

Optimization of the synthesis of mesoporous titanosilicate ETS-10: Problems and unexpected difficulties

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Abstract: We focused on the synthesis and subsequent use of mesoporous titanosilicate ETS-10 for industrial water purification. Numerous attempts have been made to optimize the conditions and reagents used for the synthesis of the ETS-10. The main problem we faced in the synthesis of ETS-10 is the production of "pure" phase and it was related to the type of titanium source. Various sources of titanium were used - titanium tetrachloride, anatase (anatase 92% and rutile 6%), nanosized titanium dioxide (Degussa P25) etc. The use of liquid titanium tetrachloride, due to its high hydrophilicity, leads to difficulties in reproducible control of the quantities of used reagents, which leads to the formation of unwanted crystalline phases, especially if the synthesis is carried out in small volumes. In addition, the optimized by us synthesis attempts included a reduced reaction time - up to 24 hours - and lower temperatures (up to 200 °C). For comparison standard synthesis is carried out for 72 h at 230 °C. As a result of the experiments, ETS-10 with minimal SiO₂ residues was obtained in 24 hours at 200 °C using nanosized anatase.

Keywords: ETS-10, SYNTHESIS, TITANOSILICATE, MESOPOROUS

1. Introduction

The interest in titanium-silicate microporous and mesoporous zeolite materials is huge. This is due to their wide application in catalytic reactions [1], as sorbents [2], ion exchangers [3] etc. Therefore, a lot of research is being done on optimizing their synthesis. Our main two goals are to synthesize a pure phase of mesoporous titanosilicate ETS-10, and exploit the sorption properties of this material.

ETS-10 was first synthesized by Engelhard in 1989 [4, 5]. It is one of the titanosilicates molecular sieves that have octahedrally coordinated titanium in its frame. Indeed, the building blocks of the ETS-10 structure are SiO₄ tetrahedra and TiO₆ octahedra. The bonding of these units through a shared/bridging oxygen produces a 7- and 12-membered rings. In turn those rings arrange to produce three-dimensional framework containing smaller and bigger channels with pore size of about 0.5 and 0.8 nm respectively. Only the channels generated by 12-membered rings are easily accessible and thus suitable for ion exchange. The basic formula of ETS-10 is (Na,K)₂TiSi₅O₁₃ [6]. The theoretical Ti/Si ratio is 0.2 but due the presence of structural defects it is generally higher (> 0.25). This framework allows the adsorption of cations with larger ionic radii which attracted our interest [7].

A number of different methods of synthesizing ETS-10 are known from the literature. First, syntheses with different sources of Ti and Si are possible: tetraethyl orthosilicate (TEOS), Sodium silicate aqueous solution [8], TiCl₃ [9], TiCl₄ [10], TiF₄ [11], Ti₂O, commercial Degussa P25 [8, 12], sodium hydroxide, (TiSO₄)₂ [13], (TiSO₄)₃ [14] NaF, NaCl and potassium hydroxide, KF, KCl, ash from rice husks as a source of silicon etc. [7, 11, 12, 15-21]. Then, mesoporous titanosilicate ETS-10 can be synthesized with or without the addition of organic template molecules [16, 22, 23]. The organic template is environmentally undesirable and unprofitable because the removal of clogged templates requires calcination e.g. high temperature, and can damage the framework. Finally, time and temperature can be varied. Thus it is desirable to synthesize ETS-10 in the absence of organic template agents, at lower temperatures and reduced time.

2. Materials and methods

Synthesis.

For the low-temperature hydrothermal synthesis of ETS-10, a number of experiments were performed with different sources of titanium, silicon, sodium, and potassium according to procedures described in the literature. The experiments aimed at optimizing the synthesis conditions e.g. without template and optimizations of temperature and time conditions.

The reagents used in our study for the synthesis of ETS-10 are: NaOH, KOH, KF, TiCl₄, TiO₂ (Degussa P25) and (anatase 92% and rutile 6%), nanosized Si₂O and Si₂O with size < 10 μm. The optimized synthesis system from us is: 0.42Na₂O-0.03K₂O-0.1TiO₂-0.5SiO₂-5.5H₂O, in which the reaction conditions such as

alkali cations, content water and ratio Si/Ti, pH, etc. were changed. A typical recipe for synthesis of ETS-10 used in this work is presented below.

Synthesis procedure: 3.36 g of NaOH are added to 8 ml of water, stirred until clear (first solution). A second solution was prepared in parallel - 0.797 g of TiO₂ (anatase) and 1.6 H₂SO₄ were added to 2 ml of water. 3.30 g of SiO₂ (nanosized) are then added to solution 1 and stirred for 20 minutes. Then the two solutions (Ti: Si) are slowly mixed, stirred for about 20 minutes on a magnetic stirrer without heating and the pH measured. Then 0.871 g of KF were added, with stirring for additional 20 minutes. After that the gel mixture is transferred in stainless steel Teflon lined autoclave and the autoclave placed in preheated oven heated to 200 °C for 22 hours. The obtained product is centrifuging and dried at 90 °C for 2-3 hours.

Methods.

The main method for characterizing the phases is powder X-ray diffraction (PXRD). Samples were measured at room temperature on an Empyrean MalvernPanalytical diffractometer, the Netherlands. Data collection was performed with Cu radiation (λ = 1.5406 Å) at 40 kV and 30 mA and PIXcel3D detector in the range 2 - 90° 2θ and step mode 0.013° 80 seconds and experiment duration 35 minutes.

Wave-dispersive X-ray fluorescence spectroscopy (WDXRF) was used to determine the chemical composition of the phases. The spectrometer is Rigaku Supermini200, Japan. Data collection was performed operating mode at 50 kV and 4.00 mA. The sample is crushed and then pressed. The ratio of sample amount (in grams) to the amount of glue (Acrawax C powder) is 5:1 g. The sample is placed in a holder with an irradiated area of 30 mm in diameter. The analysis used a semi-quantitative method to determine the elemental composition. The results obtained by the "SQX" semi-quantitative analysis method allow the determination of the chemical composition of samples without the need for reference materials (standards). One WDXRF measurement has a duration 30 minutes.

Scanning electron microscopy (SEM) is used to determine the morphology and size of the crystals. Scanning electron microscopy (SEM) was performed on a Philips 515 microscope operating at 20 keV in secondary electron mode. The samples were mounted on a sample holder with a conductive carbon coating.

3. Results and discussion

Titanium tetrachloride synthesis

Figure 1a shows a diffraction pattern of synthesis with the following molar composition: 0.59Na₂O-0.69K₂O-0.1TiO₂-3.95SiO₂-267H₂O. The initial pH is about 12. Nano-sized SiO₂ was used. The synthesis temperature is 200 °C and the duration is 24 hours.

On the Figure 1b the diffraction pattern with molar ratio: 0.29Na₂O-0.35K₂O-0.1TiO₂-1.98SiO₂-133H₂O is presented. The initial pH is about 13. As Si source SiO₂ with crystallite size <10μm

was used. The synthesis temperature is 200 °C and the duration is 24 hours.

In a later synthesis of ETS-10 was used following molar composition: $0.59\text{Na}_2\text{O}-0.69\text{K}_2\text{O}-0.1\text{TiO}_2-3.95\text{SiO}_2-267\text{H}_2\text{O}$. The initial pH is about 11. For source of Si was used micrograin SiO_2 with size of crystallites less than $10\mu\text{m}$, as well hydrochloric acid. The synthesis temperature is 200 °C and the duration is 24 hours. (Fig. 1c).

In the synthesis of ETS-10 with different amounts of titanium tetrachloride for 24 hours, at 200 °C and different sources of SiO_2 (nanosized and micrograins $< 10\mu\text{m}$), as well as the use of hydrochloric acid from Fig. 1 one can see that mostly quartz and ETS-4 are obtained.

For the conditions in Fig. 1a the amount of titanium tetrachloride is very low and the source of SiO_2 is nanosized in contrast to those in figure 1b. Under such conditions, quartz begins to form. Using low amounts of TiCl_4 , micrograin SiO_2 and HCl (to control the pH) the amount of quartz increases at the expense of ETS-4 (Fig. 1c).

These results are an indication that at 200 °C for 24 hours and with the selection of the listed reagents it is impossible to obtain ETS-10, instead ETS-4.

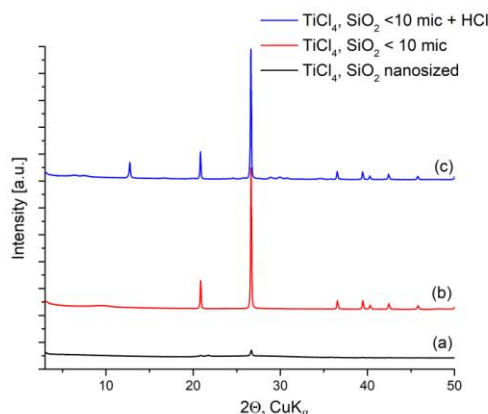


Fig. 1 XRD ETS-10 synthesized with TiCl_4 and nanosized SiO_2 under the same conditions -200°C/24h: **a)** Quartz; **b)** Quartz-80% and ETS- 4-20%; **c)** Quartz-85% and ETS- 4-15%

Additional syntheses with a source of Ti - TiCl_4 were performed, in which both the amount of titanium and water were changed.

The characteristics of the synthesized phases under different conditions of the system are presented in Fig. 2. The results show that by hydrothermal synthesis at 200 °C for 24 h, the use of increased amounts of titanium tetrachloride and less water ETS-4 with impurities is obtained (Fig. 2a). When the amount of titanium tetrachloride is decreased and the amount of water increased, a mixture of ETS-10 / ETS-4 / Quartz is obtained (Fig. 2b).

Titanium dioxide – anatase synthesis

The system and procedure described below was used for the synthesis of ETS-10 with minimal amounts of quartz (Fig. 2c).

The most optimal of our tested conditions are those using nanosized titanium dioxide - anatase, nanosized silicon dioxide, increased amounts of sodium hydroxide and the use of potassium fluoride as sources of alkalis, sulfuric acid, pH=10.6 and reducing the synthesis time to 22 hours (Fig. 2c).

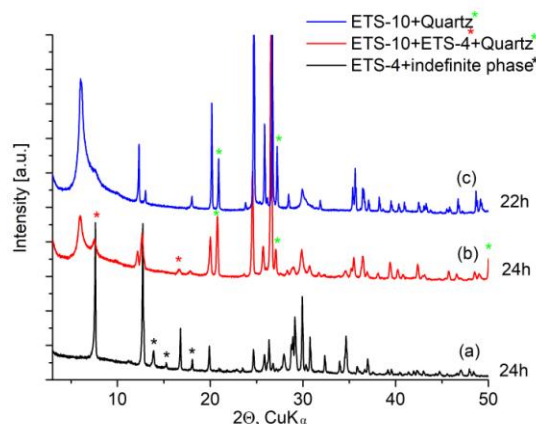


Fig. 2 XRD ETS-10 synthesized at different times with different precursors; **a)** ETS-10 -200°C/24h, TiCl_4 , **b)** ETS-10 -200°C/24h, $<\text{TiCl}_4>\text{H}_2\text{O}$; **c)** ETS-10 -200°C/22h, TiO_2 (anatase).

The result of the SEM images (Fig.3) shows that the ETS-10 crystals morphology is cubic and the size of the crystallites is $\sim 5\mu\text{m}$. This is a characteristic morphology for the synthesis of ETS-10 with nanosized titanium dioxide - anatase, established by Rocha in 1998.

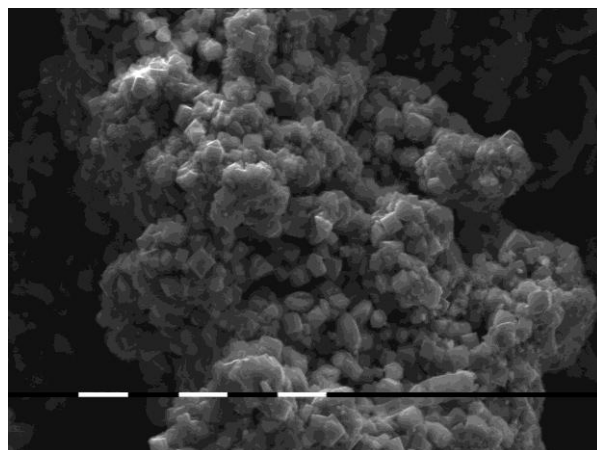


Fig. 3 SEM images of the ETS-10 (particle size $5\mu\text{m}$)

The chemical results from WDXRF are presented in Table. 1 and correspond to the stoichiometric formula: $(\text{Na}_{1.10}\text{K}_{0.28})\text{Ti}_{0.91}\text{Si}_5\text{O}_{13}$ which is in agreement with $(\text{Na,K})_2\text{TiSi}_5\text{O}_{13}$. The table shows that no significant amounts of chlorine were found in the product.

Table 1. Chemical composition of the final product (ETS-10) synthesized by nanosized TiO_2

Oxide	Mass %
N_2O	10.2057
K_2O	3.6023
SiO_2	72.4312
TiO_2	13.7135
Cl	0.0472

To determine the Si/Ti ratios, an elemental analysis of WDXRF was performed (Table 2). The results show that the Si/Ti ratio is 2.6, which is less than reported by Rocha 5-6 for pure ETS-10 phase. In our experiments for the synthesis of ETS-10, we found that with such a ratio (2.6) we obtain the phase with a small contamination with quartz, which contradicts Rocha's statement that quartz is formed mainly at a Si/Ti ratio above 6 [8].

Table 2: Elements composition of the final product (ETS-10) synthesized using TiO₂ (anatase, temperature 200°C/22h)

Elements	Mass %
Na	10.3135
K	7.3170
Si	59.4409
Ti	22.7390
Cl	0.0985
Si/Ti	2.6140
(Na+K)/Ti	0.7753

4. Conclusion

From the experiments conducted so far, it is clear that the ETS-10 synthesis system is sensitive to many of the parameters such as titanium source, alkali, pH, content water, temperature, time of synthesis. For example, when using titanium tetrachloride, as it is hydrophilic and changes the whole stoichiometry, the amount must be accurately estimated, because otherwise it has a negative effect on the final product.

We achieved the preparation of the ETS-10 phase at 200 °C for 22 hours, with minimal impurities of quartz without the use of SDA. The ETS-10 phase can be obtained with minimal impurities only when using a combination of reagents nanosized source of TiO₂ - anatase, nanosized source of SiO₂, H₂SO₄, KF and NaOH.

To obtain a pure phase, the sources of titanium and alkali must be carefully selected and the temperature raised to 230 °C.

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