STUDY OF THE TPA-SILICALITE CRYSTALLIZATION-PREPARATION AND STRUCTURAL FEATURES

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INTRODUCTION

The design of zeolites with well determined morphology requires the understanding of their nucleation and growth mechanisms. Because of the wide applications of zeolites as catalysts, molecular sieves, additives etc, there is a growing need to purpose-tailor and control the desired performance of zeolites. For this purpose it is a necessary to know every step of crystallization starting from the nucleation in gel [1-3].

Silicalite is a pure silica zeolite that belongs to the MFI type family. Because of its specific network (consisting of channels and caves with an aperture of about 0.6 nm) has various applications in petrochemical and oil industry that makes it a very important material.

EXPERIMENTAL

The synthesis of silicalite was carried out using fumed silica as the silicate source and TPABr as structure directing agent. The synthesis mixture was $2.5Na_2O\times$ 8TPABr $\times$ 60 $SiO_2\times$ 800 H_2O. The mixture was put in steenless steel autoglaves and heated for 4h at 443 K at static conditions. The freshly prepared gel and the solid samples drawn off during the reaction were characterized by infrared spectroscopy (IR), x-ray diffraction, electron diffraction, high resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM), scanning electron microscopy, optical microscopy and positron annihilation lifetime spectroscopy (PALS).

RESULTS AND DISCUSSION

In the synthesis of silicalite, as structure directing agent, TPABr (tetra propyl ammonium bromide) is used. The alkyl chains of TPA^+ cation and the hydrophobic silicate species join together through Van der Waals forces resulting in an inorganic-organic composite [4]. At the very beginning AFM shows agglomerate particles of 2 and 10 nm size. (Fig.1A) The gel sample is characterized by X-ray diffraction as amorphous (Fig.1B)

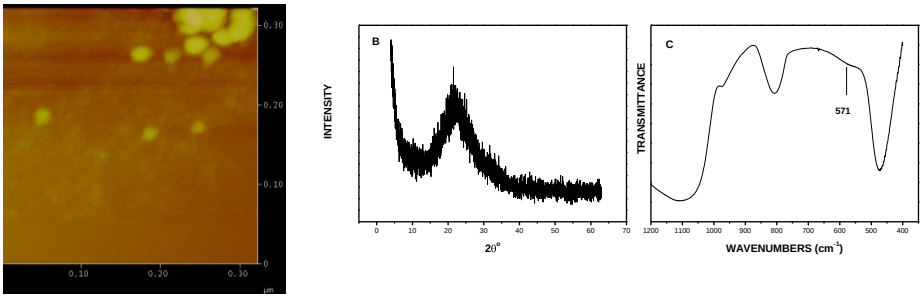

Figure 1. AFM image of the primary particles in gel (A) X-ray pattern (B) and Infrared spectra of the gel (C).

but infrared spectra shows a weak band at 571 cm-1 which is assigned to external vibrations related to the double D5 rings (5-5SBU) in silicalite, proving the existence of some short range ordered structure (Fig.1C). It is proposed [5] that these organic-inorganic composites are responsible for the nuclei formation. The amorphous agglomerate particles with short ordered structure act as nuclei for the further crystallization.

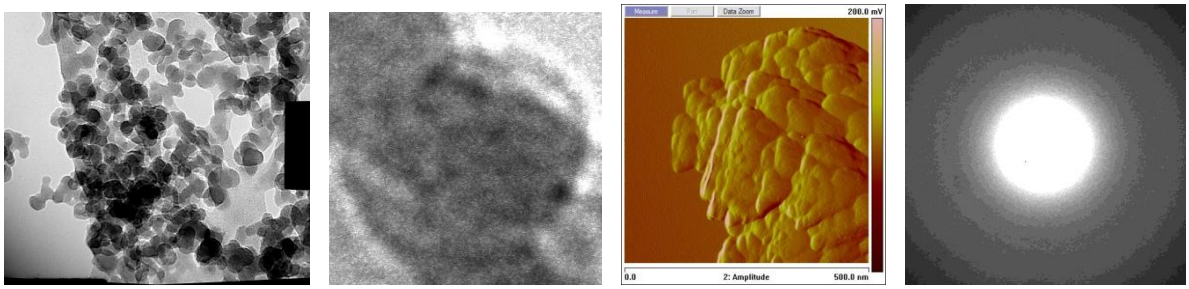

Figure 2. HR-TEM image (A), magnification x 200000 Details from Image A (B), AFM image (C) and electron diffraction (D) of the sample heated at 443K for 2h.

HR-TEM image taken after 2h of hydrothermal treatment at 443 K confirmed the size of particles to be 10 nm as it is calculated by X-ray diffraction measurements and also shows some particles having lattice fringes (fig.2A, B). The distance of the lattice fringes corresponds to two nanometers which is the size of the elementary cell in a and b direction.

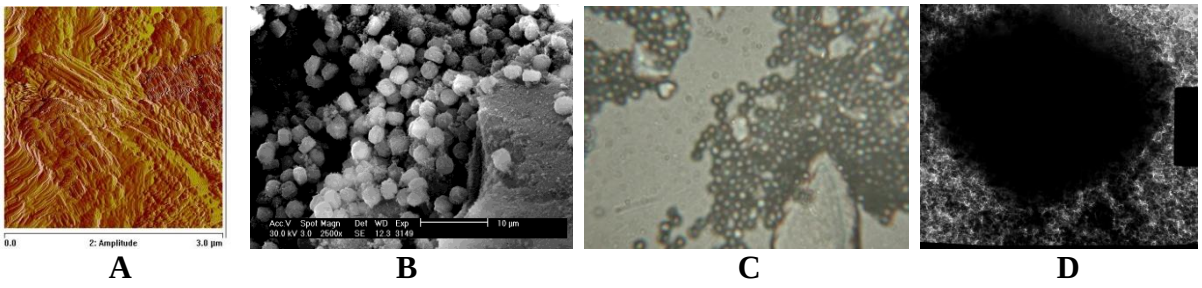

Figure 3. AFM image (A), SEM micrograph (B), optical micrograph (C) and HR-TEM image (D) of the sample heated at 443K after 3h.

After 3h of hydrothermal treatment the AFM images (fig.3A) clearly show the characteristic terraces of the silicalite structure, SEM (fig.3B) and optical micrograph (fig.3C) show simillar morphology of the sample which is estimated to be crystalline in over 50% wt. The cystallites size calculated from the X-ray diffraction measurements is about 60-70 nm in contrast to the value of 2-3μm obtained by SEM and optical microscopy measurements.
The big particles shown in SEM are not transparent for TEM but the edges show that they contain subgrains which confirms the conclusion that silicalite is a polycrystalline material. Electron diffraction after 3h indicates the setting in of long range arrangement in the sample (fig 4A).

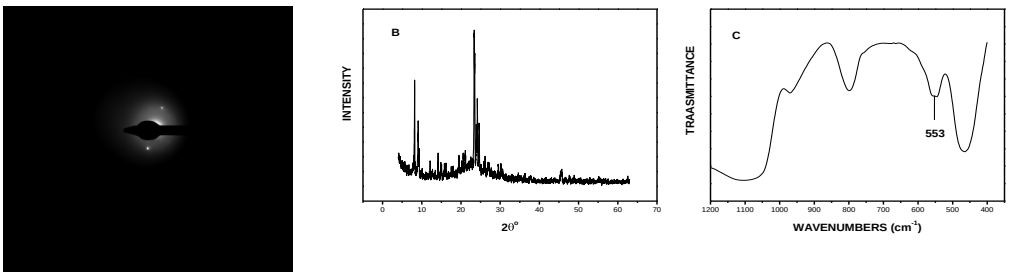

Figure 4. Electron diffraction image (A), x-ray pattern (B) and infrared spectra (C) of the sample heated at 443K for 3h.

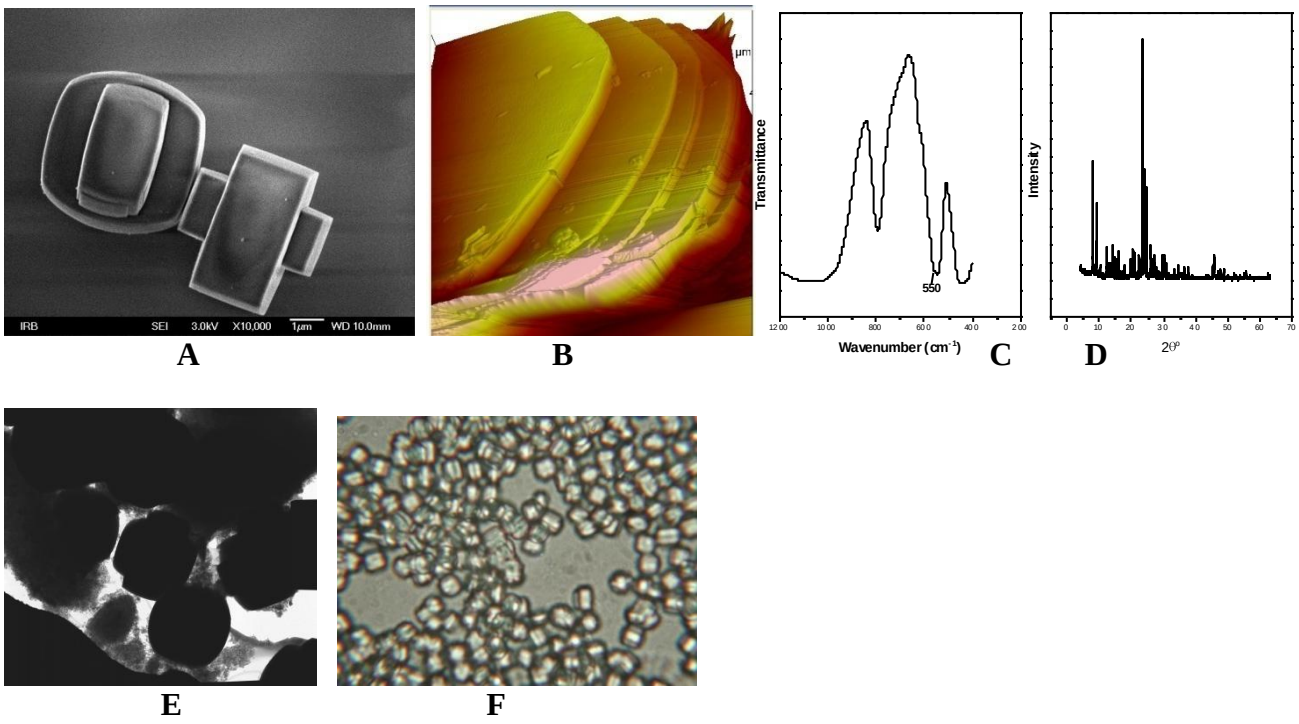

Figure 5. SEM (A), AFM micrograph (B), infrared spectra (C), x-ray pattern (D), HR-TEM (E) and optical micrograph (F) of the sample heated at 443K for 4h.

The end product after 4h of hydrothermal treatment is 100% crystalline silicalite (01-070-4743) with 5 μm size particles which are consisted of subgrains having size 80 nm according to X-ray patterns. The surface of the crystal has the characteristic terraces as it is presented by AFM micrograph (fig 5B).

The PALS measurements, performed on samples at various stages of the crystallization revealed a large change in the long-living positronium components in the lifetime (LT) spectra, indicating a large change in the availability of free volume. Furthermore, the trends of partial intensities of the long components in the LT spectra imply a sensitivity to the presence of template rest, as will be discussed in details separately [6].

CONCLUSIONS

TPA^+ cations linked together with silicate species by Vand der Waals forces and form short range ordered units with size of 2 nm that correspods to the size of a unit cell.
The units agglomerate and form particles with size about 10 nm that was confirmed by AFM and TEM. These entities acts as the nucleation centers.

During the hydrothermal treatment the size of the consisted cystallites in the grains, as obtained by X-ray diffraction and confirmed by AFM and TEM, is increasing and is about 80 nm in the end product which haves size about 5 μm.
This is also a confirmation that silicalite is a polycrystalline material.

The PALS results indicate that positron annihilation spectroscopy may expose free volume pattern enfolding which is not seen by other techniques. It is suggested that the progression of the LT spectra upon changes in the samples should be considered in a complex way, observing the whole LT pattern simultaneously.

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STUDIJ KRISTALIZACIJE TPA-SILICALITE –PRIPRAVA I STRUKTURNI OBLIK

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SAŽETAK

Modeliranje zeolita sa dobro definiranom morfologijom zahtjeva razumjevanje mehanizama nukleacije i kristalnog rasta. Zbog široke primjene zeolita kao katalizatora, molekularna sita, aditiva itd postoji rastuća potreba za ciljanim kreiranjem i kontrolom željenih svojstava zeolita. Iako postoje dobro primjenjene tehnike kao što su nuklearna magnetska rezonanca (NMR), infracrvena spektroskopija (IR), Ramanova spektroskopija, rasipanje svijetla pri niskom kutu, rasipanje svijetla, Rentgenska diffrakcija, visoko rezolutna transmisijska elektronska mikroskopija (HR-TEM), pretražna elektronska mikrografija (SEM) itd., za studiranje konstrukcije zeolita, vanjska struktura površine je nedovoljno istražena osim nekoliko studija učinjenih pomoću HR-TEM. U ovom je radu mikroskopija atomskih sila (AFM) u kombinaciji sa drugim navedenim metodama korištena da bi se istražili početni stadiji nukleacije i tijek kristalizacije na površini gela. Positronska anihilacijska lifetime spektroskopija korištena kao dodatna metoda za pružanje informacije o promjeni slobodnih volumena u strukturi tijekom kristalizacije.

Za tu su svrhu ispitane krute faze odvojene iz svježe pripremljenog natrij silikatnog hidrogela i tijekom njegove hidrothermalne obrade pri 443 K.
AFM analiza u kombinaciji sa rezultatima dobivenih HR-TEM mikroskopijom and FT IR spekroskopijom pokazuje da gel sadrži primarne čestice s uređenjem «kratkog dometa» veličine 2 nm koje agglomeriraju u djelomično kristalizirane entitete veličine10 nm koji se dalje ponašaju kao nukleusi u daljnjoj kristalizaciji zeolita.

Tijek kristallizacije praćen je Rentgenskom diffrakcijom koja ukazuje na stvaranje polikristalliničnog materijala sa veličinom kristala od 5μm i veličinom sadržanih kristalita od 80 nm.

Ključne riječi: silikalit-1, nukleacija, infracrvena spektroskopija, mikroskopija atomskih sila, transmisijska elektronska mikroskopija, Rentgenska diffrakcija