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Cu-Al-O Powders Prepared from Zeolite Precursors by Combination Treatment of Ball Milling and Heating

Cleo Kosanović,^{a,*} Mirko Stubičar,^b Ana Mužić,^a and Nenad Tomašić^c

^a*Ruđer Bošković Institute, Bijenička c. 54, HR-10000 Zagreb, Croatia*

^b*Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, HR-10000 Zagreb, Croatia*

^c*Institute of Mineralogy and Petrography, Faculty of Science, University of Zagreb, Horvatovac bb, HR-10000 Zagreb, Croatia*

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By applying combination of mechanochemical and thermal treatment important materials that could be used in sensor and semiconductor technology as well in catalysis are obtained. High energy ball milling was applied to prepare powder samples by treating mixture consisted a) of Cu and ammonium exchanged zeolite A and b) of CuO and ammonium exchanged zeolite A. According to X-ray powder diffraction the mechanical treatment resulted in mixture of amorphous phase and low size crystal particles. After 3 h of milling the samples were isothermally treated at the appropriate temperature yielding crystalline mixtures with a dominant phase of CuAlO₂. Thermal treatment of Cu-exchanged zeolite A resulted in a crystalline sample with dominant phase CuAl₂O₄.

INTRODUCTION

Copper-aluminum oxides are important materials in sensor and semiconductor technology as well as in heterogeneous catalysis due to their high thermal stability and specific catalytic and/or electronic properties. Transparent conducting oxides are materials that exhibit high electrical conductivity and high optical transmittance in the visible range.

A lot of effort has been done in preparation of CuAlO₂ films used as new p-type transparent semicon-

ductors.^{1,2} Solution methods such as sol-gel processing and nitrate processes,³ as well as the citrate process⁴ are used for the preparation of metal oxides. Other techniques such as PLD (pulsed laser deposition), dc reactive magnetron sputtering,^{5,6} and chemical vapor deposition technique⁷ are commonly used for the preparation of transparent copper-aluminum oxide semiconductor films.

In this study nanosized crystalline Cu-Al-O powders are obtained by using metal and metal oxide in combination with zeolite precursor as starting materials. High en-

* Author to whom correspondence should be addressed. (E-mail: cleo@rudjer.irb.hr)

ergy ball milling, recognized as a powerful tool in preparing novel materials in the field of materials science, was applied in order to obtain homogeneous powders of new non-equilibrium phase materials with functional characteristics, which very often could not be produced by other common processing techniques. The obtained materials were isothermally treated and the phase obtained by solid state transformations was expected to be copper-aluminium oxide.

EXPERIMENTAL

NH₄-exchanged zeolite A (NH₄A) and Cu-exchanged zeolite A (CuA) were prepared by the following procedure: Zeolite Linde 4A prepared by a known method⁸ in our laboratory was used as a starting material. Ion-exchange of the original Na⁺ ions from the zeolite with NH₄⁺ ions and then with Cu²⁺ ions was carried out as follows: 10 g of powdered zeolite A was placed in a stainless steel reaction vessel containing 250 ml of 0.5 mol dm⁻³ solution of NH₄Cl, preheated at 70 °C. The suspension was stirred for 2 h at 70 °C and thereafter the solid phase was separated from the solution by filtration. The residue on the filter paper was re-dispersed in a fresh 250 ml portion of 0.5 mol dm⁻³ solution of NH₄Cl, and stirred again for 1 h at 70 °C. After the final solid/liquid separation, the residue on the filter paper was rinsed with distilled water until the reaction of the filtrate with AgNO₃ yielded a negative result, and then was dried at 105 °C for 24 h. The same procedure was carried out with 250 ml of 0.5 mol dm⁻³ solution of Cu(NO₃)₂ in order to obtain Cu exchanged zeolite A.

The two other samples used in this study were prepared as follows:

The mixture of NH₄-exchanged zeolite A and CuO (a product of Johnson Matthey Materials Technology U.K.) in a mass ratio of 1:0.5, as well the mixture of NH₄-exchanged zeolite A and Cu (a product of Ventron GMBH) in a mass ratio of 1.5:0.5, were mechanically treated in a planetary ball mill (Fritsch Pulverisette type 7). A certain amount of the mixture (1.15 g) was put in an agate vessel containing 10 agate balls (*f* = 10 mm) and 4 agate balls (*f* = 12 mm), and then milled for predetermined time *t_m*.

The starting materials and the milled samples were characterized as follows:

- XRD diffractograms of the samples were taken by a Philips PW 3040/60 X'Pert PRO powder diffractometer with a graphite monochromised Cu-Kα irradiation. Powder diffraction data were collected in the 2*Q* range of 4–60° in steps of 0.02°. The observed *d*-spacings and the relative intensities of the X-ray diffraction lines were compared with the literature values reported.⁹

- The mass fractions of crystalline and amorphous phases were calculated by the mixed method¹⁰ using the integral value of the broad amorphous peak and the corresponding sharp peaks of crystalline phases.

- Thermal analysis of the sample obtained after 6 h of milling was done by a Netzch STA 409 simultaneous ther-

mal analysis apparatus under a constant air flow of 30 cm³ min⁻¹. Pt crucibles and alumina as a reference were used. The heating rate was 10 K min⁻¹.

RESULTS AND DISCUSSION

In order to achieve a dispersed system, a mixture of Cu and NH₄ exchanged zeolite A, (0.5 + 1.5) g, and a mixture of CuO and NH₄ exchanged zeolite A, (0.5 + 1) g, were mechanically treated and the changes occurred during milling were monitored by X-ray powder diffraction. In the first case, the system became amorphous by the milling process (Figure 1, Table I). Taking into consideration that the mass fraction of Cu in the initial mixture was 25 %, by analyzing the phases formed during milling it can be concluded that after 5 h of milling nearly the whole amount of zeolite was amorphized and the Cu partially oxidized forming CuO [PDF 45-0937], followed by the lowering of the particle size of the remaining crystalline Cu [PDF 04-0836]. A small amount of the low temperature quartz was also formed [PDF 46-1045].

In the second case (Figure 2, Table I), the NH₄ exchanged zeolite A was after 3 h of milling completely transformed in the low temperature quartz and an amorphous phase, since CuO remained crystalline in the form of tenorite [PDF 45-0937]. The changes in the phases were not significant after 5 h of milling, so the samples milled for 3 h were selected for further treatment.

Cu-exchanged zeolite A was another interesting starting material that was prepared for the synthesis of copper-aluminium oxides via solid state transformation.

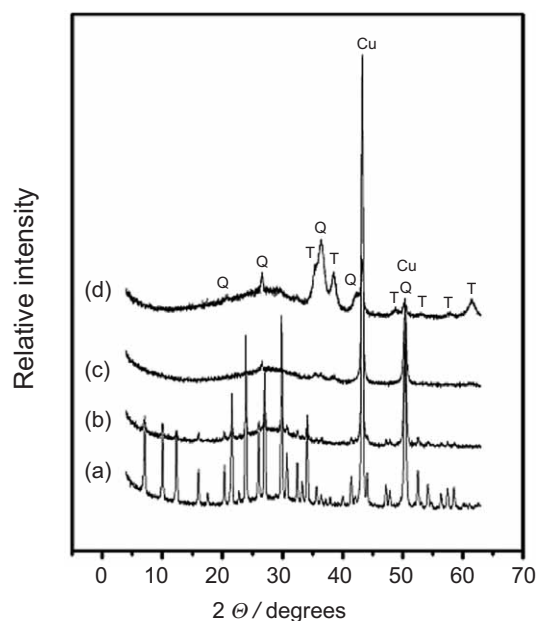


Figure 1. X-ray diffractograms of products obtained by ball-milling the mixture of zeolite NH₄A and Cu (mass ratio 1.5 : 0.5) for 10 min (a), 1 h (b), 3 h (c) and 5 h (d). Symbols: T – CuO (tenorite), Q – SiO₂ (low temperature quartz), Cu – copper.

TABLE I. Changes in components fraction and phase of the crystalline mixture of zeolite NH_4A and $\text{Cu}^{(a)}$ and of the crystalline mixture of zeolite NH_4A and $\text{CuO}^{(b)}$ obtained for different milling time

Time of ball milling	Cristallinity / %	Obtained phases
$\text{NH}_4\text{A} + \text{Cu}^{(a)}$		
10 min	99.0	$\text{NH}_4\text{A} + \text{Cu} + \text{traces of amorphous phase}$
1 h	54.0	$\text{NH}_4\text{A} + \text{Cu} + 46 \% \text{ amorphous phase}$
3 h	33.0	$\text{SiO}_2 \text{ (low temp. quartz)} + \text{Cu} + \text{CuO (tenorite)} + 67 \% \text{ amorphous phase}$
5 h	25.0	$\text{CuO (tenorite)} + \text{Cu syn.} + \text{SiO}_2 \text{ (low temp. quartz)} + 75 \% \text{ amorphous phase}$
$\text{NH}_4\text{A} + \text{CuO}^{(b)}$		
10 min	95.0	$\text{NH}_4\text{A} + \text{CuO (tenorite)} + \text{traces of amorphous phase}$
1 h	76.0	$\text{NH}_4\text{A} + \text{CuO (tenorite)} + 24 \% \text{ of amorphous phase}$
3 h	50.0	$\text{CuO (tenorite)} + \text{SiO}_2 \text{ (low temp. quartz)} + 50 \% \text{ of amorphous phase}$
5 h	48.0	$\text{CuO (tenorite)} + 52 \% \text{ of an amorphous SiO}_2 \text{ phase} + \text{amorphous phase}$

^(a) Mass ratio 1.5 : 0.5. ^(b) Mass ratio 1.0 : 0.5.

The temperature of the solid state transformation of the three samples was obtained by thermal analysis (Figure 3) as the exothermic peak in the DSC curves (Table II). The sharpest peak at higher temperatures was chosen for each sample. At lower temperature the phase transformation is taking place because of the damage of the zeolite structure that was gradually turning into amorphous phase. The endothermic peaks below 673 K belonged to the loss of the "zeolitic" water from the crystal structure and the ones at about 373 K belonged to the moisture loss from the sample.

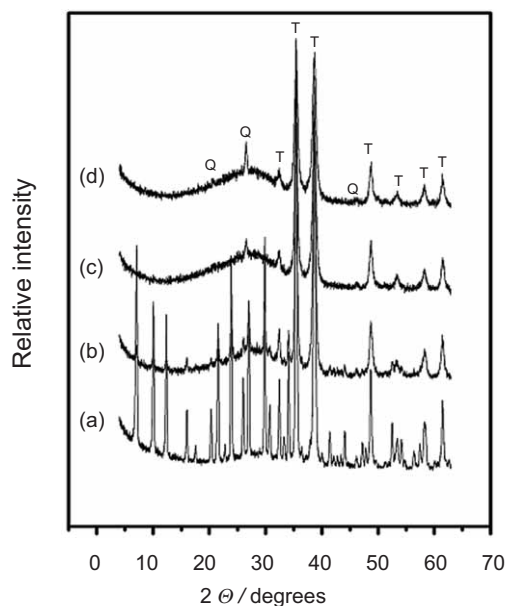


Figure 2. X-ray diffractograms of products obtained by ball-milling the mixture of zeolite NH_4A and CuO (mass ratio 1 : 0.5) for 10 min (a), 1 h (b), 3 h (c) and 5 h (d). Symbols: T – CuO (tenorite), Q – SiO_2 (low temperature quartz).

NH_4 -exchanged zeolite A was treated as follows. First step was the ion-exchange (Figure 4a, Table II):

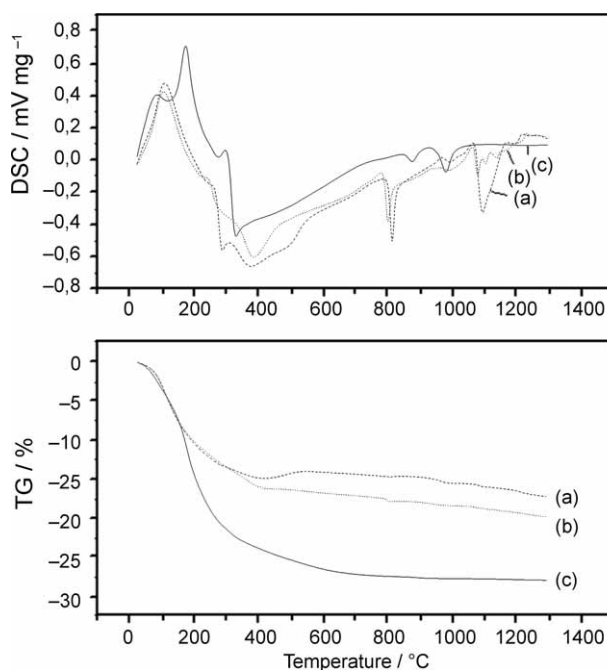
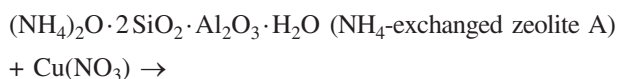


Figure 3. DSC and TG curves of the mixture of NH_4 -exchanged zeolite A and Cu (mass ratio 1.5 : 0.5) milled for 3 h, dashed line --- (a); NH_4 -exchanged zeolite A and CuO (mass ratio 1 : 0.5) milled for 3 h, dots ... (b) and Cu -exchanged zeolite A, solid line — (c).

TABLE II. The obtained phases after isothermal treatment of the Cu-exchanged zeolite A, of the milled mixture of zeolite NH₄A and Cu, and of the milled mixture of zeolite NH₄A and CuO at the temperature of their DSC peak

	CuA	Cu + NH ₄ A ^(a)	CuO + NH ₄ A ^(b)
Time of milling / h	–	3	3
Time of heating / h	3	3	3
Temperature of heating (DSC-peak) / K	1273	1368	1354
Total mass loss / %	28.02	17.26	19.87
Obtained phases	Copper aluminium oxide (CuAl ₂ O ₄) + Silicon oxide (SiO ₂)	Copper aluminium oxide, CuAlO ₂ (2H- and 3R-polytype) + Copper oxide (CuO) + Spinel	Copper aluminium oxide, CuAlO ₂ (2H- and 3R-polytype) + Copper oxide (CuO)

^(a) Mass ratio 1.5 : 0.5. ^(b) Mass ratio 1.0 : 0.5.

Then the calcination was performed isothermally at 1273 K (Figure 4b, Table II):

CuO·2SiO₂·Al₂O₃·2.1H₂O (Cu-exchanged zeolite A) → CuAl₂O₄ (copper aluminum oxide) [01-078-0556] + SiO₂ (silicon oxide) [01-076-1390]

The milled mixture of Cu and NH₄ exchanged zeolite A (0.5:1.5) (Figure 4c, Table II) after heating at 1368 K for 3 h gave CuAlO₂ [01-075-2357, 00-040-1037] (Figure 4d) as a dominant phase and the copper phase was oxidized to CuO [01-080-1916]. The reaction did not occur in stoichiometric way. The aluminum oxide content from the zeolite precursor was calculated to be ≈ 0.5 g that could react with ≈ 0.6 g of Cu. Silicon oxide, also originating from the zeolite precursor, remained as an amorphous phase that could be removed by an alkaline treatment.¹¹

The milled mixture of CuO and NH₄ exchanged zeolite A (0.5:1) (Figure 4e, Table II) after heating at 1354 K for 3 h produced CuAlO₂ [01-075-2357, 00-040-1037] (Figure 4f) as a dominant phase, containing small amounts of CuO that did not react. Since 1 g of zeolite precursor contained about 0.325 g of aluminum oxide that could react with 0.5 g of CuO, it could be concluded that the remained amorphous phase of 5 %, as it is calculated by a method described in Ref. 10, was composed of a mixture of amorphous SiO₂ and Al₂O₃.

It does not matter whether Cu or CuO was used in milled mixture with NH₄ exchanged zeolite A, after thermal treatment CuAlO₂ occurred as both 2H- and 3R-polytype.

CONCLUSION

This study had shown that powder mixtures of metal and metal oxides with zeolite precursors may be used for the preparation of copper-aluminium oxides via solid state

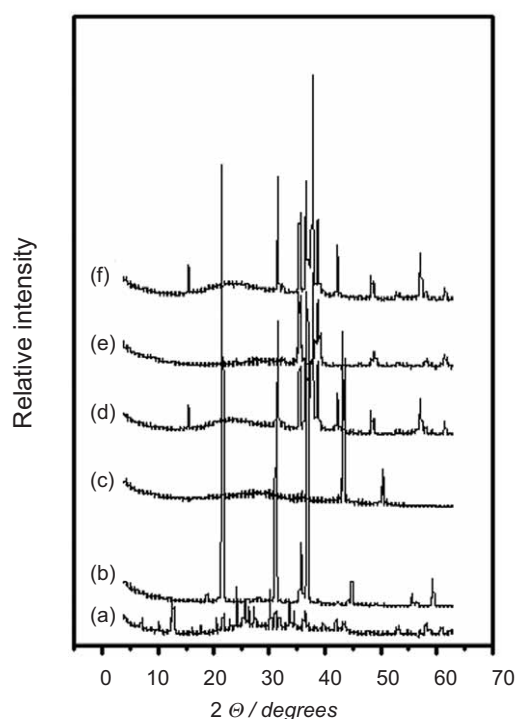


Figure 4. X-ray diffractograms of the Cu-exchanged zeolite A milled for 3 h (a) and heated at 1273K (b), the mixture of zeolite NH₄A and Cu (mass ratio 1.5 : 0.5) milled for 3 h (c) and heated at 1368 K (d), the mixture of zeolite NH₄A and CuO (mass ratio 1 : 0.5) milled for 3 h (e) and heated at 1354 K (f).

transformation processes. High energy ball mill was used to partially amorphize the mixture or to decrease the particle size of the constituents in order to achieve better homogeneity of the formed materials. Different Cu/Al ratio was obtained in the end product when the Cu constituent was incorporated in the zeolite structure.

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SAŽETAK**Cu-Al praškasti oksidi pripremljeni iz zeolitnih prekursora kombiniranim djelovanjem kugličnog mljevenja i termičke obrade****Cleo Kosanović, Mirko Stubičar, Ana Mužić i Nenad Tomašić**

Kombinacijom mehanokemijske i termičke obrade dobiveni su važni materijali koji se mogu koristiti kao senzori, poluvodiči i katalizatori. Visoko energetska mljevenja (engl. *high energy ball milling*) je korišteno za dobivanje praškastih smjesa koje se sastoje: a) od Cu i amonijeve forme zeolita A, b) od CuO i amonijeve forme zeolita A. Iz rentgenskih difraktograma je vidljivo da mehaničko tretiranje rezultira stvaranjem amorfnih faza i smanjenjem veličine čestica. Nakon 3 h mljevenja, uzorci su tretirani izotermički na odgovarajućim temperaturama te su dobivene smjese sa dominantnom fazom CuAlO₂. Termičko tretiranje same Cu-forme zeolita A rezultira stvaranjem kristalnog materijala s dominantnom fazom CuAl₂O₄.