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Synthesis of mesoporous aluminophosphates-based materials using various copolymers as templates

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ABSTRACT

The aim of this work was to study the effect that various copolymers and several synthesis conditions may have on the properties of mesoporous aluminophosphates obtained using $AlCl_3$ and H_3PO_4 as aluminium and phosphorous precursors, respectively under non-aqueous conditions. Poly(styrene-co-allyl alcohol) and various triblock type copolymers were used as structure-directing agents in an acidic medium. The parameters investigated using the poly(styrene-co-allyl alcohol) included stirring time, Al/P mole ratio, synthesis time at 40 °C, calcination temperature and the type and amount of polymer used. The resulting materials were characterized by nitrogen adsorption at −196 °C, X-ray diffraction (XRD), temperature-programmed ammonia desorption (TPD-NH_3) and transmission electron microscopy (TEM). Mesoporous aluminophosphates with surface areas up to 540 m^2/g were obtained.

1. Introduction

Since the new family of ordered mesoporous silicate and aluminosilicate materials was prepared by researchers of the Mobil Oil Co. utilizing supramolecular arrays of surfactants as structure-directing templates [1,2], a series of materials have been synthesized. In the research of zeolites-type materials, aluminophosphates and substituted aluminophosphates molecular sieves have been studied [3,4]. Extension of the synthesis of mesostructured silica to aluminophosphates seemed to be a logical progression because of similarities between their chemistry and structures.

Microporous aluminophosphates, materials of pore size less than 2 nm, were reported by Wilson et al. [3] as the first example of an inorganic molecular sieve composed of a material other than aluminosilicates with framework topology identical or similar to aluminosilicate zeolites. The structure of aluminophosphates consisted of alternating tetrahedral AlO_4 and PO_4 connected by shared oxygen atoms. The main difficulty encountered during the synthesis of these solids was the ordered organization of two different units without the formation of the single oxides. A further key development in the area was the successful synthesis of mesoporous aluminophosphates with pores up to 4 nm. The larger pores facilitate the application of catalytic or adsorption processes.

Mesoporous aluminophosphate materials are generally prepared under hydrothermal conditions from gels containing sources of aluminium, phosphorous and an organic surfactant. The surfactant can be cationic, anionic or neutral [5], typically cetyltrimethylammonium. The procedure is lengthy and requires careful pH adjustment before hydrothermal treatment. The step involving the removal of the surfactant, usually by treatment at high temperature, can result in the complete collapse of the ordered structure [6]. An alternative method is the surfactant removal by solvent extraction, used if the interaction between the surfactant and the solid is not particularly strong. For example, Masson et al. reported the successful surfactant removal using an alkaline extraction procedure followed by calcination for the preparation of aluminophosphate and magnesium-aluminophosphate mesoporous solids [7].

Various synthesis strategies have been developed to prepare a more robust solid thus preventing the collapse of the prepared ordered material during the surfactant removal step. These strategies include employing novel precursors such as the use of microporous silicoaluminophosphate for the formation of mesoporous silicoaluminophosphate [8]. Novel synthesis routes have also been reported for example, the solvent-free synthesis of mesoporous aluminophosphate and metal substituted aluminophosphate [9], and the use of microwave irradiation in a three-component eutectic mixture [10]. Surfactants such a semi fluorinated surfactants have also been shown to produce more stable aluminophosphates and Fe-aluminophosphates [11].

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Block copolymers have been used as templates for the synthesis of ordered large-pore silica and other metal oxides because of their facile structure-directing ability and degradability under oxidant conditions [12]. These surfactants have also been used in the synthesis of mesoporous aluminophosphates, not only improving the thermal stability, but also extending the pore size of the hexagonal or disordered aluminophosphate structure [13–17]. The structure of a typical triblock copolymer used in the preparation of mesoporous solids is PEO–PPO–PEO or poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide). The first and third blocks have the same chemical nature (hydrophilic) and molecular weight whereby the middle block differs in chemical nature (hydrophobic). This amphiphilic character of the surfactant allows the condensation of the inorganic sources, under non-aqueous conditions, of the materials and the formation of the mesoporous structure. The solids obtained present high thermal stability, between 600 and 900 °C [13,18]. Other surfactants also reported for the formation of stable aluminophosphates are the simple alkyl poly(ethylene oxide) [17–21]. The appropriate choice of the inorganic sources of Al and P is also the key to the successful synthesis of the mesoporous materials.

In this paper we report the effect of several synthesis conditions on the properties of mesoporous aluminophosphates obtained using $AlCl_3$ and H_3PO_4 as aluminium and phosphorous precursors, respectively, under non-aqueous conditions. Also investigated is the effect of different structure-directing agents, poly(styrene-co-allyl alcohol) and various triblock type copolymers, on the overall properties of the synthesized aluminophosphate. Characteristics investigated were surface area of the final solid, the pore structure/size and the surface acidity with a view of looking at these solids for potential catalysts for acid based reactions.

2. Experimental section

2.1. Preparation of the materials

Mesoporous aluminophosphates (AlPO) were prepared using aluminium and phosphorous precursors under non-aqueous conditions based on a method developed by Wang et al. [14]. The sources of P and Al were phosphoric acid (H_3PO_4, Aldrich) and aluminium chloride ($AlCl_3$, Aldrich), respectively, and ethanol (Aldrich) was also used during the synthesis. Other chemicals used in this study included the copolymer poly(styrene-co-allyl alcohol) (Aldrich), (PEO)*x*–(PPO)*y*–(PEO)*x* triblock type copolymers: Pluronic F65, Pluronic F103, Pluronic F123 and Pluronic F127 (supplied by BASF, USA) and (PEO)*x*–(PPO)*y*–(PEO) polymers; R0.8, R3 and R5 (supplied by Polyscience, Germany). Some information on the copolymers used is summarized in Table 1.

The synthesis of AlPO was typically carried out using the following method: 5 mmol (0.67 g) of $AlCl_3$, 5 mmol (0.5 g) of H_3PO_4 and copolymer (0.07 mmol (1.5 g) of poly(styrene-co-allyl alcohol) or 0.1 mmol of polymer (PEO)*x*–(PPO)*y*–(PEO)*x* or (PEO)*x*–(PPO)*y*–(PEO) were added to 0.65 mol (30 g) of ethanol. The mixture was stirred vigorously for 2 h at room temperature. The resulting gel was transferred to an evaporating dish and the ethanol was removed by placing the dish in an oven at 40 °C for 6 h and then at 80 °C for an additional 12 h. Finally, the template was removed by heating the sample in air (100 cm^3/min) to 550 °C at a rate of 1 °C/min. The temperature was held at 550 °C for 6 h. Several parameters were modified during the synthesis using the poly(styrene-co-allyl alcohol) in an effort to determine the effect that these parameters had on the characteristics of the final solid. Parameters investigated included stirring time, the Al and P content in the synthesis gel, synthesis time at 40 °C, calcination temperature and the type and amount of polymer used.

2.2. Characterisation of the materials

Nitrogen adsorption/desorption experiments were performed at −196 °C using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). 0.1 g of the samples were degassed for 24 h at 150 °C at a pressure lower than 0.133 Pa. The specific surface areas (S_{BET}) were calculated using the BET method, taking the cross-sectional area of the nitrogen molecule as 0.162 nm^2 [22]. The total pore volume (Vp) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.95, assuming the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at −196 °C (0.81 g/cm^3) [22]. The mesopore size-distributions of the samples were carried out from the Barrett–Joyner–Halenda method applied to the desorption isotherm [22]. X-ray diffraction (XRD) patterns of the materials in low scattering angles were obtained using a Philips X'Pert Pro (Panalytical) diffractometer with nickel filtered Cu Kα radiation (λ = 0.1542 nm). The step size and scanning speed were 0.02° and 0.5°/min. Temperature-programmed ammonia desorption (TPD-NH_3) experiments were used to characterize the acidic properties of the solids. In each experiment, 0.15 g of a sample was placed in a quartz reactor and was pretreated at 500 °C for one hour in helium and then cooled to room temperature. A flow of 4% NH_3/He was then passed over the pre-treated material for 25 min. Following this ammonia adsorption procedure, the reactor was purged with helium for 30 min to remove residual/physisorbed ammonia. The sample was then heated to 500 °C at 10 °C/min in 20 cm^3/min helium and the ammonia desorption recorded continuously by the thermal conductivity detector (TCD). Transmission electron microscopy (TEM) was performed using a Jeol 2011 microscope over samples ground and dispersed in ethanol by using an ultrasonic apparatus; then, a drop of the suspension was placed on a carbon-coated copper grid and air dried before the study.

3. Results

3.1. Preparation of AlPO using poly(styrene-co-allyl alcohol) as template

A series of experiments were carried out to find the optimum AlPO synthesis conditions using the non-ionic block copolymer

Table 1
Some characteristics of the copolymers studied.

Name	Formula	Structure	Average molecular weight (g/mol)
F65	PEO_{19}–PPO_{29}–PEO_{19}	$H(-OCH_2CH_2-)_{19}[-OCH(CH_3)CH_2-]_{29}(-OCH_2CH_2-)_{19}OH$	3400
F103	PEO_{17}–PPO_{59}–PEO_{17}	$H(-OCH_2CH_2-)_{17}[-OCH(CH_3)CH_2-]_{59}(-OCH_2CH_2-)_{17}OH$	4950
F123	PEO_{20}–PPO_{70}–PEO_{20}	$H(-OCH_2CH_2-)_{20}[-OCH(CH_3)CH_2-]_{70}(-OCH_2CH_2-)_{20}OH$	5750
F127	PEO_{100}–PPO_{65}–PEO_{100}	$H(-OCH_2CH_2-)_{100}[-OCH(CH_3)CH_2-]_{65}(-OCH_2CH_2-)_{100}OH$	12600
R0.8	PEO_{28}–PPO_{26}–PEO	$H(-OCH_2CH_2-)_{28}[-OCH(CH_3)CH_2-]_{26}(-OCH_2CH_2-)_2OH$	2900
R5	PEO_{164}–PPO_{25}–PEO	$H(-OCH_2CH_2-)_{167}[-OCH(CH_3)CH_2-]_{25}(-OCH_2CH_2-)_2OH$	8750
R3	PEO_{225}–PPO_{57}–PEO	$H(-OCH_2CH_2-)_{225}[-OCH(CH_3)CH_2-]_{57}(-OCH_2CH_2-)_2OH$	13300