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Layered titanosilicates for size- and pattern- controlled overgrowth of MFI zeolite

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Abstract

Size- and pattern- selective overgrowth of MFI-type zeolite (silicalite-1) on the layered titanosilcates JDF-L1 (Jilin Davy Faraday - Layered solid 1, also known as Aveiro Manchester - 1, AM-1) and AM-4 (Aveiro Manchester – 4) is realized. The shell of MFI is grown as closely packed monolayer of submicron cask-like particles following the surface contour of the core of plate-like particles of JDF-L1. The overgrowth of MFI on AM-4 carries the characteristics of hetroepitaxial interconnection. Isolated crystals (5-10 μm) of MFI are closely embedded along various orientations to the plate-like particles of AM-4. The thermal behaviour of the interconnected materials was evaluated by in situ high-temperature powder X-ray diffraction. The realized hetrochemical and heterostructural interconections show that the surface of the layered titanosilicates can act as multi- and single- nucleation site. This finding might be applied to other members of the family of tetrahedral-octahedral molecular sieves and may be important for design of hierarchical catalysts and adsorbents with mixed properties.

1. Introduction

The current industrial zeolite catalysts and adsorbent materials are physical mixtures of micrometer-sized, phase- pure crystals shaped into larger bodies such as extrudates or granulates[1]. However, there is considerable interest in the development of alternative zeolite catalysts and adsorbent materials as continuous zeolite films on various supports or interconnected zeolite reactors for multiple molecular-sieving and catalytic functions with improved performance [2]. The majority of work is dedicated to porous aluminium silicates as zeolites and the interconnection between tetrahedral and transition-metal tetrahedral-octahedral porous materials is limited to MFI/ETS-4 (Engelhard titanosilicate – 4) and MFI/ETS-10 (Engelhard titanosilicate – 10)[3]. To date, there are just a few synthetic titanium silicates with a layered structure – bafertisite, natisite, paranatisite, JDF-L1 and AM-4. Among them JDF-L1 and AM-4 are the most studied members[4-24]. JDF-L1 ($Na_4Ti_2Si_8O_{22}$•$4H_2O$) is one of the few synthetic titanium silicates containing 5-coordinated titanium[12, 25]. The structure is composed of titanosilicate layers built up of interconnected 4-rings of SiO_4 tetrahedra and isolated TiO_5 pyramids that contain only one unshared vertex pointing to the interlayer space. In this space reside water molecules and Na^+ cations that compensate the negative charge of the layers. AM-4 ($Na_3(Na,H)Ti_2O_2[Si_2O_6]$•$2.2H_2O$) is a synthetic analogue of the mineral lintisite. The structure can be described by interconnected chains of SiO_4 tetraheda and TiO_6 octahedra that form titanosilicate layers[10]. Similar to JDF-L1 in the interlayer space reside Na^+ cations and water molecules.

The layered character and presence of titanium in different coordination attracted substantial interest in possible exfoliation and pillaring, preparation of composite materials, membranes, solids for biocide applications and potential catalysts. On the other hand, zeolites with MFI structure are composed of interconnected SiO_4 tetrahedra forming a framework with 10-ring channels. These materials are well-known catalyst commercialized for acid-catalyzed reactions such as hydrocarbon isomerization and the alkylation of hydrocarbons[26, 27].

In this paper, two types of layered titanosilicates (JDF-L1 and AM-4) are shown to control the pattern and size of the overgrown of MFI zeolite.

Experimental

Layered titanium silicates JDF-L1 and AM-4 were prepared according to previously reported procedures [13, 15]. Namely, in a typical synthesis of JDF-L1, 2.96 g SiO_2 (Aldrich) was added to a solution of 2.2 g NaOH (Aldrich) in 40 ml distilled water. Subsequently, 0.66 ml $TiCl_4$ (Aldrich) hydrolyzed in 20 ml distilled water was added to the above solution. AM-4 was prepared by dissolving 2.97 g SiO_2 in solution of 40 ml H_2O and 7.1 g NaOH. This mixture was added to a solution containing 20 ml H_2O and 1.1 ml $TiCl_4$.

In both cases the obtained gel was homogenized for 40 min by a magnetic stirrer and then transferred into 45 ml Teflon-lined autoclaves. The crystallization was performed under static conditions at 200 °C for 24 h (JDF-L1) and 5 days (AM-4). After fast cooling with flowing H_2O the samples were filtered and washed with distilled water and dried at 50 °C for 2–3 h.

The overgrowth of MFI (silicalite-1)/layered titanium silicate was realized as follows: 0.5 g of JDF-L1 or AM-4 was dropped in a solution prepared by mixing 8.5 g TPAOH, 5 g of TEOS and 5.18 g H_2O. After homogenization (10 min) by a magnetic stirrer the mixture was placed in a Teflon-lined autoclave and heated at 150 ^{o}C for 5 days. The run product was filtered, washed with distilled water and dried at 50 ^{o}C.

The powder XRD patterns were collected on a θ–θ diffractometer Bruker D8 Discover working with CuK$\alpha_{1,2}$ radiation in $\theta/2\theta$ scan regime, 2θ range 5–50^{o}, step 0.04^{o} and time per step 1 s. The phase identification, refinement of the lattice constants and estimation of the amount of the run product (MFI/titanoasilicate) were performed by the software package TOPAS-3 [Bruker AXS GmbH, Karlsruhe, Germany]. The *in situ* powder XRD experiments were performed by high-temperature chamber Anton Paar HTK 1200N.

The SEM images EDS probing were carried out with NanoSEM-FEI Nova 200 and (FEG/SEM) EDAX - Pegasus X4M (EDS/EBSD).

2. Results and discussion

Powder XRD patterns of the obtained MFI/JDF-L1 and MFI/AM-4 overgrowths were refined by the method of Le Bail[28]. No impurities were detected and the overgrowths preserved the crystal structure of the titanosilicate core (Figures 1 and 2). Among the obtained unit cell parameters (JDF-L1: space group: $P42_12$; $a = b = 7.36(8)$, $c = 10.66(8)$ Å; AM-4: space group: A2/a; $a = 28.58(3)$, $b = 8.60(1)$, $c = 5.21(1)$ Å, $\beta = 88.8(1)^o$; MFI: space group: *P*nma; $a = 20.03(6)$, $b = 19.86(2)$, $c = 13.36(8)$ Å) only AM-4 show slight distortion when compared with the with values reported in the literature (JDF-L1: $a = b = 7.3740(10)$, $c = 10.709(2)$ Å; AM-4: $a = 5.2012(8)$, $b = 8.573(2)$, $c = 29.300(6)$ Å, $\beta = 89.26(1)°$; MFI: $a = 20.02(2)$, b = 19.89(9), c = 13.38(3) Å) [10, 12, 25, 29] and the pure phases synthesized in this work (Figure S1). Using the method of Rietveld it was estimated the following rough ratios of the run product: MFI/JDF-L1 = 4; MFI/AM-4 = 1. These values are in agreement with the collected SEM images and indicate that higher-silica (Si/Ti = 4) titanosilicate (JDF-L1) contributes for crystallization of larger amount of MFI when compared with lower-silica (Si/Ti = 1) AM-4.

MFI/titanosilicate overgrowths were subjected to calcination observed by in-situ powder XRD diffraction. Figure 3a shows that the overgrowth of MFI on JDF-L1 decreases the thermal stability of the later. At 150 ^{o}C the reflections (00l) disappear which is at drastically lower temperature when compared with the thermal stability of single phase of JDF-L1[16]. This indicates that the overgrowth of MFI induce instability in JDF-L1. When the overgrowth of MFI is realized on low-silica titianosilicate as AM-4 the result is opposite. Figure 3b shows that up to 350 °C the long range order of the titanosilicate layers is preserved and the decrease of the interlayer space is only 2 Å.

Concerning the effect of the temperature on MFI it was estimated that the lattice recovered after heating up to 350 °C show different volumes. The structure of MFI is preserved but the decrease of its unit cell volume is smaller for MFI/JDF-L1 (0.85 %) when compared with the one of MFI/AM-4 (1.5 %) (Figures S4 and S5). The primary reason for this shrinkage is the removed organic template but the difference in dimension of change must be related to the influence of the titanosilicates on MFI structure.

Structurally, MFI, JDF-L1 and AM-4 share similar structural units of SiO_4 tetrahedra. The framework of MFI is composed of only SiO_4 tetrahedra whose 3D interconnection can be described in various ways. In this respect, 4-rings of SiO_4 tetrahedra are common for MFI and JDF-L1 (Figure 4). This similarity is enhanced by the small bond length difference (~ 4%) between the oxygen atoms of two adjacent SiO_4 tetrahedra. However, the access to SiO_4 units is shielded by TiO_5 semi-octahedra whose vertexes represent the rigid surface of the layer (Figure 1). On contrary, the SiO_4 tetrahedra in AM-4 are not shielded and accessible in any direction (Figure 2) but the inter-tetrahedral length difference between two adjacent SiO_4 units of the titanosilicate and MFI is much larger (23%) (Figure 4). This suggests that for the realization of overgrowth it should has local polyhedral distortion or concentration of defects on the crystal surface.

Figure 5 shows SEM images of MFI grown over JDF-L1. The distinction between the titanosilicate and MFI was based on EDS probing and crystal shape characteristics. Aggregates of plate-like crystals of JDF-L1 (20-40 µm) are covered with monolayer of regularly packed submicron (500 – 800 nm) crystals of MFI with typical cask-like morphology. On average in every 25 µm^2 of the JDF-L1 plate-like crystals there are around 50 MFI crystals. It is interesting to notice that MFI crystals grown on JDF-L1 are smaller than the ones that are not attached to the titanosilicate matrix (Figure 5). This suggests that the surface of JDF-L1 favours the simultaneous nucleation and growth or crystals with regular shape and size. The monolayer of MFI crystals is not restricted to any crystal face of JDF-L1 indicating that the rate of heterogenous nucleation is higher than the lateral growth of the 2D nuclei at any part of the crystal. Considering that the plate-like surface of JDF-L1 crystals is composed of titanosilicate layer whose only unshared polyhedral vertex belongs to TiO_5 semi-octahedron one can suggest that this structural unit serve as centre for heteronucleation whose “projection” is a monolayer of MFI crystals. The heterostructural interconnections MFI/JDF-L1 could be achieved via unshared SiO_4 vertexes uncovered by leached TiO_5 polyhedra or via other defect sites.

Figure 6 shows SEM images of MFI grown over AM-4. Unlike JDF-L1, plate-like crystals of AM-4 act as single-nucleation site and only isolated crystals of MFI (5-10 µm) are attached. There is no specific preference for nucleation and MFI grows from sides perpendicular or parallel to the layers of AM-4 and the contact surface of MFI follows the morphology of AM-4. No cracks between the two surfaces are visible which suggests a possible heteroepitaxial inteconnection. Interesting fact from these observations is that the surface of high-silica (Si/Ti = 4-5) titanosilicates (JDF-L1, ETS-10[3]) favours the overgrowth of numerous small (submicron) crystals of MFI, and the low-silica (Si/Ti = 1-3) tianaosilicates (AM-4, ETS-4[3]) promotes overgrowth of bigger (5-10 μm) and separate crystals of MFI. This means that at the given conditions the amount of titanium in the core structure govern the nucleation and growth of the shell structure.

4. Conclusions

The work presents the first overgrowthof MFI/layered titanium silicates. Plate-like crystals of two titanium silicates (JDF-L1 and AM-4) demonstrate different influence on the size and arrangement pattern of the overgrown MFI zeolite. While the high-silica JDF-L1 favours nucleation and growth of monolayer of submicron crystals of MFI, the low-silica AM-4 favours the formation of micrometric, differently oriented isolated crystals of MFI. The presented overgrowths can serve for preparation of regularly interconnected materials with mixed properties.

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Figure 1. Experimental and calculated XRD patterns of the MFI/JDF-L1 overgrowth. Polyhedral representation of both structures is also shown (red - SiO_4 tetrahedra; green – TiO_5 semi-octahedra).

Figure 2. Experimental and calculated XRD patterns of the MFI/AM-4 overgrowth. Polyhedral representation of both structures is also shown (red - SiO_4 tetrahedra; green – TiO_6 octahedra).

Figure 3. In situ XRD patterns of the MFI/JDF-L1 (a) and MFI/AM-4 (b) overgrowths collected at different temperatures. The most characteristic changes in the diffraction reflections of the layered titanosilicates are indicated by lines.

Figure 4. Similar structural fragments of SiO_4 tetrahedra included in the structures of AM-4, JDF-L1 and MFI.

Figure 5. SEM images of monolayer of cask-like crystals of MFI grown over plate-like crystals of JDF-L1.

Figure 6. SEM images of separated crystals of MFI grown over plate-like crystals of AM-4.

Figure 1:

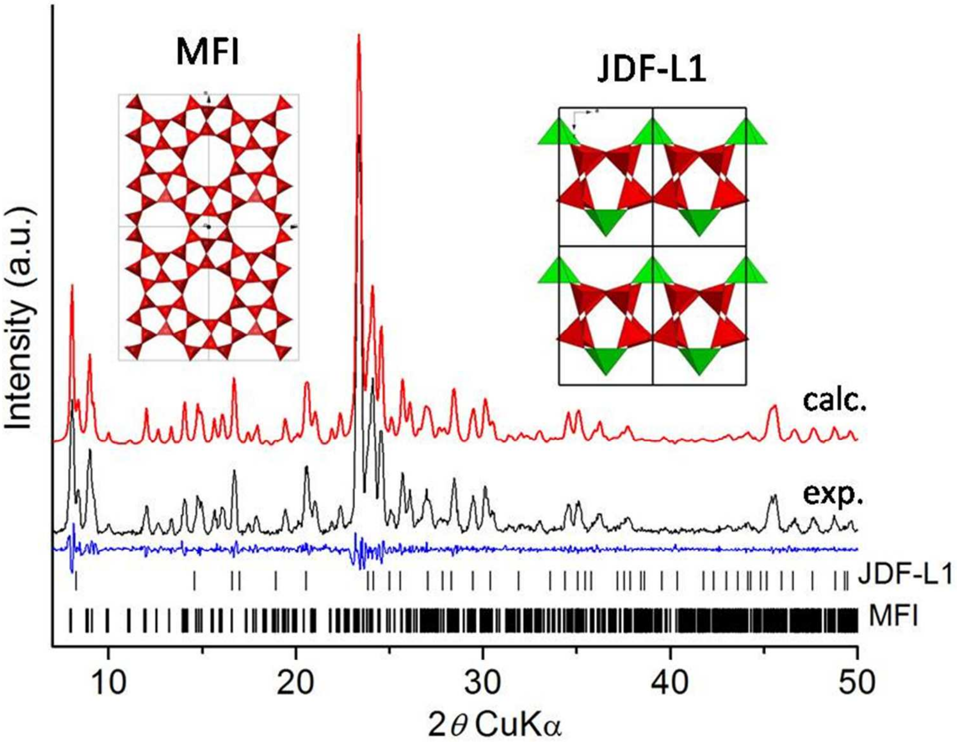


Figure 2:

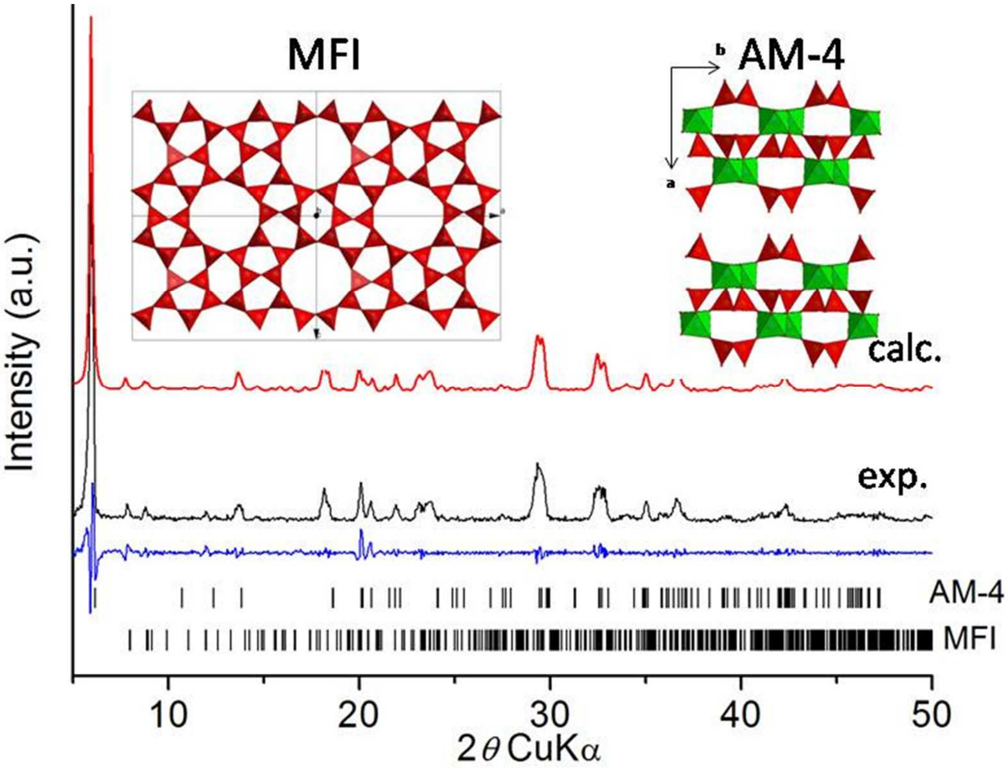
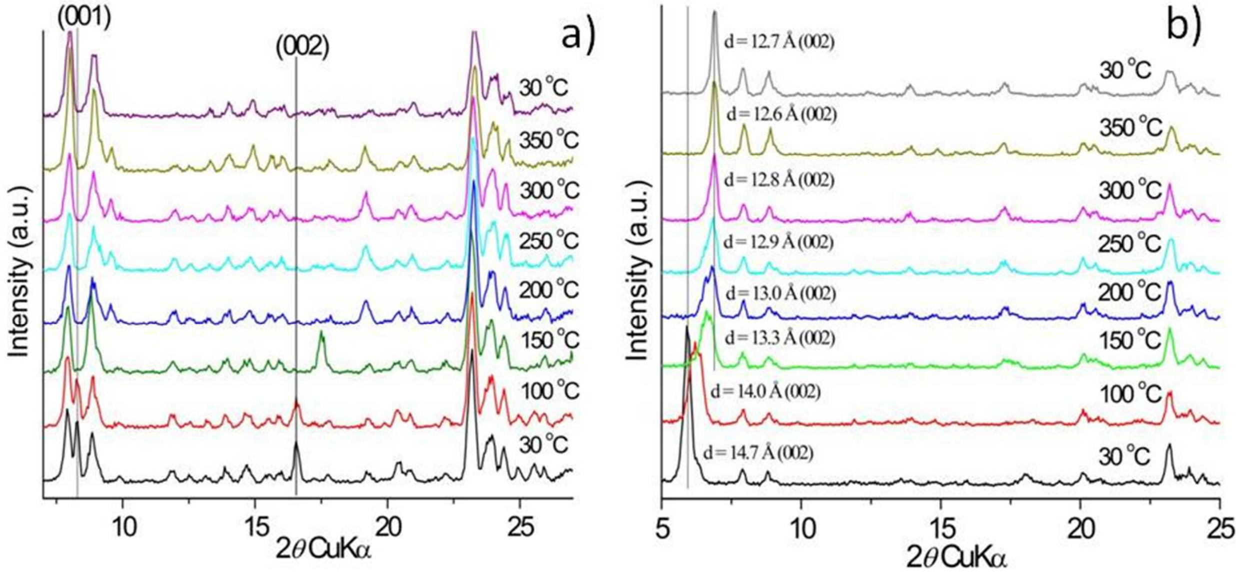


Figure 3:



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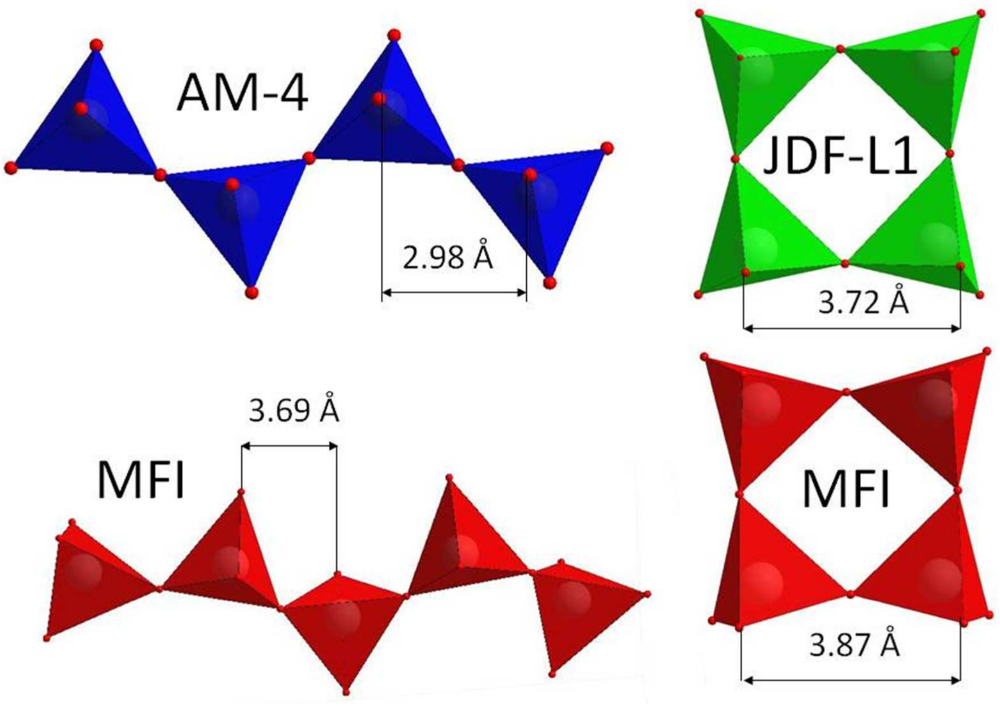

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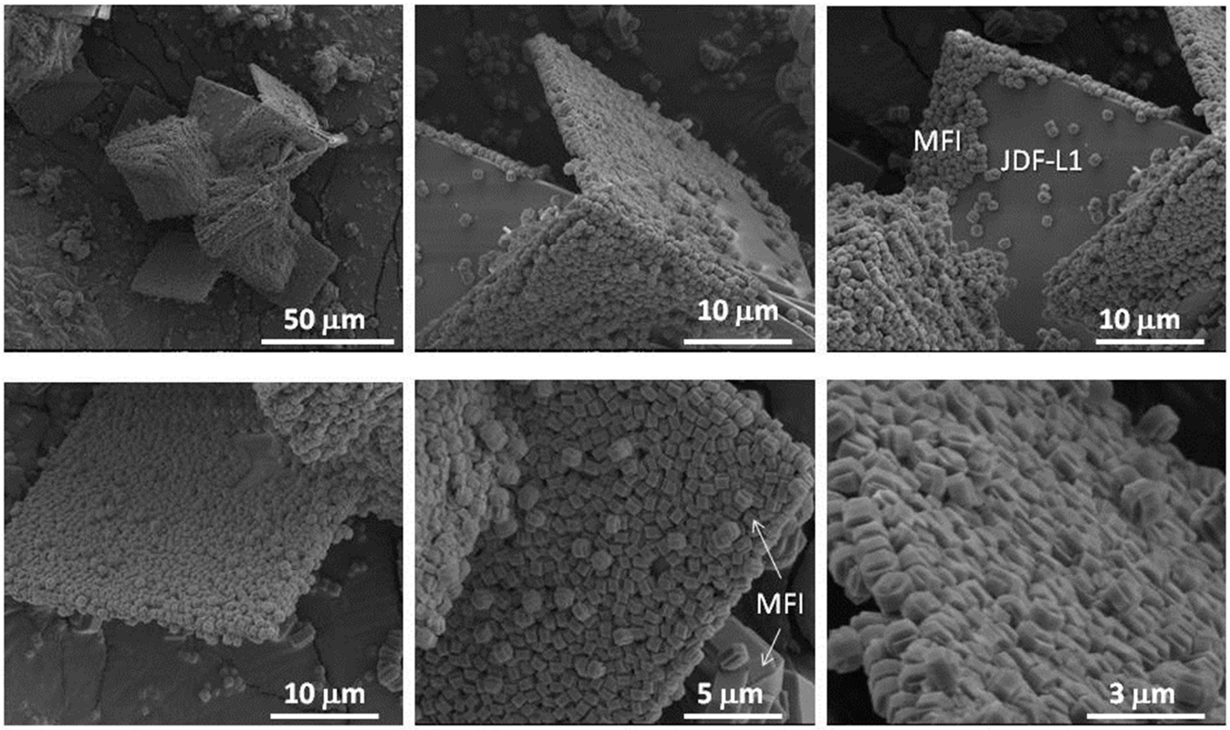

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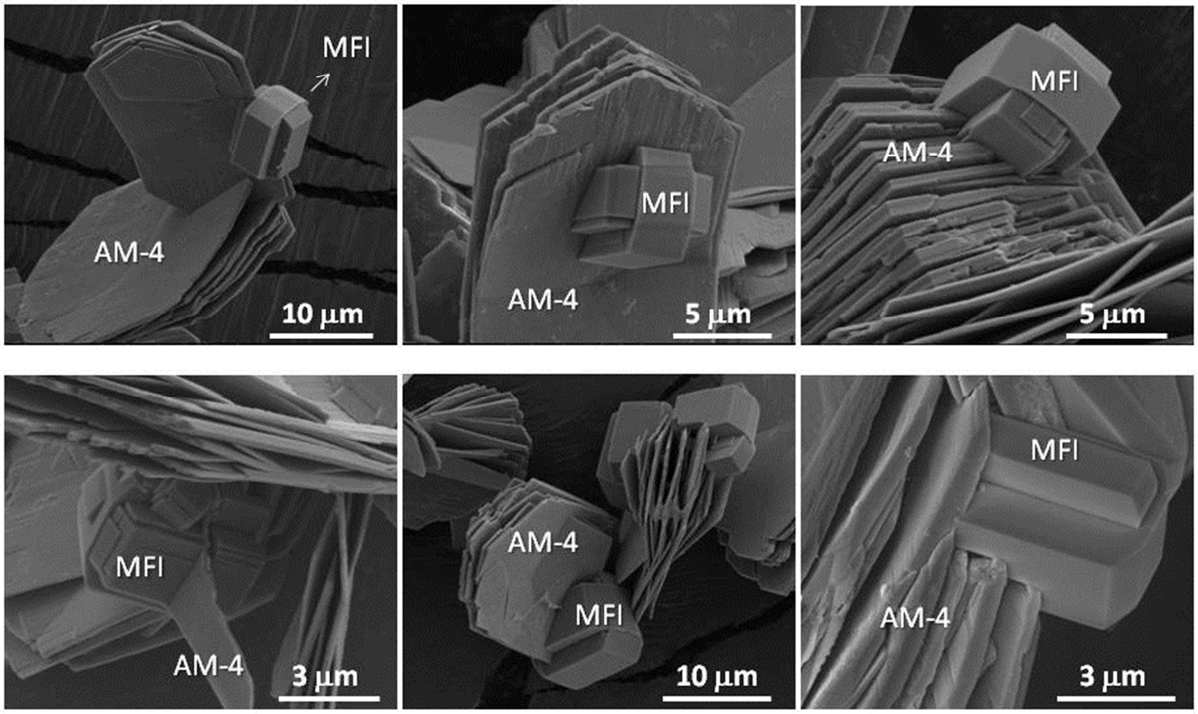

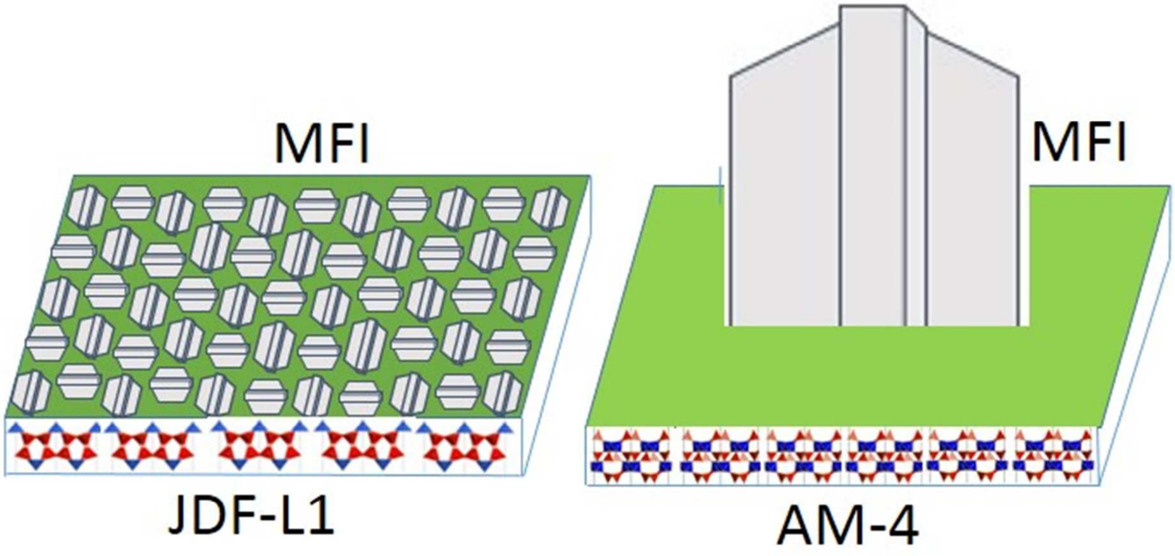

Layered titanosilicates (JDF-L1 and AM-4) revealed size and pattern dependent overgrowth of MFI-type of zeolite.