Materials Chemistry and Physics xxx (2016) 1–10

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# Structural and surface properties of highly ordered mesoporous magnesium-aluminium composite oxides derived from facile synthesis

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## HIGHLIGHTS

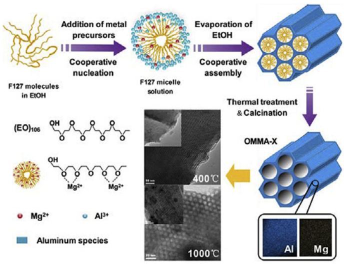
- Mesoporous Mg-Al composite oxides with excellent structural and surface properties.
- A highly homogeneous incorporation of Mg into the mesoporous framework of alumina.
- A superior structural stability up to 1000 °C coupled with a large surface area.
- A salt effect from the addition of $Mg(NO_3)_2 \cdot 6H_2O$ to explain the formation mechanism.

## ARTICLE INFO

*Article history:*
Received 17 October 2016
Received in revised form
17 November 2016
Accepted 20 November 2016
Available online xxx

*Keywords:*
Ordered mesoporous materials
Mg-Al composite oxides
Cooperative assembly
Structural stability
Surface properties

## GRAPHICAL ABSTRACT



## ABSTRACT

Highly ordered mesoporous magnesium-aluminium composite oxides (denoted as OMMA-x) with a variety of $n_{Al}/n_{Mg}$ ratios have been successfully synthesized via a facile strategy, and a salt effect was proposed to explain the formation mechanism. The incorporation of Mg can significantly improve the structural and surface properties of ordered mesoporous alumina (OMA) material. The resultant OMMA-x exhibited a much more ordered 2-D hexagonal mesostructure, a narrower pore size distribution, a higher specific surface area and pore volume, and a stronger basicity than those of OMA. More importantly, the highly homogeneous incorporation of Mg at the atomic level and the formation of framework Mg—O—Al bonds could effectively suppress the formation of crystalline alumina during the calcination process. As a result, OMMA-x demonstrated a superior thermal stability. For example, the ordered mesostructure of OMMA-8 could be well maintained with a high surface area of 182 $m^2/g$ even after thermal treatment at 1000 °C.

## 1. Introduction

The use of ordered mesoporous alumina (OMA) materials as host, which possess highly uniform channel, high specific surface area, large pore volume, narrow pore size distribution, and tunable pore size ranging from several to scores of nanometers, could give fresh impetus to the development of novel catalysts and adsorbents for diverse applications [1–4]. However, the synthesis of OMAs is much more difficult than their silica analogues; typical preparation recipes for ordered mesoporous silica-based materials could not

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http://dx.doi.org/10.1016/j.matchemphys.2016.11.038
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Please cite this article in press as: D. Pan, et al., Structural and surface properties of highly ordered mesoporous magnesium-aluminium composite oxides derived from facile synthesis, Materials Chemistry and Physics (2016), http://dx.doi.org/10.1016/j.matchemphys.2016.11.038

effectively act on the synthesis of OMA, due to the complicated hydrolysis behavior of aluminium precursor and phase transitions accompanied by the mesostructural collapse during the calcination process at high temperature [2,5]. Consequently, in most reported cases, disordered mesostructures with low surface area and poor thermal stability were fabricated [6–8], which seriously impede the practical application of mesoporous alumina materials. Therefore, it is still a great challenge to synthesis OMA materials with well-defined mesopores and highly structural stability.

At present, OMA materials are commonly synthesized through two general strategies: (1) a nanocasting method using silica or carbon with ordered mesostructure as hard templates [9–11], and (2) a modified sol-gel self-assembly process with the presence of a soft template (including cationic and anionic surfactant, as well as nonionic block copolymer) as the mesostructure-directing agent [2,12–14]. Compared with the first pathway requiring more than once impregnation and calcination steps, the soft-template synthesis procedure is a very attractive alternative way to obtain OMA materials with well-defined structural, textural, and chemical properties via a one-step process. In this method, the composite mesostructure, i.e., ordered arrays of surfactant micelles embedded within alumina matrices, is generally formed during the evaporation-induced self-assembly (EISA) process, and unidimensional OMA materials are further obtained after the thermal decomposition of the template micelles. In 2005, Niesz et al. [15] firstly reported the successful synthesis of OMA using the triblock copolymer P123 as the template by controlling the hydrolysis conditions of aluminum precursor and conducting the EISA process under a nitrogen flow. Since then, a significant breakthrough has been realized following a facile and reproducible sol-gel pathway reported by Yuan et al. [2], in which the EISA process was carried out in air and the necessity in strictly controlling the hydrolysis-condensation conditions of aluminium precursors could be effectively obviated. Obviously, such synthesis method can substitute competently the cooperative assembly process between inorganic species and organic templates typically employed to synthesize ordered mesoporous silica-based materials, and has been widely exploited for the synthesis of OMA-based materials with ordered 2-D hexagonal mesostructure and high specific surface area [3,4,16]. However, the thermal stability of OMA synthesized by Yuan is still far from satisfactory. After thermal treatment at 1000 °C for 1 h, the mesostructure of OMA was remarkably destroyed, along with a relatively low specific surface area (116 $m^2/g$) [2].

The recent investigations have shown that via the sol-gel procedure, the doping of suitable element into alumina matrix plays an important role in restraining the crystallization of alumina during the thermal treatment process at high temperature [17,18]. Magnesia features a unique basic characteristic, and the thoughtful combination of both magnesia and OMA allows the fabrication of new types of mesoporous materials with enhanced thermal stability and interesting basic properties (strength and amount of basic sites) [1,19], which have been employed as catalysts or supports in many reactions, for instance, heterogeneous production of biodiesel [1,20] and catalytic conversion of carbon dioxide [19,21,22]. In the past few years, to avoid structural damage of OMA in post-treatment process, great efforts have been made to directly prepare Mg-Al oxides [20,23,24]. However, it is difficult to achieve the mesoporous magnesia-alumina materials with high degree of atomic mixing, thus the resulting mesoporous phases generally were the mixture of alumina and periclase or the mixture of hydrotalcite and periclase [20]. Until now, few reports are available on the direct synthesis of mesoporous Mg-Al composite oxides with a long-range periodic ordered mesostructure, high specific surface area and pore volume, and highly homogeneous incorporation of MgO.

Recently, we introduced a facile synthesis method to incorporate metal heteroatoms into the mesoporous framework of alumina, and the incorporation of heteroatoms may endow OMA-based materials with many excellent properties [5,17,25]. Inspired from our previous works, herein, highly ordered mesoporous $MgO-Al_2O_3$ composite materials (OMMA-x) with a variety of $n_{Al}/n_{Mg}$ ratios were designed and successfully synthesized. The resultant materials exhibit an improved structural stability and a highly homogenous distribution of Al and Mg at the atomic level, and possess a well-defined ordered 2-D hexagonal mesostructure, a narrow pore-size distribution, and a high specific surface area and pore volume. The effects of incorporating Mg on the structural and textural properties, thermal stability, and basicity of OMMA-x along with the possible formation mechanism were investigated.

## 2. Experimental

### 2.1. Synthesis for OMMA-x

The OMMA-x materials were synthesized via a similar method described in the literatures [5,25]. Fig. 1 shows the schematic illustration for the synthesis of OMMA-x materials, where x stands for the molar ratio of Al/Mg. In a typical synthesis, 3.2 g of triblock copolymer F127 ($M_w = 12600$, $EO_{106}PO_{70}EO_{106}$) and a required amount of $Mg(NO_3)_2 \cdot 6H_2O$ (0.41, 0.51, 0.68, and 1.02 g, respectively) were dissolved in 20 mL anhydrous ethanol containing 2.0 g of 37 wt% hydrochloric acid and 0.4 g of citric acid. Then, 3.26 g of aluminum isopropoxide was slowly added into the above clear solution. After vigorously stirring under the sealed conditions at 30 °C for 24 h, the resultant reaction sol was transferred to a dish and then underwent successively solvent evaporation at 45 °C for 24 h, thermal condensation treatment at 100 °C for 24 h, and calcination at 400 °C for 5 h to obtain the final solid products.

As a comparison, MgO-supported mesoporous alumina material with Al/Mg molar ratio of 8 was prepared by a traditional incipient wetness impregnation (IWI) method. The OMA support was prepared using the same strategy as that of OMMA-x excluding the addition of magnesium precursor, and then added into 20 mL anhydrous ethanol solution dissolved $Mg(NO_3)_2 \cdot 6H_2O$. The resultant mixture was stirred at 30 °C for 24 h and later dried at 100 °C for 24 h. The final solid was calcined at 400 °C for 5 h and named as Mg/OMA-8.

### 2.2. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 diffractometer using Ni-filtered Cu K$\alpha$ (0.154 nm) radiation at 40 kV and 30 mA. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F electron microscope attached with an energy-dispersive X-ray (EDX) spectrometer. Elemental mapping measurements were performed on a Hitachi Model S-4800 scanning electron microscopy instrument with an acceleration voltage of 25 kV. Nitrogen adsorption-desorption isotherms were measured on a Quantachrome analyzer at −196 °C. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface area. Pore size distributions were derived from the adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method. The total pore volume ($V_P$) was determined according to the nitrogen amount adsorbed at a relative pressure of 0.99. $^{27}Al$ MAS NMR spectra were recorded on a Bruker AVANCE$^{III}$ 500 spectrometer operating at a frequency of 156.37 MHz (3.98 $\mu s$ as a pulse width), a pulse delay of 4 s, and an acquisition time of 0.014 s. Differential thermogravimetric (DTG) analysis of as-synthesized samples was performed by use of a Netzsch STA449F3 instrument in air with a heating rate of

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