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Peculiarities of formation of phase composition, porous structure, and catalytic properties of tungsten oxide-based macroporous materials fabricated by sol–gel synthesis

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ARTICLE DATA

Article history:
Received 17 September 2013
Received in revised form 3 December 2013
Accepted 3 December 2013

Keywords:
Nanostructures
Oxides
Sol–gel synthesis
Surface properties
Phase transition

ABSTRACT

The method of template sol–gel synthesis of tungsten oxide-based macroporous materials using 'core–shell' latex particles as colloid templates is described. The chemical composition and structural characteristics of the synthesized macroporous oxide systems have been investigated. The peculiarities of formation of material phase composition and macroporous structure under different template thermal destruction conditions have been revealed. An optimal method of a targeted synthesis of the crystalline tungsten(VI) oxide having a defect-free macroporous structure (average pore size 160 nm) and efficient catalytic properties under organic liquid phase oxidation conditions has been suggested. The prospects of the fabricated material application as catalysts of hydrothermal oxidation of radionuclide organic complexes at radioactive waste decontamination have been demonstrated.

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1. Introduction

The specific features of the structural organization and chemical composition of inorganic materials, including oxide systems, to a great extent determines their functional properties, in particular, their frequently manifested activity in the processes of heterogeneous catalytic transformation of organic substances [1–3]. Fabrication of nanostructured materials is possible through application of a generally known sol–gel synthesis, which enables one to form an inorganic material base of a specified porous structure and, as a result, predetermined properties [4–6]. In spite of a certain progress in the field of template synthesis of porous inorganic systems, many experimental and theoretical problems remain to be solved. The problem focus here consists in the fact that to obtain a specific porous material, including tungsten oxide, a

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1044-5803/$ – see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.matchar.2013.12.003

great variety of templating agents can be used: liquid crystal surfactant systems [7], colloid crystals [8], block copolymers [9], bioorganic substances [10], microemulsions [11], latexes [12] etc., whereas the sol–gel process mechanism is specific in each individual case. For most of the nanostructured systems, the principles of selection of the method of specific template removal and its effect on the inorganic base and material porous structure formation have been studied to a rather insufficient degree. The principal importance of the theoretical grounding of the regularities of change in the sequence "synthesis conditions–composition–structure–properties" was demonstrated in [4,13,14] for some inorganic oxides and hybrid components. In these works, the authors defined specific features of 'soft' (alkaline or acidic dissolution) and 'hard' (thermal destruction) methods of template removal and revealed the difference in the synthesized material phase composition: amorphous state in the former case and crystalline phase in the form of the lowest oxidation number oxides or carbides/nitrides in the latter case. Besides, each individual approach to the template removal can result, aside from phase changes, in distortion of the material porous structure until the formation of nonporous crystalline macrophases. Such a situation is accompanied by reduction of the efficiency of the synthesized materials, including the catalytic activity of porous tungsten oxides that are extensively applied in practice as catalysts for liquid-phase media oxidation [15–17].

To sum up, the objective of the present study was to apply the sol–gel synthesis using the 'core–shell' colloid template in order to fabricate tungsten oxide-based macroporous materials and study the effect of the conditions of the process of thermal destruction of the template on the chemical composition, porous structure, and catalytic properties of the fabricated materials.

2. Experimental

2.1. Reagents

A commercially available butylsiloxane–acrylate latex (KE 13–36) of the 'core–shell' structure manufactured by JSC "Astrokhim" (Elektrostal', Russia) according to the method similar to the one described in [18] was used as a template. Latex was supplied as dispersion in water with solid content 50% and used as received. Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$, chemical pure grade) was used as a tungsten precursor. $TiCl_3$ (3% solution in hydrochloric acid, chemical pure grade) was used as a reducer.

2.2. Synthesis

20 mL of a solution of sodium tungstate containing 0.5 g/mL of $Na_2WO_4{\cdot}2H_2O$ was added to 55 ml of butylsiloxane–acrylate latex dispersion (solid content 4.5%) upon stirring and reduced to tungsten blue by the addition of 45 mL of 3% solution of $TiCl_3$ in hydrochloric acid. The solution pH, which must not fall below 4, was adjusted by the addition of 5 N NaOH. The obtained dispersion was intensively stirred on a magnetic stirrer for 1 h and left for settling. The precipitated hydrogel was filtered through white ribbon filter paper, thoroughly washed by distilled water, and dried at 90 °C for 2 h to remove the excessive moisture. The obtained xerogel was annealed in a Nabertherm RSR-B 120/500/11 horizontal tube furnace (Germany) at 400–900 °C in inert atmosphere (argon) or oxidizing medium (air) or reducing medium (hydrogen)—see Table 1 for conditions. The heating rate was 5 °C/min and the holding time at final temperature was 1 h.

2.3. Characterization Methods

The phase composition of the fabricated samples was determined by the X-ray diffraction analysis (XRD), CuKα-radiation, the mean wavelength (λ) 1.5418 Å, Ni-filter, on a DRON-3 multipurpose diffractometer (Russia). The particles size and electrokinetic potential were determined using the methods of photon correlation spectroscopy and laser Doppler electrophoresis on a Zetasizer Nano ZS device (Malvern, Great Britain). The pore size distribution was determined on an AutoPore IV mercury porosimeter (Micromeritics, USA). The analysis of solid surface area and porosity was carried out using an ASAP 2020 MP device (Micromeritics, USA). The sample SEM images were obtained using a HITACHI S-3400N scanning electron microscope (Hitachi, Japan).

2.4. Investigation of Catalytic Properties

The catalytic properties of the synthesized materials were investigated in liquid phase oxidation of methylene blue (MB) dye (8 mg/L) by hydrogen peroxide (0.36%). The dye oxidation was followed by the decrease of solution optical density

Table 1 – Chemical composition and structural characteristics of macroporous materials based on tungsten oxides.

Sample	Thermal treatment conditions		Material composition	S_{spec}, m^2/g	$V_{macropore}$, cm^3/g
	T, °C	Gas medium	XRDΦA	Porosimetry	
W(Ar)-400	400	Argon	–	16.87	0.22
W(Ar)-600	600		WO_2; $WO_3Ti_{54}W_{46}O_2$ (traces)	18.12	0.35
W(Ar)-800	800		WO_2; $WO_3Ti_{54}W_{46}O_2$ (traces)	18.81	0.32
W(Ar)-900	900		W; WO_2; $WO_3Ti_{54}W_{46}O_2$ (traces)	7.7	0.19
W(Ar/H_2)-600(900)	600(900)	Argon (hydrogen)	W; TiO_2 (traces)	9.1	0.26
W(O_2)-600	600	Air	WO_3; TiO_2 (traces)	1.0	0.08
W(Ar/O_2)-600(300)	600(300)	Argon (air)	WO_3; TiO_2 (traces)	16.34	0.32

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