Developments in Strategic Materials and Computational Design III

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Edited by

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The American Ceramic Society

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A Collection of Papers Presented at the 36th International Conference on Advanced Ceramics and Composites
January 22–27, 2012
Daytona Beach, Florida

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Preface

Contributions from two Symposia and two Focused Sessions that were part of the 35th International Conference on Advanced Ceramics and Composites (ICACC), in Daytona Beach, FL, January 22–27, 2012 are presented in this volume. The broad range of topics is captured by the Symposia and Focused Session titles, which are listed as follows: Focused Session 1—Geopolymers and other Inorganic Polymers; Focused Session 2 - Computational Design, Modeling Simulation and Characterization of Ceramics and Composites; Focused Session 4—Advanced (Ceramic) Materials and Processing for Photonics and Energy. And Symposium 10—Thermal Management Materials and Technologies.

Focused Session 1 on Geopolymers and other Inorganic Polymers was the 10th continuous year that it was held. It continues to attract growing attention from international researchers and it is encouraging to see the variety of established and new applications being found for these novel and potentially useful materials. Six papers are included in this year's proceedings. The ability to decorate metakaolin with nanosilver particles is reported as the first step to biocidal porous geopolymer ceramics. The field of low pH, phosphoric acid reacting with fly ash to form chemically bonded phosphate ceramics is discussed. Such studies are welcome in the pursuit of sustainable and environmentally friendly ceramic composites.

Focused Session 2 was dedicated to design, modeling, simulation and characterization of ceramics and composites so as to further optimize their behavior and facilitate the design of new ceramics or composites with tailored properties. Thirty six technical papers were presented regarding the prediction of the crystal structure and properties of new ceramics, materials design for extreme/harsh environments, virtual materials design for new innovative materials, application of novel simulation methods for materials processing and performance, and the characterization and modeling of surfaces, interfaces, and grain boundaries at multiple scales. Six papers from this particular focused session are included in this issue.

The debut of Focused Session 4 was held during ICACC 2012. This session focused on synthesis, structural and functional characterization of self-organized materials and nanostructures of all ceramic materials with application potentials as functional materials, with particular consideration given to the capability to tailor and control material properties via surface and structural modifications. Two papers are included in this issue.

Symposium 10 discussed new materials and the associated technologies related to thermal management. This included innovations in ceramic or carbon based materials tailored for either high conductivity applications (e.g., graphite foams) or insulation (e.g., ceramic aerogels); heat transfer nanofluids; thermal energy storage devices; phase change materials; and a slew of technologies that are required for system integration. Two papers were submitted for inclusion in this proceedings issue.

The editors wish to thank the symposium organizers for their time and labor, the authors and presenters for their contributions; and the reviewers for their valuable comments and suggestions. In addition, acknowledgments are due to the officers of the Engineering Ceramics Division of The American Ceramic Society and the 2012 ICACC program chair, Dr. Sanjay Mathur, for their support. It is the hope that this volume becomes a useful resource for academic, governmental, and industrial efforts.

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Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of nine issues that has been published based on content presented during the 36th International Conference on Advanced Ceramics and Composites (ICACC), held January 22–27, 2012 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 36th ICACC hosted more than 1,000 attendees from 38 countries and had over 780 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following symposia and focused sessions:

Symposium 1	Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	9th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics
Symposium 5	Next Generation Bioceramics

Symposium 6	International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
Symposium 7	6th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications
Symposium 8	6th International Symposium on Advanced Processing & Manufacturing Technologies (APMT) for Structural & Multifunctional Materials and Systems
Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Thermal Management Materials and Technologies
Symposium 11	Nanomaterials for Sensing Applications: From Fundamentals to Device Integration
Symposium 12	Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13	Advanced Ceramics and Composites for Nuclear Applications
Symposium 14	Advanced Materials and Technologies for Rechargeable Batteries
Focused Session 1	Geopolymers, Inorganic Polymers, Hybrid Organic-Inorganic Polymer Materials
Focused Session 2	Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites
Focused Session 3	Next Generation Technologies for Innovative Surface Coatings
Focused Session 4	Advanced (Ceramic) Materials and Processing for Photonics and Energy
Special Session	European Union – USA Engineering Ceramics Summit
Special Session	Global Young Investigators Forum

The proceedings papers from this conference will appear in nine issues of the 2012 Ceramic Engineering & Science Proceedings (CESP); Volume 33, Issues 2-10, 2012 as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites VII, CESP Volume 33, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments II, CESP Volume 33, Issue 3 (includes papers from Symposia 2 and 12 and Focused Session 3)
- Advances in Solid Oxide Fuel Cells VIII, CESP Volume 33, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VIII, CESP Volume 33, Issue 5 (includes papers from Symposium 4)

- Advances in Bioceramics and Porous Ceramics V, CESP Volume 33, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology VI, CESP Volume 33, Issue 7 (includes papers from Symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials VI, CESP Volume 33, Issue 8 (includes papers from Symposium 8)
- Ceramic Materials for Energy Applications II, CESP Volume 33, Issue 9 (includes papers from Symposia 6, 13, and 14)
- Developments in Strategic Materials and Computational Design III, CESP Volume 33, Issue 10 (includes papers from Symposium 10 and from Focused Sessions 1, 2, and 4)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 37th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2013) January 27 to February 1, 2013 in Daytona Beach, Florida.

Michael Halbig and Sanjay Mathur
Volume Editors
July 2012

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Geopolymers and Other Inorganic Polymers

METAKAOLIN-NANOSILVER AS BIOCIDE AGENT IN GEOPOLYMER

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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 CO_2 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 SiO_2, 33.0 Al_2O_3, 0.19 TiO_2, 0.76 Fe_2O_3, 0.03 CaO, 0.37 MgO, 0.67 K_2O, 0.02 Na_2O, 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 $AgNO_3$ as silver precursor and following two different reduction *vias*: the first by thermal reduction at 350 °C for 2 h in H_2 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 ^{27}Al and ^{29}Si NMR spectra were obtained at room temperature, using an Avance (Bruker) spectrometer, operating at 104.3 MHz for ^{27}Al and 79.5 MHz for ^{29}Si (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 μs) pulses, 5s inter-accumulation intervals and 125 kHz filterings were used. All spectra were referred to TMS (tetramethylsilane) and $Al(H_2O)_6^{3+}$ 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 μL form 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 μL 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 $Al\text{-}O^-$ and $Si\text{-}O^-$ 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-NNR 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} ($Si\text{-}O\text{-}Al^{(VI)}$) [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. ^{29}Si-NMR is capable of distinguishing SiO_4 tetrahedra, with connectivity ranging from 0 to 4 (Qm 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 ^{29}Si-NMR spectra, which corresponds to Si atoms in tetrahedral layers of layer silicates (Q^3 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 ^{27}Al 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 aluminun free Q^4(0Al) species, i.e. pure SiO_2 phase, and homogeneously distributed $Si(Al)O_4$ units [Q^4(1Al)]. 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 tree 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 structured 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 innoculating 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 η) 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 innoculum 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].