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Calcination and thermal degradation mechanisms of triblock copolymer template in SBA-15 materials

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Abstract

The calcination under air and degradation under inert atmosphere of as made SBA-15 surfactant templated mesostructured silica materials were studied using a combination of N_2 sorption at −196 °C, mass spectrometry (MS) monitored temperature programmed oxidation and degradation, thermogravimetric analysis (TGA), ^{13}C MAS NMR and Fourier transform infrared (FTIR) spectroscopy. The characterization of the materials treated at different temperatures under oxidative and inert atmospheres indicated that both processes follow stepwise mechanisms. SBA-15 materials exhibit three families of pores: primary main mesopores, complementary intrawall mesopores (>2 nm) and intrawall micropores (<2 nm). Under oxidative atmosphere, the primary mesopores and the larger framework intrawall pores are first emptied below 200 °C with the production of volatile organic compounds (VOCs). This step is followed by an oxidation of the PEO chains from the intrawall micropores (<2 nm) producing CO_2 by combustion. Under inert atmosphere, the degradation of the organic template also begins first in the primary mesopores. However, an increase in the pore diameter up to 550 °C indicates that the complete liberation of primary mesopores is much slower than for calcination under air and occurs simultaneously with the removal of the PEO chains occluded within framework micropores.

Keywords: SBA-15; Triblock copolymer; Calcination; Thermal degradation; Template removal

1. Introduction

Since the discovery of MCM-type mesostructured materials [1], many applications of these materials have been proposed in fields as diverse as catalysis [2,3], separation [4], electronic [5], optoelectronics [6] and nanocasting [7–9]. By using the surfactant templating pathways, substantial efforts have been deployed to synthesize new materials with different mesostructures and pore sizes [10–13]. In 1998, Zhao et al. developed a new mesostructured material by using non ionic triblock copolymers as structuring agent in acidic medium [14,15]. Compared with the previous M41S family, the SBA-15 type silica shows an enhanced hydrothermal stability because of thicker and more condensed silica walls [16,17].

Nevertheless, several aspects of the synthesis of these materials remain to be improved to develop more valuable solids for a wider range of applications. An important aspect of the synthesis of these mesostructured materials is the removal of the organic template occluded within the pores. Several methods have been developed to remove the organic template from hybrid mesophase such as oxidative ozone treatment [18,19], supercritical fluid extraction [20,21], microwave digestion [22] and ether cleavage by an acid [23,24], but the most popular ones are calcination under air and extraction with an organic solvent [25–29]. Several studies have been carried out to understand the influence of calcination on the physico-chemical properties of mesostructured SBA-15 type silica materials and showed that significant lattice shrinkage occurs upon high-temperature treatment [20,22,23,25,30,31]. However, relatively little works was done to understand the mechanism of the organic template oxidation along the calcination process [15,30].

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Several studies demonstrated that SBA-15 materials may contain intrawall pores that interconnect the ordered primary mesopores [32–35]. This porous framework is formed as the hydrophilic part of the triblock copolymer is occluded within the silica walls. These interactions between the inorganic framework and the PEO chains appear to strongly affect the calcination behavior. Kleitz et al. showed by using TG-DTA/MS that the removal of the triblock copolymer under air is a stepwise mechanism [30]. These authors showed that a decomposition step between 150 and 200 °C is responsible for the transformation of the major part of the polyalkene oxide into carbonaceous species. From XRD measurements at varying calcination temperature, they also showed that this first step was accompanied by a strong increase in the intensities of the low angle reflections. From 200 to 250 °C, the oxidation of the block copolymer produced CO_2 and H_2O. Interestingly, a noticeable decrease in the (100) reflection intensity was recorded over this temperature range and was attributed to a decrease in the scattering contrast due to the removal of the organic compounds from the intrawall pores. Moreover, by considering the relatively low temperature decomposition of the triblock copolymer (e.g. 150–180 °C) compared to that of cationic surfactants, it was also suggested that oxidation of the block copolymer is catalyzed by the inorganic framework [15,30].

The removal of the organic structure directing species by a thermal treatment under inert atmosphere is also commonly used in laboratories. The popularity of this method has recently increased with the discovery of the mesoporous polymers/carbons synthesized by a direct surfactant templating pathway [36,37]. In this case, the thermal degradation under inert atmosphere could be a good alternative to remove the structuring agent because this new class of mesostructured materials are highly sensitive to an oxidative atmosphere.

The present work is aiming at understanding the mechanisms of template removal either by calcination under oxygen or thermal degradation under inert atmosphere in the SBA-15 materials. The template removal was studied by a combination of N_2 sorption at −196 °C, TGA, MS monitored temperature programmed oxidation and degradation, ^{13}C MAS NMR and FTIR.

2. Experimental

2.1. Materials

SBA-15 material was obtained following the procedure reported by Zhao et al. [14,15]. Pluronic P123 (BASF, $M_w = 5800$ g/mol) was used as the template and tetraethyl orthosilicate (Aldrich) as the silica source. In a typical synthesis, 7.659 g of P123 was dissolved in 290 mL of a 1.6 M aqueous HCl solution. 16 g of TEOS was then added dropwise. The synthesis was carried out for 20 h at 35 °C followed by 24 h of hydrothermal treatment at 80 °C. The solid products were recovered by filtration and dried under air at 80 °C during 24 h. Prior to the calcination and degradation experiments, all the samples were again dried at 80 °C under vacuum overnight to remove the physisorbed solvent or water.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 40 mA).

Elemental analyses of carbon were performed with a Carloerba instrument 1500 Carbon, Nitrogen, Sulfur analyser.

Nitrogen adsorption/desorption isotherms at −196 °C were determined using a QUANTACHROME NOVA 2000 instrument. Before the experiments, the made sample was evacuated at 120 °C for 6 h and thermally treated samples were evacuated at 150 °C for 4 h. The specific surface area was calculated using the BET equation over the relative pressure range of 0.1–0.2. The micropore and mesopore volumes were estimated from the α_s-plot using a LiChrospher Si-1000 (EM Separations, Gibbstown, NJ) as reference material [38]. The pore size distributions were determined from the adsorption branch of isotherms using the modified BJH method [39].

Temperature programmed calcination and temperature programmed degradation monitored by mass spectrometry (TPC-MS and TPD-MS) were performed using a RXM-100 multi catalyst testing and characterization system (Advanced Scientific Design Inc.). Seventy milligram of support was placed in a U-shaped reactor coupled with a quadrupole mass spectrometer. All the experiments were carried out under a flow (50 mL/min) of 10% O_2 in He (TPC) or 100% He (TPD) from 25 °C to the various temperatures of interest with a 2 °C/min ramp and then cooled down to room temperature under the same flow. The temperature was maintained for different times after the end of the ramp to achieve polymer degradation and oxidation. The isothermal periods used during calcination and degradation of the different samples are presented in Table 1. Masses m/z 12, 14, 16, 18, 20, 26, 27–30, 36–46 and 58 were recorded using a mass spectrometer (UTI) to identify the

Table 1
Experimental conditions used during calcination (C) and thermal degradation (D) of as-synthesized SBA-15

Samples (C,D-T°C)	Ramp (°C/min)	Isothermal time (min)	Flow composition
C160	2	0	10% O_2 in He
C175	2	120	10% O_2 in He
C270	2	120	10% O_2 in He
C335	2	120	10% O_2 in He
C575	2	15	10% O_2 in He
D360	3	120	He
D450	3	120	He
D550	3	120	He
D700	3	20	He