TEMPLATE-BASED APPROACH IN THE PREPARATION OF NANOPOROUS SILICAS AND TITANIA-SILICAS

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Abstract

Mesoporous silicas and titania-silicas were synthesized with use as a template quaternary ammonium salts and their hydroxides. Fumed silica, tetraethyl orthosilicate and itanium(IV) tetraisopropoxide were applied as presursors. Syntheses were carried out in presence HCl and NH₄OH. Mesoporous titania-silicas with TiO₂ contents from 1 up to 70 mol. % were prepared. Obtained samples have been characterized by the powder X-ray diffraction data and nitrogen adsorption at 77 K. Specific surface area, total pore volume, pore volume and area distribution were determined from nitrogen adsorption isotherm for synthesized titania-silicas. It was demonstrated that the ordered structures of MCM-41 type and bimodal porous materials with maximum pore diameter of 3 and 30 nm may be prepared depending of a synthesis conditions and a precursor nature.

Introduction

Remarkable achievement of the last decade in the field of synthesis of ordered mesostructural materials is preparation of a new class MCM-41 periodic silicates, aluminosilicates [1-2] and non-silica periodic mesostructured materials [3] with pore diameter from 15 up to 100 Å and high specific surface area (more than 1000 m²/g) with the use of surfactants as supramolecular templates. Such materials are used as catalyst carriers due to their unique geometrical structure, high thermal stability and adsorptivity [4-5]. Considerable recent attention has been focused on synthesis of MCM-41 materials contained in their structure the ions of transition metals, in particular titanium [5-11], for preparation of materials with high catalytic activity and which are stable at heating and in conditions of hydrothermal treatment [5]. So in the work [5], hydrothermal stability up to 800 °C and stability in acid medium (pH=2) was distinguished for obtained Ti-MCM-41 materials in contradistinction to zeolites which are much less stable in the same conditions. Inclusion of titanium into the skeleton of mesoporous silica matrices permits one to create new materials with pore diameter in the range 15-100 Å, high specific surface area and with catalytic activity in oxidation reactions of large organic molecules, for which adsorption space of known perspective Ti-containing catalysts of a TS-1, TS-2 and Ti-B types is inaccessible [6]. The works [7,8] dealing with synthesis of Ti-MCM-41 and Ti-HMS must be pointed out in this direction. It has been shown, in particular, that Ti-MCM-41 materials, alongside with TS-1 and Ti-HMS, are effective catalysts for hydroxylation reaction of benzene to phenol. The catalytic activity of Ti-HMS and Ti-MCM-41 in the reaction of 2,6-di-tert-butyl phenol oxidation was also demonstrated [7]. Titanium containing silicates demonstrate also photocatalytic activity [11-13]

The aim of this work is to continue systematic research in the field of synthesis and characterization of nanoporous pure silicas and titania-silicas bearing various amounts of titanium.

Experimental

For preparation of mesoporous silica and titania-silicas tetraethyl orthosilicate (TEOS) and Aerosil 300 was used as a silica source and titanium(IV) tetraisopropoxide Ouaternary ammonium salts titanium source. a chosen as was (ODTMACI, C18CD and octadecyltrimethylammonium chloride hexadecyltrimethylammonium bromide (HDTMABr, C16Br) and tetramethylammonium bromide (TMABr, C1Br) was applied as template. These salts were transformed into hydroxyl form with an use of the ion-exchange column filled by the AB-17-8 anionite in hydroxyl form.

Synthesis of mesoporous silicas from fumed silica. Fumed silica (aerosil) was suspended in water or in aqueous solution of quaternary amine hydroxide at intensive stirring. Resulting silica concentration was about 30 wt %. Silica/amine ratios are indicated in the Table 1. Obtained suspensions allow to stand for 24-28 hrs at room temperature, then were dried up at 150°C and calcinated at 540 °C for 6 h on air.

Synthesis of MCM-41 pure silica [14]. Weighed portion of the surfactant (8.3 g CTMABr) was dissolved in 42 ml of concentrated ammonia solution and intermixed to homogeneous milk-white mixture. After addition of 9.67 ml TEOS the mixture obtained was stirred up to gel-like product formation. The samples prepared were dried up at air and calcinated at 540 °C for 6 h on air.

Synthesis of titania-silica in presence of HCl. Mesoporous titanosilicas with molar ratios Ti/(Ti + Si) equal 1, 15, 30, 50, and 70 % were synthesized using the technique described in the work [7]. The necessary $Ti(i-OC_3H_7)_4$ amount was added by small portions at stirring to TEOS solution in mixture of ethanol and isopropanol. Weighed portion of ODTMACl was dissolved at intensive stirring in water with addition of small amount of concentrated HCl. Obtained homogeneous milk-white suspension was added to initial mixture at intensive stirring and heating up to 60 °C for the gel preparation (for 1.5 h). The gel was subjected to aging for 18 h on air. Samples were dried up at 120 °C for 3 h, and then were calcinated at 540 °C for 6 h on air.

Synthesis of titania-silica in presence of NH_4OH . 0.124 ml (0.00043 mol) TiPOT was added by small portions at stirring to 9.52 ml (0.0426 mol) TEOS (Ti/(Ti+Si)x100=1%). Concentrated ammonia solution (42 ml) was added at stirring to the weighed portion of the surfactant 8.3 g CTMABr (0.0228) mol. Obtained milk-white mixture was drawn together with an initial solution and was stirred up to gel-like product formation (5 hrs). Solid products were calcinated at 540 °C for 6 h on air. Samples with the titanium contents 15, 30, μ 50% were prepared in a similar manner.

Characterization of the synthesized samples was performed by the powder X-ray diffraction (XRD) data (automated diffractometer DRON-3M, CuK_{α} radiation) and nitrogen adsorption isotherm measurements at 77 K on ASAP-2000 Micromeritics equipment. Average pore diameter was estimated by Gurvich method (d=4V/S). The specific surface area, S_{BET}, was determined from the linear part of the BET equation (at p/p_s = 0.05-0.35). Pore volume distribution was calculated from desorption branch of an isotherm of nitrogen adsorption using the Barrett-Joyner-Halenda (BJH) formula [16,17]. Comparative α -plots [16,18,19] were constructed using standard nitrogen adsorption data for silica of Jaroniec at al. [20].

Results an

The si aluminium ic cations. Thus rather import long-stage hy geometrical cl

Table 1. Geor

Sample	pr
Si	A
SiC1	A
SiC16	A
MCM-41	T
TilSiC16a	T
Ti15SiC16	T
TilSiC18	T
Til5SiC18	T
Ti30SiC18	T
Ti50SiC18	TR
Ti70SiC18	TE
TilSiC16b	TF
Til5SiC16	TE
TIB0SiC16	TE
TisosiC16	TE

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Results and discussion

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The sources of silica aerosil and tetraethyl orthosilicate practically do not contain of minimise ions and sodium. All syntheses were carried out also in absence of inorganic encoder. Thus, obtained silicas and titania-silicas do not contain extraneous impurity, that is inder important for their use in catalysis. Besides use of TEOS allows one to avoid a tog-stage hydrotermal treatment and to carry out of synthesis at room temperature. Some cometrical characteristics of the prepared samples are submitted in the Table 1.

Table 1. Geometrical characteristics of mesoporous silicas anf titania-silicas.

Sample	SiO ₂ precursor	TiO2 content	Template	Template /Oxide	Media	BET surface	Total pore	Pore diameter,
		s, mol.%		molar ratio		area, m²/g	volume, cm ³ /g	Å
Si	Aerosil	0		· · · ·	H ₂ O	253	1.32	208
SiC1	Aerosil	0	TMA-OH	0.20	H ₂ O	206	1.08	210
SiC16	Aerosil	0	C16-OH	0.10	H ₂ O	416	1.42	136
MCM-41	TEOS	0	C16-Br	0.53	NH ₄ OH	1291	1.30	40
TilSiC16a	TEOS	1	C16-Br	0.27	HC1	1284	0.89	28
Ti15SiC16	TEOS	15	C16-Br	0.27	HC1	987	0.79	32
TilSiC18	TEOS	1	C18Cl	0.27	HC1	924	0.47	20
Ti15SiC18	TEOS	15	C18Cl	0.27	HC1	805	0.45	22
TE30SiC18	TEOS	30	C18Cl	0.27	HCl	702	0.52	30
TE50SiC18	TEOS	50	C18Cl	0.27	HCl	529	0.59	46
Ti70SiC18	TEOS	70	C18C1	0.27	HC1	353	0.45	51
TilSiC16b	TEOS	1	C16-Br	0.53	NH4OH	900	0.98	43
Ti15SiC16	TEOS	15	C16-Br	0.53	NH4OH	618	1.04	67
TI30SiC16	TEOS	30	C16-Br	0.53	NH4OH	459	0.94	82
Ti50SiC16	TEOS	50	C16-Br	0.53	NH4OH	340	0.48	57

Funded silica is often applied for preparation of aerosilogel, suitable for use as a carrier various catalysts including enzymes. As it is visible from Fig.1 aerosilogel has no corpores. Practically all its specific surface consists from a surface of mesopore wall with the meter 200Å and above. At realization of syntheses at presence of trymethylammonium introvide the total specific surface area is decreased and pore diameter calculated by Gurvich was unchanged. However, as shown in Fig 2 the sample has microporosity. It is possible to explain this fact by action tetramethylammonium ions as a template. Use more the total specific surface area equal to those calculated by Gurvich method (136 Å), 2 there are two maxima on a curve of pore distribution at 30 and 300Å and practically the pore diameter 30 Å in this sample corresponds to pore diameter of materials MCM-41 however in XRD pattern of this sample does not find out presence of the ordered the tord of the presented in Table 2. This sample is shown in Fig.4 and lattice prediameters is represented in Table 2. This sample exhibited XRD pattern with diffraction the substant of which are characteristic of well-ordered hexagonal structure (4 reflections). Fig. 5

demonstrates adsorption isotherm and pore distribution which is typical for high-quality materials of MCM-41 type.

800 B11

800

400

200

BTP



Fig. 1. Comparative α_s -plot for aerosilogel (Sample Si in Table1)











Table 2. X-ray diffraction data of MCM-41 Hexagonal unit cell parameter, a=45.3 Å

hkl	Experimental d-values, Angstrom	Calculated d-values, Angstrom	
100	39.26		
110	22.66	22.67	
200	19.64	19.63	
200	14.85	14.84	









Volume adsorbed, colg 8TP 600

500 400 300

200

100

0

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Fig. 6. Comparative α_s-plot for mesoporous titania-silica prepared in HCl media (1) (BET surface area 1284 m²/g, S_{ext}=14 m²/g, Sample Ti1SiC16a) and in NH₄OH media (2), (BET surface area 900 m²/g, S_{ext}=211 m²/g, Sample Ti1SiC16b).





From Fig. 6, curve 1 is visible that titania-silica obtained in HCl media has not emificant external surface in contrast of the sample prepared in NH₄OH media (Fig. 6, curve 2). At synthesis titania-silica by technique used for synthesis of pure MCM-41 silica becagonal structure is kept up to 15 % of the contents of titanium (Fig. 7 and Table 3).

Diffractograms of the obtained titanium-containing materials prepared in HCl are resented on Fig. 8. It is necessary to note that though samples of titania-silicas received by in HCl media have a extremely high specific surface area and uniform pore distribution are not well ordered.











Fig. 9. Pore volume distribution for mesoporous titania-silicas with 1, 15, 30, 50, and 70 mol. % titanium (1-5 respectively). Template C18Cl in HCl.

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Availability of small-angle peak on XRD pattern of the mesoporous silica, containing 1 mol. % of titanium, testifies about existence in this sample of ordered structure, but no structural information can be extracted from this diffractograms [21]. Peaks at $2\theta \approx 25^{\circ}$ is characteristic of anatase structure tended to increase with increase in metal contents in titanium-containing silicas.

Based on adsorption research it was shown that values of specific surface area in the titanium-containing silicas, determined by BET method, decrease with the increase of titanium contents both in acid and base conditions (Table1).

For sample obtained in HCl media with C18Cl template the pore diameters, calculated by Gurvich method, are increased from 20 up to 51 Å at slightly varying total pore volume ($0.45-0.60 \text{ cm}^3/\text{g}$). As the titanium content in the samples is increased, the shape of the nitrogen adsorption isotherms is changed from I up to IV type with occurrence of hysteresis loops characteristic of mesoporous structures and close under form to H1 type [16]. The curves of pore volume distributions on pore diameter for the synthesized titanium-containing mesoporous materials are submitted on Fig. 9. At low titanium contents in samples (down to 30 mol. %) the narrow volume pore distribution on pore diameter is observed.

Conclusion

The obtained experimental data testify an opportunity of template synthesis of nanoporous silica and titania-silicas with high titanium contents and advanced specific surface areas. More ordered structures of pure silica and titania silica MCM-41 type is possible to prepare in NH₄OH media.

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Abstract

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