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Synthesis of Sn–silicalite from hydrothermal conversion of SiO_2–SnO_2 xerogels

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ABSTRACT

For the first time, the synthesis of Sn–zeolites starting from SiO_2–SnO_2 xerogels is described. The influence of several synthesis parameters in the physico–chemical properties of the xerogels and the zeolites subsequently generated has been investigated. Two different tin sources were assayed in the synthesis of xerogels (anhydrous $SnCl_4$ and $SnCl_4 \cdot 5H_2O$) as well as two gelation agents (NH_3 and TPAOH). Though both bases led SiO_2–SnO_2 xerogels mainly showing tetrahedrally coordinated tin centres, regardless the tin source, only TPAOH derived materials were easily transformed into MFI-type zeolites showing tin incorporation. On the other hand, NH_3 gelified xerogels were difficult to crystallize, being this fact attributed to the retention of NH_3 species in the xerogels because of the tin Lewis acidity, avoiding its inclusion in the zeolite crystalline framework. Studies on the crystallization time and temperature allowed to optimize the transformation of TPAOH gelified SiO_2–SnO_2 xerogels into tin-containing MFI zeolites showing isomorphically incorporated tin centres. The so-obtained materials were compared with conventionally synthesized SnS-1 zeolite showing better quality in terms of tin incorporation.

1. Introduction

The interest of tin incorporation into zeolites dates from decades ago [1–3]. In these first articles, the substitution of Si by Sn into zeolite frameworks, particularly in MFI materials, was supported by different characterisation techniques. However, their catalytic activity was not relevant as they were not probably tested in the appropriate reactions. In order to expand the applicability range of these tin-containing materials, zeolite structures with higher pore size, like Sn-beta and Al-free Sn-beta, were prepared and tested in the oxidation of aromatic compounds [4]. A few years later, the report of the excellent catalytic behaviour of Sn-containing beta zeolites in Baeyer Villiger reaction [5] – with practically 100% conversion and 100% selectivity for certain subtracts – renewed the interest on tin-functionalized zeolites and related materials [6–11].

Sn-beta zeolite is difficult to synthesize since it seems not to spontaneously crystallise from Sn-contained gels. This is overcome by the addition of some seeds of nano-crystalline pure-silica beta to the gel [5], being therefore essential two proper syntheses of the two BEA-structured materials, with and without tin atoms. The incorporation of tin into BEA framework by this method is limited to a Si/Sn ratio higher than 120 [11,12], probably as a consequence of the substitution of Sn atoms in the BEA framework is an endothermic process [13]. Higher Sn content into the gel implies the presence of undesired extra-framework Sn species in the final samples.

Similar problems were described for the incorporation of Ti in zeolites. Their catalytic activity was found to depend on the amount of isomorphically substituted Ti into the zeolite framework [14,15]. The incorporation of Ti into MFI-structured zeolites was limited to a particular content, regardless the synthesis method [16,17]. In this context, the preparation of zeolite TS-1 from wetness impregnated SiO_2–TiO_2 xerogels was proposed as an alternative [18] since, unlike the conventional crystallization of zeolites, its transformation from xerogels is given by a solid–solid mechanism [19,20]. Ti (and also Sn [21]) substitution limit in xerogels is very much higher than that in zeolites [22], because the former does not force the metal to occupy a particular spatial position. On the other hand, there is not doubt about the chemical similarities of Sn^{4+} and Ti^{4+}. For instance, both are the most stable oxidation state of their atoms in aqueous solution, and both corresponding oxides have rutile-like topology. Moreover, the incorporation of both ions into the zeolite framework produces similar electronic properties since they are equally interpreted by diffuse-reflectance UV–vis (DR-UV–vis) and Fourier transform infrared (IR) spectroscopies [23].

Herein we present the first study of the transformation of SiO_2–SnO_2 xerogels into Sn–zeolites. In particular, this work is focused on MFI, the topology being studied in the transformation of xerogels in zeolites.

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2. Experimental

2.1. Synthesis of the materials

SiO_2–SnO_2 xerogels were prepared by a two-step sol–gel method. Tetraethylorthosilicate (TEOS) and either $SnCl_4$ (previously dissolved in freshly-distilled anhydrous ethanol in a dry box) or soluble-in-water $SnCl_4 \cdot 5H_2O$ were added to a 0.05 M HCl aqueous solution and partially hydrolysed for 1 h under stirring. The two-phase mixture became a unique phase after 5 min under agitation. Next, an aqueous base (NH_4OH 1 M or TPAOH 20 wt%) was dropwise added until the gel point was reached. The so-formed gel was dried at 110 °C becoming a xerogel.

The resultant xerogels were wetness impregnated with TPAOH (1.6 g per 1 g of xerogel) [20] and the mixture were hydrothermally treated at different crystallization temperatures (150–190 °C) for different times (1–30 days). The solids were washed and dried at 110 °C overnight. Finally, the samples were calcined at 550 °C under air atmosphere for 5 h to remove the template.

The samples will be named as follows: the xerogels will be identified with letter X followed by a number representing the content of Sn, being 3, 6 and 9 wt%; in the case of zeolites, their names starts with Z followed by a number, only indicating an arbitrary order.

2.2. Characterisation techniques

Phase purity of the samples was checked by X-ray diffraction (XRD). XRD patterns were acquired on a Philips X'PERT MPD diffractometer using Cu Kα radiation. Crystallinity of Sn–zeolites with MFI topology was calculated from the area below the curve in the range 22.4–24.7°, referenced to the same reflections of the XRD pattern of a silicalite-1 sample, considered as 100% crystalline, which was prepared from a pure silica xerogel. The tendencies in crystallinity were corroborated by the intensity variations of the double five-ring lattice vibration band at ca. 550 cm^{-1} in the FT-IR spectra [24].

DR-UV–vis spectra were recorded on a Varian CARY-500 spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range from 200 to 600 nm. A halon white reflectance standard was used as a reference material.

Tin content was determined by ICP-atomic emission spectroscopy. The samples (100 mg) were dissolved in aqueous hydrofluoric acid. After dissolution, the samples were diluted in water until filling a 1 l calibrated flask. An absorption standard solution of Sn (1000 $\mu g\ ml^{-1}$ in water) was used for the calibration of the equipment.

Scanning electron microscopy (SEM) images and micro-elemental analysis (EDX) were carried out on a XL30 ESEM Philips, operating at 30 kV.

Thermogravimetric analysis (TGA) were performed in N_2 flow on a TA instrument SDT 2960 thermobalance, with a heating rate of 5 °C min^{-1} up to 800 °C.

FT-IR spectra of fresh catalysts were recorded on a Mattson Infinity Series spectrophotometer using the potassium bromide wafer technique.

^{119}Sn magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded using a Varian Infinity-400 spectrometer (9.4 T) at 149.0 MHz, using a 7-mm probe. Spinning rates of 6 kHz, pulse lengths of 1.7 μs ($\pi/4$) and pulse delays of 40 s were applied. ^{119}Sn chemical shifts were referenced against tetramethyl tin, taken as 0 ppm.

Acidity of the samples was determined by ammonia temperature programmed desorption (TPD) in a Micromeritics 2910 (TPD/TPR) equipment. The calcined samples were outgassed under a helium flow (50 N ml min^{-1}) with a heating rate of 15 °C min^{-1} up to 560 °C and kept at this temperature for 30 min. After cooling to 60 °C, an ammonia flow of 35 N ml min^{-1} was passed through the sample for 30 min. The physisorbed ammonia was removed by flowing helium at 60 °C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550 °C with a heating rate of 15 °C min^{-1}, maintaining afterwards this temperature for additional 30 min. The ammonia concentration in the effluent stream was measured through a thermal conductivity detector. Acidity of the samples were quantified by comparing the area of the TPD bands with that of a zeolite Al-ZSM-5 (Si/Al = 30), considering that every Al atom is incorporated into the zeolite framework generating a Brönsted acid site.

3. Results and discussion

3.1. Xerogels

Fig. 1 shows the DR-UV–vis spectra of xerogels prepared with either anhydrous or $SnCl_4$ pentahydrate for three different tin contents. All of them were gelified with a 1 M aqueous solution of NH_4OH. Regardless the Sn source, it is evident that Sn is mainly tetrahedrally coordinated and scarce contribution of Sn species with higher coordination, if any, is detected. Therefore, there is not a discernible effect of the nature of the tin source on the tin coordination in the SiO_2–SnO_2 xerogels. Other physico–chemical properties of the xerogels prepared with different tin sources were studied by an exhaustive characterisation study including techniques such as chemical analysis by ICP-AES, TGA, N_2 adsorption–desorption isotherms at 77 K, FT-IR spectroscopy, and NH_3–TPD (results not shown). Significant differences between xerogels were not found in any of these techniques, excepting that the TGA weight loss of NH_3 was observed at higher temperatures in the xerogels prepared with anhydrous tin source (254 °C for a xerogel containing 3 wt% of Sn) than in those prepared with $SnCl_4 \cdot 5H_2O$ (233 °C for a xerogel with the same tin content). Because of the experimental simplicity in preparing xerogels with the soluble-in-water $SnCl_4 \cdot 5H_2O$ and especially because their better transformation to zeolites MFI (see below), pentahydrate tin chloride will be the precursor of the SiO_2–SnO_2 xerogels discussed from now on, unless other thing will be stated.

DR-UV–vis spectra shown in Fig. 1 also evidences that tin coordination does not vary with the Sn content, at least in the studied range 3–9 wt% of Sn, for any of both Sn sources. ICP-AES analyses confirmed that all Sn and all Si are found in the final xerogels. The homogeneity in tin coordination is additionally supported by ^{119}Sn MAS NMR studies (Fig. 2). The ^{119}Sn NMR spectra of the xerogels with 3 and 9 wt% of Sn prepared with $SnCl_4 \cdot 5H_2O$ are dominated by a broad but symmetrical signal without any other significant contribution. The large width of the signal must be related with the amorphous nature of the xerogel, which would provide a wide distribution of environments for a given Sn coordination. The main difference between the ^{119}Sn NMR spectra of the xerogels with different tin content seems to be the intensity of that resonance. More importantly, the ^{119}Sn chemical shift of this signal is centred at ca. −688 ppm, very different from the δ ^{119}Sn of SnO_2 (−605 ppm) and very similar to that of hydrated Sn-beta [12], Sn-MFI [25], Sn-MEL [3] and Sn-MCM-41 [26], which where assigned to tetrahedral, octahedral and even penta-coordinated Sn, but located into the framework in any case. The high Sn content able to be incorporated into the SiO_2 matrix of a xerogel (at least, 9 wt% of Sn, that is, Si/Sn ratio of 19.4) as it is deduced from DR-UV–vis and ^{119}Sn MAS NMR, supports our hypothesis about a minor restriction to accommodate tin in xerogels compared the crystalline zeolite.