

Geopolymers and Other Inorganic Polymers

COPYRIGHTED MATERIAL

METAKAOLIN-NANOSILVER AS BIOCIDES AGENT IN GEOPOLYMER

José S. Moya^a, Belén Cabal^a, Jesús Sanz^a, Ramón Torrecillas^b

^aInstituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Cantoblanco, 28049, Madrid, Spain

^bCentro de Investigación en Nanomateriales y Nanotecnología (CINN), Consejo Superior de Investigaciones Científicas (CSIC) – Universidad de Oviedo (UO) – Principado de Asturias, Parque Tecnológico de Asturias, 33428, Llanera, Spain

ABSTRACT

Metakaolin is an aluminosilicate mineral product which is produced in quantities of several million tons per year worldwide and used in applications including supplementary cementitious materials in concretes, an intermediate phase in ceramic processing, as a paint extender, and as a geopolymer precursor. Meanwhile, geopolymers are also being considered for a variety of applications including low CO₂ producing cements, fiber-reinforced composites, refractories, and as precursors to ceramic formation.

Given the importance of metakaolin in several industry sectors, and also taking into account the possible large spectrum of applications, incorporating silver nanoparticles could provide an additional biocide functionality. In this regard, further studies of their structural evolution are required because of the presence of silver nanoparticles. For this purpose, this work is mainly focused on the evaluation of the effect of the presence of silver nanoparticles on kaolin/metakaolin structures and also on the study of their biocide capacity.

1. INTRODUCTION

Geopolymers are a class of inorganic polymers that are based on aluminosilicates. They are usually produced by adding a reactive aluminosilicate precursor, such as fly ash or metakaolin, to a highly alkaline silicate solution in order to facilitate the break-up of the primary aluminosilicate framework, leading to polymerisation and solidification. Then curing at 25–90 °C in a humid atmosphere completes the process. Geopolymers have received considerable attention because of their low cost, excellent mechanical and physical properties, low energy consumption and reduced “greenhouse emissions” at the elaboration process [1].

Metakaolin is preferred by the niche geopolymer product developers due to its high rate of dissolution in the reactant solution, easier control on the Si/Al ratio and the white colour. Metakaolin is formed by the dehydroxylation of kaolin. When kaolin is heated beyond the temperature of the dehydroxylation, endothermic metakaolin is formed. Between 500 and 900 °C, this is the main product obtained. The exact temperature range depends on the starting kaolin and on the heating regime.

Kaolin possesses a two-layered structure where a sheet of octahedrally coordinated aluminium is connected to a tetrahedrally coordinated silicon sheet. Sanz et al. [2] studied the kaolinite-mullite transformation by magic-angle spinning nuclear magnetic resonance (MAS-NMR) and determined the presence of Al in tetra- and pentacoordination in metakaolinite. The heat treatment at 700 °C alters the structure of kaolin, the main change being the dehydroxylation of the octahedra. Above 800 °C, tetrahedral sheets are broken making possible silica and alumina segregations. These modifications eliminate long-range order and make possible the formation at 980 °C of amorphous mullite precursors. Dehydroxylation treatments cause the clay to become chemically reactive.

On the other hand, with the emergence and increase of microbial organisms resistant to multiple antibiotics, and the continuing emphasis on health-care costs, the development of materials with the ability to inhibit bacterial growth has been of great interest in recent years. The antimicrobial activity of silver has been known since ancient times. In the course of this work, a simple and fast method to prepare monodispersed silver nanoparticles embedded into kaolin and metakaolin is presented. These new silver-based nanostructured materials could have potentially wide-ranging applications, among others they could be used as precursors in geopolymer synthesis providing additional biocide functionality. Based on this, this work is mainly focused on the evaluation of the effect of the presence of silver nanoparticles on the structures of kaolinite/metakaolin and also on the study of their biocide capacity.

2. EXPERIMENTAL SECTION

2.1. Materials

Kaolin from CAVISA, La Coruña, Spain, with the following chemical analysis (wt.%): 54.3 SiO₂, 33.0 Al₂O₃, 0.19 TiO₂, 0.76 Fe₂O₃, 0.03 CaO, 0.37 MgO, 0.67 K₂O, 0.02 Na₂O, was used as raw material. Metakaolin was obtained after calcination of kaolin at 700 °C for 24 h in air. Silver nanoparticles supported on kaolin were obtained using AgNO₃ as silver precursor and following two different reduction *vias*: the first by thermal reduction at 350 °C for 2 h in H₂ atmosphere and the second one by chemical reduction employing sodium borohydride as a reducing agent. In the case of metakaolin, only chemical reduction was performed.

2.2. TEM and FTIR characterization

The morphological aspects of the samples were studied by transmission electron microscopy (TEM) (Jeol microscope model FXII operating at 200 kV). Infrared spectroscopy was done in transmission in a vacuum atmosphere with a Fourier transform infrared spectrometer (Bruker IFS 66v/s).

2.3. MAS-NMR measurements

The ²⁷Al and ²⁹Si NMR spectra were obtained at room temperature, using an Avance (Bruker) spectrometer, operating at 104.3 MHz for ²⁷Al and 79.5 MHz for ²⁹Si (9.4 T external magnetic field). The samples were loaded in 4 mm rotors and spinned at 10 kHz during MAS-NMR spectra recording. In this study, $\pi/2$ (5 μ s) pulses, 5s inter-accumulation intervals and 125 kHz filterings were used. All spectra were referred to TMS (tetramethylsilane) and Al(H₂O)₆³⁺ as external standards. The error in chemical shift values was estimated to be lower than 0.5 ppm.

2.4. Antibacterial tests

Antibacterial tests were performed to investigate the effect of the kaolin/metakaolin/nAg powder on two different micro-organisms: *Escherichia coli* JM 110 (Gram-negative bacteria), *Micrococcus luteus* (Gram-positive bacteria). The two different bacteria were incubated in a liquid media overnight at 37 °C. After that, 10 μ L from each culture was diluted to 1 mL, using suitable media, and cultured at 37 °C for 6 h. The media used were Luria Bertani (LB). Subsequently, 150 μ L of an aqueous suspension of kaolin/metakaolin/nAg composite (30 wt.%) was added to a final concentration of silver in each culture of 0.036 wt.%. A silver free media (a mixture of water containing the corresponding nutrient) was used as control. The microorganisms were tested for viability after culture on appropriate dilution from the corresponding cultures. The inocula were incubated at 37 °C with horizontal shaking for 48 h. The number of viable colonies was counted every 24 h.

3. RESULTS AND DISCUSSION

3.1. Characterization and effect of the presence of silver nanoparticles on the structure

The morphology of the samples was studied by TEM (Figure 1). A size distribution was carried out from different TEM images. There is a size distribution of globular-shaped silver nanoparticles that range between $d_{50} \sim 12 \pm 7$ nm in the case of kaolin samples and $d_{50} \sim 30 \pm 15$ nm for metakaolin. TEM images (Figure 1) also provide evidence for different distributions of silver nanoparticles, depending on the kind of support (i.e., kaolin or metakaolin) and on the reduction treatments used (for the different treatment see section 2.1). As it is clearly seen, in the case of the sample of chemically reduced kaolin (Figure 1.A), silver nanoparticles are anchored preferably on the crystal edges (the distribution of silver nanoparticles corresponds to 68 % at edges versus 32 % at basal surface), whereas in the case of the thermally reduced kaolin (Figure 1.B) and of the metakaolin (Figure 1.C), the distribution is more homogeneous (ca. 48 % at edges and 52 % at basal surface). Taking into account the structure of kaolin, silver nanoparticles could be bonded to the clays substrate *via* electrostatic interaction between the negatively charged and edge Al-O⁻ and Si-O⁻ groups of the surface clays, or with the anionic basal silicate planes if hydrogen bonds tightly linking contiguous layers are broken, before or during the incorporation of silver. It can be inferred that the adhesion of silver nanoparticles is closely related to the amount of surface hydroxyl groups located at the crystal edges. A decrease in hydroxyl groups of the clay leads to a more homogeneous distribution of silver nanoparticles, but with the disadvantage that their size is larger.

Although there are some studies in the literature about the synthesis of silver nanoparticles-kaolin composite materials [3, 4, 5], there are none on metakaolin particles. In order to obtain more information about the interaction of silver nanoparticles with metakaolin and whether or not its structure is modified, FTIR and MAS-NMR investigations have been performed.

The transformation of kaolin to metakaolin can be clearly deduced from the lattice region, 1400-400 cm^{-1} , of FTIR spectra (Figure 2). The kaolin starting material gives at least 10 well-defined IR bands in this region due to Si-O, Si-O-Al, and Al-OH vibrations: 1113, 1031, 1009, 699, 471, and 432 cm^{-1} (Si-O); 938 and 912 cm^{-1} (Al-OH); 792, 756, 539 cm^{-1} (Si-O-Al^(VI)) [6]. The conversion to metakaolin totally removes these bands. In general, changes in the Si-O stretching bands and the disappearance of the Si-O-Al bands suggest strong modifications in tetrahedral and octahedral layers of the metakaolin. The incorporation of silver nanoparticles, both in kaolin and metakaolin, does not modify the positions of vibrational bands in the region 1100-400 cm^{-1} , indicating a small interaction between silicate layers and silver nanoparticles.

Magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy was employed with the aim of further clarifying the mode of bonding between the silver nanoparticles and the clay substrates. ²⁹Si-NMR is capable of distinguishing SiO₄ tetrahedra, with connectivity ranging from 0 to 4 (Q_m species, with m standing for the number of bridging oxygens) [7]. In the original kaolin (Figure 3), two sharp absorptions at -91.5 ppm with full width at half maximum (FWHM) of 1 ppm were detected in ²⁹Si-NMR spectra, which corresponds to Si atoms in tetrahedral layers of layer silicates (Q³ polymerization state) [2]. The incorporation of silver nanoparticles, following a chemical or thermal reduction (Figure 3), does not change the structure of kaolin. The spectra obtained in both cases are similar to the kaolin. Only in the case of the sample thermally reduced at 350 °C (Figure 3) it was observed a slight broadening of the main peak at -91.5 ppm and the formation of a new small broad band at -97 ppm. This could indicate the formation of a small fraction of amorphous silica. The ²⁷Al NMR spectrum of kaolin (Figure 4) shows a single peak at 0 ppm, characteristic of Al in octahedral coordination. No differences were detected when silver nanoparticles were supported on it chemically or thermally.

Metakaolin shows a very wide and asymmetric ^{29}Si resonance band (Figure 3) with two intense signals of different linewidth at -107.8 and at -101.4 ppm. This suggests the coexistence of aluminum free $\text{Q}^4(0\text{Al})$ species, i.e. pure SiO_2 phase, and homogeneously distributed $\text{Si}(\text{Al})\text{O}_4$ units [$\text{Q}^4(1\text{Al})$]. When silver nanoparticles are supported on metakaolin (Figure 3), the intensity of the peak at -107.8 ppm is maintained but the peak at -101.4 ppm shifts to -103.6 ppm. From these results, a variation in the chemical environment of the silicon nuclei of the metakaolin upon incorporation of silver nanoparticles can be inferred.

The ^{27}Al NMR spectrum of metakaolin (Figure 4) contains three peaks at 4, 28 and 54 ppm, attributed respectively to the presence of octahedral, pentahedral and tetrahedral aluminum [2]. The incorporation of silver nanoparticles to metakaolin stabilizes in some way the unstable structure of metakaolin. When spectra of starting and treated metakaolin are compared (Figure 4), a slight increase of hexacoordinated at expenses of tetrahedral and pentahedral aluminium is observed.

From the comparative analysis of ^{29}Si and ^{27}Al MAS-NMR spectra of starting materials and those of silver-kaolin or silver-metakaolin composites, it can be concluded that the silver particles interact preferentially with tetrahedral sheets and in a minor extent with octahedral layers of metakaolin particles. In this case some stabilization of hexacoordinated aluminium is favoured by incorporation of silver particles.

3.2. Biocide Activity

To investigate the antibacterial effect of n-Ag containing powders, a biocide test was performed inoculating 10^{10} colonies forming units into 1 mL of the corresponding medium with *Escherichia coli*, *Micrococcus luteus*. The microorganisms were tested for viability after culture on appropriate dilution from the corresponding cultures. During this test, the viable microorganisms were counted after 24 and 48 hours. As a control, silver free media (a mixture of water and the corresponding nutrient) was cultured under the same conditions.

The logarithm reduction ($\log \eta$) has been used to characterize the effectivity of the biocidal agent:

$$\log \eta = \log A - \log B \quad (1)$$

where A is the average number of viable cells from inoculum controls after 24, 48 h, and B is the average number of viable cells from the substance after 24, 48 h.

As it can be seen in Figure 5 after 24 h, the presence of silver nanoparticles on kaolin surface, at the concentration of 0.036 wt.% of silver, reduces completely the number of colonies of *E.coli* and *M. luteus*, achieving a logarithm reduction higher than 10 which means a completely safe disinfection. Its high effectiveness is pointed out against both bacteria. In the case of metakaolin-silver nanocomposite, higher times are required to obtain quite similar results (i.e., $\log \eta \sim 8$ for *E. coli* and $\log \eta > 10$ for *M. luteus*). This behaviour could be attributed to the different sizes of silver nanoparticles in both materials. Previously, it was mentioned that silver nanoparticles embedded in kaolin are significantly smaller [$d_{50} \sim 12 \pm 7$ nm] than when they are in metakaolin [$d_{50} \sim 30 \pm 15$ nm]. The size of nanoparticle implies that it has a large surface area coming into contact with the bacterial cells and hence, it will have a higher percentage of interaction than the one with bigger particles.

The mechanism of bactericidal action of silver nanoparticles embedded into an inorganic matrix is still not fully known [8]. The silver nanoparticles show efficient antimicrobial property compared to other salts due to their extremely large surface area, which provides better contact with microorganisms. Sulphur-containing proteins in the membrane or inside the cells as well as phosphorous-containing elements are likely to be the preferential sites for silver nanoparticles binding. The nanoparticles release silver ions in the bacterial cells, which enhance their bactericidal activity [9].

The presence of low concentration of silver nanoparticles and silver ions involves a cytotoxic effect on human fibroblast stabilizing the cytotoxic limit above 30 ppm for silver nanoparticles and 1 ppm for silver ions [10]. In order to determine the toxicity of these materials, silver concentration in the resulting supernatant after 48 h was measured by Inductively Coupled Plasma (ICP) analyses. The results obtained are shown in Table 1. The concentration of silver nanoparticles in solution when metakaolin-nAg is used was about 4 times higher than in the case of kaolin-nAg, for all microorganisms studied. This can be due to the notable difference on particle size. Kaolin/metakaolin/nAg powders release significantly less fraction of silver keeping the concentration of silver below the cytotoxic level.

CONCLUSIONS

Following a simple and low-cost method it was possible to obtain silver dispersed nanoparticles attached to a kaolin/metakaolin matrix. The uneven distribution of the silver nanoparticles on the kaolin plates has been related to the presence of AlOH and SiOH at the edges of the plates. Conversely, silver nanoparticles are homogeneously distributed in metakaolin. When ^{27}Al and ^{29}Si MAS-NMR spectra of two modified supports are compared, it was concluded that silver particles interact in a preferential way with tetrahedral layers of metakaolin materials. The bactericidal activity results show that these nanocomposites are strongly active against some of the most common Gram positive and negative bacterial strains, which could open the possibility to use them as precursors to fabricate biocide geopolymers with a large spectrum of applications.

ACKNOWLEDGEMENT

The authors acknowledge the financial support from ITMA, Spain (Ref. 010101090014) and the regional CAM Government (project S-2009/PPQ 1626).

REFERENCES

- [1] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer. Geopolymer technology: the current state of the art. *Journal of Materials Science* 42 (2007) 2917-2933.
- [2] J. Sanz, A. Madani, J.M. Serratosa, J.S. Moya, S. Aza. Aluminum-27 and silicon-29 magic-angle spinning nuclear magnetic resonant study of the kaolinite-mullite transformation. *Journal of American Ceramic Society* 71 (1988) C-418-C421.
- [3] K. Burridge, J. Johnston, T. Borrmann. Silver nanoparticles-clay composites. *Journal of Materials Chemistry* 21 (2011) 734-742.
- [4] R. Patakfalvi, I. Dékány. Synthesis and intercalation of silver nanoparticles in kaolinite/DMSO complexes. *Applied Clay Science* 25 (2004) 149-159.
- [5] R. Patakfalvi, A. Oszkó, I. Dékány. Synthesis and characterization of silver nanoparticles/kaolinite composites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 220 (2003) 45-50.
- [6] E. Kristoff, A.Z. Juhasz, I. Vassanyi. The effect of mechanical treatment on the crystal structure and thermal behaviour of kaolinite. *Clay and Clay Minerals* 41 (1993) 608-612.
- [7] G. Engelhardt, D. Michael. High Resolution Solid-State NMR of silicates and zeolites. John Wiley & Sons Ltd. 1987.

- [8] C. Marambio-Jones, E.M.V. Hoek, A review of the antibacterial effects of silver nanomaterials and potencial implications for human health and the environment, *J. Nanopart. Res.* 12 (2010) 1531-1551.
- [9] M. Rai, A. Yadav, A. Gade, Silver nanoparticles as a new generation of antimicrobials, *Biotechnol. Adv.* 27 (2009) 76-83.
- [10] A. Panáček, M. Kolář, R. Večeřová, R. Prucek, J. Soukupová, V. Kryštof, P. Hamal, R. Zbořil, , L. Kvítek, Antifungal activity of silver nanoparticles against *Candida* spp. *Biomaterials*. 30 [31] (2009) 6333-6340.

Correspondence address

Prof. José S. Moya

ICMM-CSIC

Sor Juana Inés de la Cruz, 3, 28049 Cantoblanco, Madrid, Spain

Tel. +34 91349000

Fax. +34 913720623

E-mail: jsmoya@icmm.csic.es

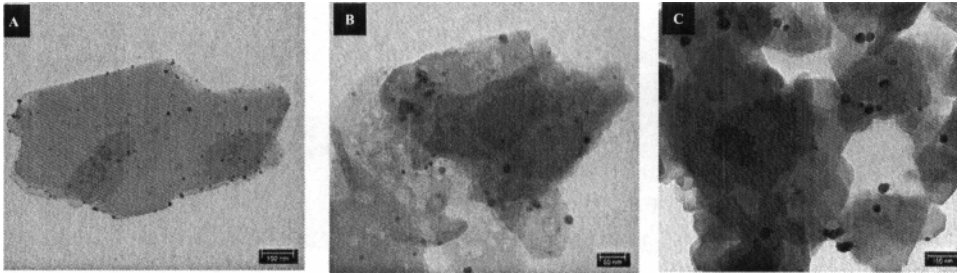


Figure 1. TEM micrographs corresponding to: A) kaolin-nAg (chemically reduced), B) kaolin-nAg (thermally reduced) and C) metakaolin-nAg.

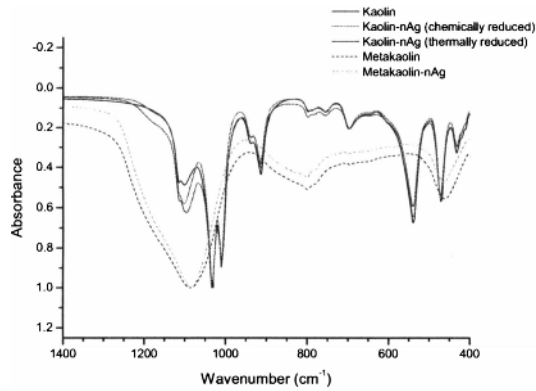


Figure 2. FTIR spectra of kaolin's and metakaolin's sample.

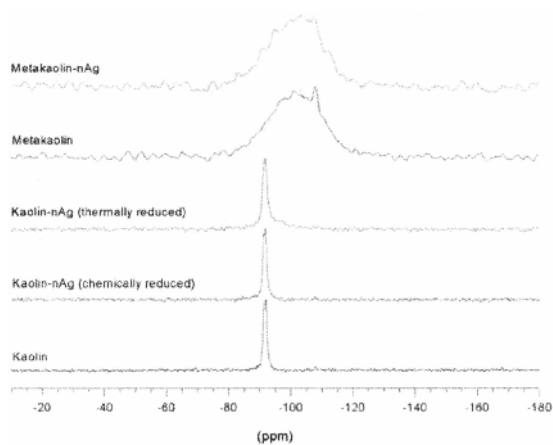


Figure 3. Comparison of ^{29}Si MAS-NMR spectra of the samples of kaolin and metakaolin.

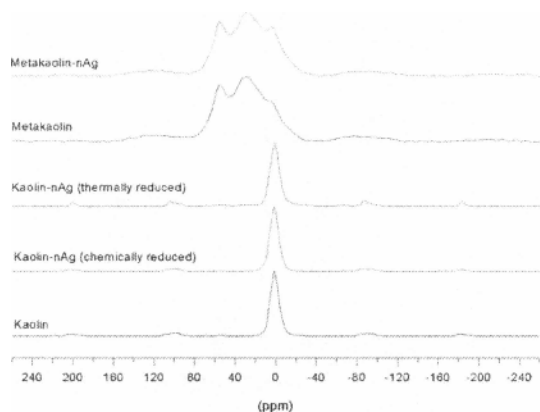


Figure 4. Comparison of ^{27}Al MAS-NMR spectra of the samples of kaolin and metakaolin.

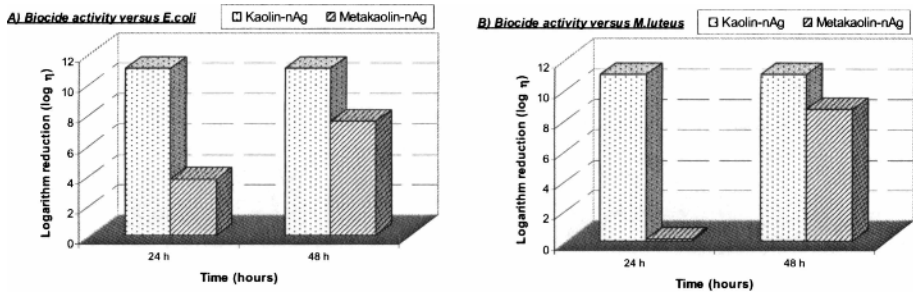


Figure 5. Logarithm reduction (log η) of: A) *E. coli* and B) *M. luteus* at 24 and 48 h corresponding to kaolin-nAg and metakaolin-nAg.

Table 1. ICP analysis of silver lixiviated after 48 h of biocide test

Bacteria strains	Ag lixiviated (ppm)	
	Kaolin-nAg	Metakaolin-nAg
<i>E. coli</i> (Gram -)	2.27	8.91
<i>M. luteus</i> (Gram +)	2.81	8.06

