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Hydrophilicity and surface heterogeneity of TiO_2-doped silica materials for membrane applications

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ABSTRACT

Silica materials containing different amount of titania (namely from 0 to 33%) were prepared, characterized and tested to evaluate their hydrophilic features in order to design a good membrane material for water purification. XRD, HRTEM, nitrogen gas-volumetric adsorption at 77 K were applied to obtain a complete structural and morphological description of the systems. Material stability in alkaline solutions was clearly enhanced by adding TiO_2 to the silica material. Adsorption microcalorimetry and microgravimetric measurements were used to study water and toluene adsorption, respectively, in order to assess the hydrophilic and hydrophobic behaviors of the materials using polar (water) and non-polar (toluene) probe molecules. Microcalorimetric data allowed to describe also the energetic features of the water adsorption giving interesting information on the microscopic environment of the adsorption sites. The analysis procedure applied in this study can constitute a valid approach to determine *a priori* the behaviors of membrane materials.

1. Introduction

Microporous and mesoporous materials with narrow pore size distribution and high pore volume are of great interest for membrane applications [1,2]. Especially materials with 1–2 nm large pores can be used as a nanofiltration layer for water softening [3] or for the removal of emerging pollutants (e.g. pharmaceuticals [4], hormones [5], and pesticides [5,6]). Thus, the development of such materials might have a high impact on water purification technologies.

Over the last twenty years, silica has been widely considered as membrane material, because microporous [7] and mesoporous [8,9] defect-free silica layers with well-defined pore structure can be fabricated by facile sol–gel coating procedures. Highly stable silica-based membranes can be obtained by introducing organic moieties in the silica network [10–12] or by inorganic doping [13]. Both approaches have been proven to be highly effective in the stabilization of silica networks. Moreover, these modifications can change porosity, pore charge density, isoelectric point, and hydrophilicity of silica network, thus impacting membrane selectivity and permeability. Hydrophilicity is an especially important feature for membrane materials, because it can strongly affect membrane permeability to water or organic solvents. Thus, developing materials with controlled hydrophilicity is of prime importance from a membrane application perspective. The hydrophilic/hydrophobic behavior of organo-modified silica membranes has been extensively investigated, as membrane affinity for non-polar solvents can be intuitively increased via the replacement of the hydrophilic surface hydroxyl groups by hydrophobic hydrocarbon chains [14]. Membrane hydrophobicity can also be tuned by covering their pore surface with alkyl groups of various lengths. “Super-hydrophobic” silica membranes have been prepared by applying long hydrocarbon chains [15,16] or fluorinated chains [17], and highly hydrophilic membranes have been prepared by the introduction of amino groups on the pore surface [18]. Although these aspects can be very important to develop a membrane with high selectivity towards specific targets, the studies concerning truly inorganic silica membranes have been until now mainly focused on their chemical and hydrothermal stability [13,19–29], and not so much on their surface properties [27,28]. At the authors' best knowledge, change in membrane hydrophilicity upon chemical modification has been

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reported only for nickel-doped silica membranes, for which the hydrogen/steam selectivity was found to increase with the Ni/Si ratio, suggesting that membranes with higher Ni loading were more hydrophobic [29].

In this study, we investigate the impact of titania doping on the hydrophilicity of unsupported nanofiltration silica materials for membranes fabrication. TiO_2-doped silica has been selected as a suitable membrane material, because it has been shown that TiO_2 doping can increase the chemical and hydrothermal stability of silica membranes without a large reduction of membrane pore volume [13]. Moreover, the sol–gel method allow for the fabrication of membranes with high TiO_2 loading, good homogeneity and strong adhesion on the membrane support. This fabrication method consists in the use of alkoxides as precursors for the synthesis of stable nanocolloids, which are coated on a ceramic support and calcined to obtain a selective membrane layer. Finally, it was proved that TiO_2-doped silica can originate good membranes, since one of the formulation studied in this paper was used to fabricate a membrane which was applied with excellent results in water softening [14].

Mesoporous TiO_2-silica powders with different composition were prepared by the sol–gel method. Cetyltrimethylammonium bromide (CTAB) was applied as pore-forming agent, in order to imprint similar porosity in all the materials presented in this study. After morphological investigation by XRD, TEM and low-temperature N_2 adsorption analysis, and tests of stability at different pHs, the hydrophilicity of the materials was determined by means of an adsorption microcalorimeter coupled with a gas-volumetric glass apparatus. This technique allows for the quantitative measure of the amount of water adsorbed as a function of water pressure admitted on the sample and the direct measurement of molar heat of adsorption of water molecules at the surface of the membrane material as a function of the surface coverage. In general, a strongly exothermic water adsorption is an indication of a highly hydrophilic surface [30–33] and the liquefaction enthalpy of water vapor (44 kJ mol^{-1}) can be taken as threshold reference value to classify a surface as hydrophilic (enthalpies higher than 44 kJ mol^{-1}) or hydrophobic (enthalpies lower than 44 kJ mol^{-1}) [34]. Number, strength, and strength distribution of the water adsorption sites were measured as a function of surface coverage for eight TiO_2-silica powders with different composition, but similar pore structure. Surface hydrophobicity was also tested for selected materials with a different technique, i.e. microgravimetry, in order to verify the gas-volumetric results obtained with water and adsorption microcalorimetry by measuring materials affinity towards a hydrophobic vapor, namely toluene. These adsorption results, coupled with morphological characterization, allowed developing understanding on the effect of TiO_2-doping on hydrophilicity and surface heterogeneity of silica-based membrane materials, and gave interesting insights on features of colloids specifically designed for membrane fabrication [14], allowing to obtain results suitable for further development of enhanced nanofiltration membranes.

2. Experimental

2.1. Sol synthesis

Unsupported membranes were prepared by the sol–gel method. The following reagents were used: tetraethylorthosilicate (TEOS, 99.0% Sigma Aldrich), titanium(IV) tetrabutoxide ($Ti(butO)_4$, 97%, Sigma Aldrich), ethanol (99.9% Kemityl), nitric acid (69% Sigma Aldrich), cetyltrimethylammonium bromide (CTAB, Sigma Aldrich). Since $Ti(butO)_4$ is more sensitive to hydrolysis and condensation than TEOS, the sols were prepared following a two-step synthesis method, which was designed with the aim to obtaining well-developed sols avoiding gelation or precipitation, as necessary for coating during membrane fabrication, even at a high TiO_2 loading. In the first step, 1.4 N nitric acid (86 mL) was slowly dropped into a mixture of TEOS (319 g) in ethanol (276 g) under vigorous stirring. The mixture was heated at 333 K for 3 h always under stirring. After that, the mixture volume was adjusted to obtain a final 1.5 M hydrolyzed-TEOS solution, which was stored at 278 K until it was used for the preparation of the unsupported membranes.

This hydrolyzed-TEOS solution was used to prepare the TiO_2–doped silica sols with the reagents listed in Table 1. All the reagents were cooled at 278 K before mixing. The silica sol was diluted with ethanol (Dilution 1). Doping solutions were prepared by diluting $Ti(butO)_4$ in butanol (Dilution 2) under inert atmosphere in glove box, and then added to the diluted hydrolyzed-TEOS stirring vigorously. The final volume of the reaction mixture was further adjusted with ethanol (Dilution 3). The flask containing the mixture was heated at 333 K for 90 min always under stirring. Then, 7.00 g of CTAB were added to mixture. After stirring for 5 min to allow dissolution of the surfactant, the mixture was poured in Petri dishes, where the solvent was let to evaporate for 3 days at room temperature to form a gel. Then, the remaining solvent was removed by drying the gels in an oven at 393 K for 2 days. The dried materials were calcined at 723 K for 3 h at a heating/cooling rate of 2 K min^{-1}. The amount of reagents and solvents used are summarized in Table 1 together with the short names of the samples.

2.2. Material characterization

Specific surface area (*SSA*) and specific pore volume (V_P) of materials were determined by means of N_2 adsorption at liquid-nitrogen boiling point in a gas-volumetric apparatus ASAP2020 (Micromeritics, Norcross USA). Samples were outgassed at 573 K *in vacuo* (residual pressure 10^{-2} mbar, 1 mbar = 100 Pa) for about 4 h,

Table 1
Composition of the reaction mixtures used for the synthesis of the TiO_2-silica membrane materials.

Sample name	TiO_2 loading (mol%)	Hydrolized TEOS	Dilution 1	Dopant	Dilution 2	Dilution 3	Surfactant
		1.5 M solution (mL)	Ethanol (g)	$Ti(butO)_4$ (g)	Butanol (g)	Ethanol (g)	CTAB (g)
T_0.0	0	133	57.85	0.00	40.00	25.00	7.00
T_0.5	0.5	132	58.44	0.35	40.00	24.65	7.00
T_1.0	1	132	59.02	0.70	40.00	24.30	7.00
T_2.0	2	130	60.19	1.40	40.00	23.60	7.00
T_5.0	5	126	63.71	3.50	40.00	21.50	7.00
T_10	10	120	69.57	7.01	40.00	17.99	7.00
T_20	20	106	81.28	14.02	40.00	10.98	7.00
T_33	33	89	96.51	23.12	40.00	1.88	7.00