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Synthesis and characterization of microporous titanosilicate ETS-10 obtained with different Ti sources

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ABSTRACT

Titanosilicate ETS-10 crystals were prepared by hydrothermal synthesis varying Ti source ($TiCl_3$ and commercial TiO_2-anatase), time in autoclave and seeding with previously prepared ETS-10 crystals. The crystalline powders were characterized by X-ray diffraction, N_2 adsorption, thermogravimetric analysis, and scanning and transmission electron microscopies. Control of the particle size of ETS-10 crystals ranging from 0.32 μm × 0.41 μm to 16.4 μm × 32.5 μm was successfully achieved varying the seeding and synthesis conditions. In particular, it was found that the use of TiO_2-anatase alone or together with $TiCl_3$ promotes heterogeneous primary nucleation. Transmission electron microscopy demonstrated that the largest crystals obtained here were twinned.

1. Introduction

ETS-10 is a microporous titanosilicate built from orthogonal TiO_6 octahedra and SiO_4 tetrahedra linked by corner-sharing oxygen atoms forming a three-dimensional pore system with a considerable degree of disorder. Each Ti atom in a six-coordinated state carries two negative charges balanced by Na^+ and K^+ cations [1,2]. This makes ETS-10 particularly attractive in adsorption [3], photochemistry [4–7], catalysis and membrane separation processes [8,9], due to its high cation exchange capacity, good accessibility for guest molecules and the presence of electrically isolated titania rods [10].

Control of particle size is critical when synthesizing zeolitic materials and it would allow widening the knowledge of the ETS-10 morphology, structure and potential applications [11,12]. Large sizes may allow structure refinement from single crystal data, and experimental determination of the positions of the extra-framework cation sites from diffraction data [13,14]. Also, large crystals are suitable for studying the formation of intergrowth structures inside single zeolite crystals [15]. Small sizes [16] may find application in the preparation of mixed matrix membranes for molecular separations, where the tiny crystalline particles can be homogeneously dispersed in the chosen polymer, providing this with their intrinsic characteristics.

Even though the crystallization of ETS-10 has been reported in detail in many previous works, some aspects related to crystal growth and the formation of twins merit still some experimental effort. In this work, besides the influence of the hydrothermal synthesis conditions in ETS-10 crystallization, heterogeneous primary nucleation was promoted by using TiO_2-anatase together with $TiCl_3$ as Ti sources. The different synthesis conditions were evaluated by XRD, SEM, and TEM, among other techniques, in the light of the control of the size and twin formation of the crystalline product.

2. Experimental

Previously developed hydrothermal synthesis techniques [3,8,17] that allowed control of crystallinity were adapted and employed for producing ETS-10.

2.1. ETS-10 preparation (from TiO_2)

About 400-nm-sized ETS-10 crystals were prepared by hydrothermal synthesis using TiO_2-anatase (powder, 99.8 wt%, Aldrich) as Ti source. To prepare 35.06 g of gel, sodium silicate solution (27 wt% SiO_2, 8 wt% Na_2O, Merck) (12.3 g) was mixed with deionized water (16.5 g) and stirred to homogenize. Potassium chloride (99 wt%, Merck) (0.86 g), potassium fluoride (99 wt%,

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Table 1
Molar composition of synthesis gels.

Reference/gel	Ti source	Seeding	Gel molar composition
[2]	$TiCl_3$	ETS-4	$5.4Na_2O:0.8K_2O:TiO_2:5.9\ SiO_2:124H_2O$
[18,19]	$TiCl_3$	ETS-4	$3.70Na_2O:0.95K_2O:TiO_2:5.71SiO_2:171H_2O$
[5]	$TiCl_3$	ETS-10	$3.7Na_2O:0.95K_2O:TiO_2:5.7SiO_2:171H_2O$
[24]	$TiCl_3$	ETS-10	$4.8Na_2O:0.75K_2O:TiO_2:5.5SiO_2:140H_2O$
[26]	P25[a]	ETS-10	$1.6Na_2O:7.2NaCl:1.0KF:TiO_2:5.3SiO_2:110H_2O$
[17]	$TiCl_3$	ETS-10	$4.7Na_2O:1.5K_2O:TiO_2:5.5SiO_2:122H_2O$
	TiO_2	No	$5.0Na_2O:1.3K_2O:TiO_2:6.0SiO_2:122H_2O$
[20]	P25[a]	ETS-10	$3.4Na_2O:1.0K_2O:TiO_2:4.5\text{-}5.5SiO_2:150\text{-}180H_2O$
[31]	$Ti(SO_4)_2$	No	$4.2\ Na_2O:1.5KF:TiO_2:5.5SiO_2:300H_2O$
[32]	$TiCl_3$	No	$1.0Na_2O:0.6KF:1.28HCl:0.2TiO_2:1.49SiO_2:39.5H_2O$
ETS-10-$TiCl_3$-1 (this work)	$TiCl_3$	No	$4.2Na_2O:1.2K_2O:TiO_2:5.5SiO_2:336H_2O$
ETS-10-$TiCl_3$-2 (this work)	$TiCl_3$	ETS-10	$4.0Na_2O:1.2K_2O:TiO_2:5.6SiO_2:336H_2O$
ETS-10-$TiCl_3$-3 (this work)	$TiCl_3$	TiO_2	$4.1Na_2O:1.2K_2O:TiO_2:5.5SiO_2:336H_2O$
ETS-10-TiO_2 (this work)	TiO_2	No	$4.6Na_2O:1.9K_2O:TiO_2:5.5SiO_2:147H_2O$

[a] TiO_2 P25 is a highly dispersed TiO_2 manufactured by Evonik–Degusa with 76 wt% anatase and 24 wt% rutile.

Aldrich) (1.1 g) and sodium chloride (pro-analyse, Merck) (3.5 g) were added to the mixture in this order under strong stirring to obtain a thick, transparent gel. Finally, TiO_2-anatase (0.8 g) was added and stirring continued for other 30 min. Then, the obtained gel was poured into a Teflon-lined autoclave and submitted to hydrothermal synthesis at 230 °C for 24 h. After this time, the autoclave was removed from the oven and quenched under cold tap water to room temperature. The product, which will also be used as seeds in the formation of ETS-10 crystals, was washed in deionized water and centrifuged several times, then dried at 100 °C overnight. The parent gel molar composition is collected in Table 1, as ETS-10-TiO_2. For comparison purposes, similar compositions from the literature are also shown in Table 1, those using $TiCl_3$ as Ti precursor being slightly different to those with TiO_2-anatase. Finally, using this procedure, about 2.8 g of product was recovered after drying.

2.2. ETS-10 crystal synthesis from $TiCl_3$

Larger ETS-10 crystals were obtained by seeded and unseeded liquid hydrothermal syntheses. The precursor reactants were $TiCl_3$ solution (15 wt% $TiCl_3$ in 10 wt% HCl, Merck), deionized water, hydrogen peroxide (30 wt%, Riedel-de-Häen), potassium chloride, and sodium hydroxide (99 wt%, Merck) and the same sodium silicate solution aforementioned. To prepare 35.12 g of gel, $TiCl_3$ solution (5.1 g) was mixed with deionized water (21.4 g). Hydrogen peroxide (0.66 g) was added to convert $TiCl_3$ to $TiCl_4$. KCl (0.86 g), NaOH (1.0 g) were added in this order and stirred strongly to obtain a homogeneous, light orange gel, which turned to light yellow when the sodium silicate solution (6.1 g) was added. In case of seeding, previously prepared 400 nm ETS-10 or commercial TiO_2-anatase particles in 0.3 wt% with respect to the total weight of the gel were added at the end. Two different commercial TiO_2-anatase sources were used: that aforementioned with a particle size of about 300 nm [21] and another of less than 25 nm (nanopowder, 99.7 wt%, Aldrich). After complete mixing of the precursors for 30 min, the pH was measured in a 1/100 diluted (to improve contact with the pH electrode) portion of the gel, and was always in the 10.4–10.6 range (including the previously described preparation of ETS-10 from TiO_2). Gel molar compositions are collected in Table 1, as ETS-10-$TiCl_3$-X, where $X = 1$ for the unseeded synthesis, $X = 2$ for the crystals obtained with ETS-10 seeds, and $X = 3$ for the synthesis gel seeded by TiO_2-anatase. The gel was then transferred to a Teflon-lined autoclave and hydrothermal synthesis was carried out at 230 °C for 48–60 h. After hydrothermal synthesis, the same procedure described for sample ETS-10-TiO_2 was carried out, and approximately 1.5 g of product was recovered after drying, independently of synthesis time.

2.3. Characterization

X-ray diffraction analyses (Rigaku/Max System diffractometer, Cu Kα radiation with $\lambda = 1.5418$ Å and graphite monochromator) and specific surface area measurements (Micromeritics Tristar 3000, surface area and porosity analyzer) using N_2 at 77.4 K were conducted for most of the samples. Prior to the N_2 adsorption/desorption measurement, the samples were degassed under vacuum for 8 h at 250 °C. The specific surface area was calculated according to BET method and the micropore volume and external surface was estimated from the *t*-plot curves. Thermogravimetric analyses (TGA) were performed by a TGA/SDTA851^e system (Mettler Toledo) in air at a heating rate of 10 °C/min.

Scanning electron microscopy (JEOL 6400) images were obtained on gold-coated specimens by operating at 20 kV. Also, images of the ETS-10 crystals were collected using transmission electron microscopy (JEOL-2000 FXII). TEM specimens were prepared after repeated dispersion in deionized water before pouring onto the carbon grid. Some selected samples were also characterized by selected area electron diffraction (SAED) and high resolution electron microscopy (HREM) using a JEOL 3000 FEG electron microscope, fitted with a double tilting goniometer stage ($\pm 20°$, $\pm 20°$).

3. Results and discussion

ETS-10-TiO_2 possessed an average crystal size of about $0.32\ \mu m \times 0.41\ \mu m$, as shown in the TEM image corresponding to Fig. 1a and Table 2, which agreed with the data reported by other authors using TiO_2-anatase as the Ti precursor [3,17,20]. Average particle sizes in Table 2 were obtained upon the analysis of 20 specimens obtained at each synthesis condition. When compared with $TiCl_3$, TiO_2-anatase can be considered as a low solubility Ti source that many times appears unconverted at the end of the corresponding hydrothermal process carried out to synthesize microporous titanosilicates [20,21]. It would be expected that longer synthesis times give rise to less unreacted TiO_2-anatase in the final product, as will be shown later. From the obtained results, it could be inferred that the TiO_2-anatase nanoparticles would lead to the *heterogeneous primary nucleation* of ETS-10. This mechanism of nucleation, together with the TiO_2-anatase low solubility [21] would dramatically reduce the availability of nutrients for growth, thus explaining why these conditions led to the smallest crystal size.