. Beyer, *J. Chem. Soc. Fara. Trans.*, **1992**, *88 (9)*, 1345.

[22] W. Grunert, N.W. Hayes, R.W. Joyner, E.S. Shpiro, M. Rafio, H. Siddiqui, G.N. Baeva, *J. Phy. Chem.*, **1994**, *98*, 10832.

[23] G.L. Price, V. Kanazirev, D.F. Church, *J. Phy. Chem.*, **1995**, *99*, 864.

[24] I. Schay, H. Knozinger, L. Guerzi, G. Pal- Borily, *Appl. Catal. B.*, **1998**, *18*, 263.

[25] J. Varga, J. Halsasz, D. Horvath, D. Mefin, J. B. Nagy, *Stud. Surf. Sci. Catal.*, **1998**,*116*, 367.

[26] I. Halasz, G.Pal- Borbley, H. K. Beyer, *React, Kinet, Catal. Lett.*,**1997**,*61 (1)*, 27.

[27] N.N. Sazonova, O.V. Komova, E.V.Robrov, A.V. Sumakov, N.A. Kulikovskaya, V.A. Rogov, G.B. Barannik, *React, Kinet, Catal. Lett*, **1997**,*60*, 331.

[28] D. J. Liu, H.J. Robota, *Catal, Lett.*, **1993**,*21*,291.

[29] M. Iwamoto, *Stud. Surf. Sci. Catal.*, **1991**,*60*,327.

[30] Y. Li, W. K. Hall, J. Catal., **1991**, *129*, 202.

[31] B. Wichterlova, Z. Sobalik, J. Dedecek, *Catal. Today*, **1997**, *38 (2)*, 199.

[32] D. J. Liu, H.J. Robota, *J. Phy. Chem.*, **1999**, *103*, 2755.

[33] Z. Chajar, M. Primet, H. Praliaud, M. Chevrier, C. Gauthier, F. Mathis, *Appl. Catal. B.*, **1994**, *4*, 99.

[34] H.Y. Chen, L. Chen, J. Lin, K.L. Tan, *Inorg. Chem.*,**1997**, *36*, 1417.
[35] G. Spoto, A. Zecchina, S. Bordiga, G. Ricchiardini, G. Martra, G. Leofanti, G. Petrini, *Appl. Catal. B.*, **1994**, *3*, 151.
[36] T. Liese, W. Grunert, *J. Catal.*, **1997**, *172*, 34.
[37] I. Halasz, A. Brenner, *Catal. Lett.*,**1998**, *51*, 195.
[38] B. Sulikowski, J. Find, H.G. Karge, D. Herein, *Zeolites.*, **1997**, *19*, 395.
[39] R. Szostak, Handbook of Molecular Sieves, Van Nostrand Reinhold, New York, pp 518, **1992**.
[40] G. Centi, F. Fazzini, A. Galli, *Res. Chem. Inter.*, **1998**, *24 (5)*, 541.
[41] H. Praliaud, S. Mikhailenko, Z. Chajar, M. Primet, *Appl. Catal. B.*, **1998**, *16*, 359.
[42] T. Beutel, J. Sarkany, G. D. Lei, J. Y. Yan, W. M. H. Sachtler, *J. Phy. Chem.* **1996**, *100*, 845.
[43] J. Sarkany, J. L. D'Itri, W. M. H. Sachtler, *Catal. Lett.*, **1992**, *16*, 241.
[44] G. Delahay, B. Coq, L. Broussous, *Appl. Catal. B.*, **1997**, *12*, 49.