Porous nanosized oxide powders in the MgO-TiO$_2$ binary system obtained by sol-gel method

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Abstract

Mesoporous powders were obtained by sol-gel process in the MgO-TiO$_2$ system. The scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), thermogravimetric/differential thermal analysis (TG/DTA), powder X-ray diffraction (XRD) and nitrogen adsorption/desorption measurements have been used to characterize the morphology, phase evolution, crystallinity and pore structure of the obtained materials. The adsorption capacity of the synthesized powders for CO$_2$ and CO was also investigated. The results were discussed comparatively with those obtained for the monocomponent oxides in order to establish new and better potential for their applications.
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1. Introduction

Nanopowders are agglomerates of extremely small particles, namely nanoparticles (smaller than 100 nm), and they are the result of a fabrication process conceived to obtain superior products [1].

In applications, the mostly used nanoparticle categories are ceramic metal oxides and silicates due to their unique properties such as chemical, thermal, electrical, optical, mechanical, magnetic, and morphological (high specific surface area) [2–4]. Such powders may be used as pigments, catalysts, supports in chromatography or as raw materials for advanced polycrystalline ceramics preparation [5,6]. Characteristics such as large surface area, high specificity and reactivity make nanoparticles excellent candidates for adsorbent materials that can remove contaminants from gaseous [7] or liquid phases [8,9].

Among the oxide nanopowders the monocomponent as well as bicomponent ones belonging to the MgO-TiO$_2$ system

present increased interest in the field of environmental protection and decontamination, many research studies being focused on their preparation by wet chemical methods and their characterization. Also, MgO-TiO$_2$ mixed oxides nanopowders could find many useful applications, such as sensors, pigments, capacitors, catalysts, adsorbents or raw materials for advanced polycrystalline ceramics synthesis.

As chemical techniques for the fabrication of these materials, the sol-gel processing represents a moderate and adjustable method that enables the control of size, morphology, structure and chemical properties of inorganic oxide powders. The sol-gel process allows for the synthesis of powders with more elaborate structure and morphology, improving thus the reactivity of the synthesized material.

The TiO$_2$ powder is mostly studied due to its use in photocatalytic processes. The TiO$_2$ powders were prepared either by sol-gel polymeric routes [10–16] or by using chelating agents, as polyethylene glycol (PEG) [17], hydroxypropyl cellulose (HPC) [18] or carboxylate ligands [19]. The inverse micelle technique was also examined [20]. TiO$_2$ powder with a different amorphous anatase-rutile content was

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prepared by $TiCl_4$ hydrolysis and the photocatalytic activity was tested [21]. TiO_2 nanoparticles components of a superstructure were generated by thermal hydrolysis of titanium isopropoxide in the presence of p-toluensulfonic acid [22].

The sol-gel preparation of MgO powder has been less studied [23–25]. MgO nanocrystalline powders were obtained from an inorganic salt, $Mg(NO_3)_2 \cdot 6H_2O$ and an organic precursor, oxalic acid, or an inorganic one and ammonium hydroxide [7,26,27]. In some cases microwave treatment was also applied [28]. Among the alkaline earth metal oxides, MgO has been studied as a plausible CO_2 adsorbent mainly because of its low energy requirement for regeneration [29]. It was shown that the activity of MgO can be improved by mixing with another metal oxide or using templates or supporting materials [30]. Mixed oxide-based nanoparticles can have a synergistic effect resulting in adsorption properties superior to those of its pure components. To the best of our knowledge, only few papers regarding the obtaining of $MgO-TiO_2$ mixed oxide powders and investigation of their adsorption capacity for CO_2 have been reported [31].

The aim of our work was to obtain $MgO-TiO_2$ mixed oxides powders by a sol-gel process and to investigate their adsorption capacity for CO_2 and CO. Their structures and morphologies were characterized by scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), thermogravimetric/differential thermal analysis (TG/DTA), X-ray diffraction (XRD) and BET specific surface area and porosity analysis. The results were discussed comparatively with those obtained for the monocomponent oxides (TiO_2 and MgO).

2. Experimental

2.1. Powders preparation

Powders were obtained in the MgO, TiO_2 monocomponent and $MgO-TiO_2$ bicomponent systems by sol-gel method. The composition of the precursor solutions and the experimental conditions are given in Table 1.

Titanium ethoxide ($Ti(OC_2H_5)_4$) and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) were used as precursors, the ethyl alcohol (C_2H_5OH) was used as solvent, H_2O as hydrolysis reagent and the ammonia (NH_4OH) as catalyst. The obtained oxide powders were separated from the solution by filtration, washed with distilled water in order to remove the adsorbed reagents

residue, dried and then, according to the thermal analysis results, thermally treated as follows: TiO_2 at 300 °C, MgO at 450 °C and $MgO-TiO_2$ at 600 °C, with 1 h plateau and a heating rate of 1 °C /min.

2.2. Powders characterization

The synthesized powders were characterized by SEM, FT-IR spectroscopy, XRD, TG/DTA analysis and BET specific surface area and porosity analysis.

The morphology of the samples were investigated by scanning electron microscopy (SEM) using a high-resolution microscope, FEI Quanta 3D FEG model, at an accelerating voltage of 5 kV, in high vacuum mode with Everhart–Thornley secondary electron (SE) detector. Samples preparation was minimal and consisted in immobilizing the material on a double-sided carbon tape, without coating.

FT-IR spectroscopic measurements were realized in transmission mode with a Nicolet Spectrometer 6700 FT-IR in the 400–4000 cm^{-1} range. The spectra were taken from thin transparent (~ 20 mg/cm^2) KBr pellets containing approximately 0.5% wt samples. Pellets were prepared by compacting and vacuum-pressing an intimate mixture obtained by grinding 1 mg of substance in 200 mg KBr.

Powder X-ray diffraction patterns were recorded on a Rigaku Ultima IV apparatus, with CuK_α $\lambda = 1.5406$ Å radiation, in the $2\theta = 10$–$70°$ range, with a speed of 5 °C/min and a 0.02 step size, at 40 kV and 30 mA. PDXL software from Rigaku, connected to ICDD database was used for phase identification. The lattice constants and crystallite size were calculated using WPPF method and Williams Hall method. The quantitative ratio was determined by RIR method.

Thermogravimetric and thermodifferential analysis (DTA/TG) were performed using a Mettler Toledo TGA/SDTA 851[e] equipment at a heating rate of 10 °C/min, in air, with typically 20 mg sample.

Nitrogen sorption isotherms at -196 °C were recorded on a Micromeritics ASAP 2020 automated gas sorption system. The samples were outgassed at 200 °C for 3 hours under vacuum prior to N_2 adsorption. Specific surface areas (S_{BET}) were calculated according to the Brunauer-Emmett-Teller (BET) equation using adsorption data in the relative pressure range between 0.05 and 0.30. The total pore volume (V_{total}) was estimated from the amount adsorbed at the relative pressure of 0.99. The pore size distribution

Table 1
The initial composition of precursor solutions and the experimental conditions used for nanopowders synthesis.

Precursors for:	Molar ratio			pH	Reaction conditions	
	$C_2H_5OH/\Sigma precursors$	$H_2O/\Sigma precursors$	$NH_4OH/\Sigma precursors$		Temp. (°C)	Time (h)
TiO_2[a]	85	5	–	5–6	25	0.5
MgO[b]	85	5	0.4	5–6	25	1.0
$MgO-TiO_2$[c]	85	5	0.04	5–6	25	1.0

[a] precursor = $Ti(OC_2H_5)_4$
[b] precursor = $Mg(NO_3)_2 \cdot 6H_2O$
[c] precursor = both precursors from above (1:3 molar ratio)