Synthesis of large single crystals of layered **titanosilicate** JDF-L1 with orthogonally lamellar architecture

Li Zhang^a, Jian Li^a, Yingjie Jin^{a,*}, Shudong Zhang^b, Suhua Sun^b, Shanlin Zhao^{a,§}

^a Faculty of Chemistry and Chemical-Environmental Engineering, Liaoning Shihua University, Fushun 113001, Liaoning Province, PR China

^b Fushun Research Institute of Petroleum and Petrochemicals, Sinopec, Fushun 113001, Liaoning Province, PR China

Abstract: Facile procedures were reported for synthesis of sizable lamellar JDF-L1 crystals. Phase transformation between ETS-10 and JDF-L1 was experimentally demonstrated founding on the role of K⁺, Na⁺ and F⁻ ions in crystal growth. Factually, K⁺ ions were confirmed not to participate in the crystal growth of JDF-L1. High concentrations of only Na⁺ and F⁻ ions in initial gels facilitated the formation of lamellar JDF-L1 differing from normal JDF-L1 in crystal morphology and unit-cell dimensions.

Keywords: Sol-gel preparation; Crystal growth; Intergrowth; Large single crystal; Lamellar texture

1. Introduction

Titanosilicate JDF-L1 (Na₄Ti₂Si₈O₂₂·4H₂O [1]) is a unique non-centrosymmetric, tetragonal layered solid with well-defined micropore structure [2]. Particular attention has recently been drawn to JDF-L1 due to the five-coordinated Ti(IV) ions in the form of TiO·O₄(SiO₃)₄ square pyramids to form continuous sheets running along [001] direction [3]. Such structural characteristics of JDF-L1 with less Ti(IV) ligand saturation and oriented crystal habit promise specific applications in asymmetric synthesis, hybrid membranes, hydrogen storage, etc. [4, 5].

* Corresponding author. Tel.: +86 24 56860797; fax: +86 24 56860958. E-mail address: jinyingjie512@163.com (Y Jin).

§ Corresponding author. E-mail address: lnsjpaper@163.com (S Zhao).

New studies on the growth of large single crystals of zeolites are one of the important aspects of crystal engineering to provide functional materials tailored toward particular applications [6]. Of these, an important aspect is to probe the crystal orientation and morphology affected by compositions and synthesis conditions [7]. Smaller crystals like nanosized zeolites improve access to the exchangeable alkali ionic sites. However, larger single crystals with regular morphologies provide insight in the fine structural resolution since well-formed large crystals tend to convey much information on the crystal structure and growth mechanism that may be unobtainable from fine, polycrystalline powders [8]. In the quest for the synthesis of large crystals of zeolites and zeotypes, one of the classical synthetic pathways involves the use of available fluorides as a mediated mineralizing agent [9], which allows access to the growth of defect-free large zeolite crystals compared to conventional approaches [10]. In addition to the effect of fluorine anions, the presence of Na^+ and K^+ cations in initial gels is shown to induce phase transformation of titanosilicates [11], for example, the selective growth of various layered titanosilicates (JDF-L1, ETS-10, AM-4, etc. [12]) as individual dominant phases, although some mechanistic pathways concerning the role of alternative alkali cations remain open.

Herein, we report the synthesis of large single crystals of novel layered JDF-L1 with orthogonally lamellar morphology and the effects of alkali cations and concomitant F^- ions on the crystal growth regulation and on the evolution of crystal morphology.

2. Experimental

2.1. Synthesis of layered titanosilicates

Layered titanosilicates, designated ETS-10, normal JDF-L1, ETS-10/JDF-L1 intergrowth and lamellar JDF-L1, were synthesized in Na_2O – SiO_2 – TiO_2 –(KF)– H_2O systems (Table A1). For synthesis of

typically lamellar JDF-L1, 2.3 g NaOH (96 wt%) and 3.4 g $\text{KF} \cdot 2\text{H}_2\text{O}$ (99 wt%) were dissolved in 20.0 g deionized water at a room temperature. The alkali solution of containing KF was added into 11.8 g sodium silicate solution (28 wt% SiO_2 , 8.2 wt% Na_2O) to form an alkaline Si precursor solution. The Ti precursor solution was prepared by dissolving 2.5 g $\text{Ti}(\text{SO}_4)_2$ (96 wt %) in the diluted H_2SO_4 solution (20.0 g). The acidic Ti solution was poured into the alkaline Si precursor solution under stirring for 2 h. The synthetic gel was crystallized hydrothermally at 200 °C for 72 h and the resulting solids after crystallization were filtrated, washed with deionized water, and dried overnight at 110 °C.

2.2. Structural characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/max-2400 diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) in scanning range of 5–60° (2 θ). Pattern decompositions were calculated using an indexing program of MID jade 6.5. N_2 adsorption at 77 K was performed on a Micromeritics ASAP 2420 apparatus. Prior to measurement, the sample was ultrasonically treated in a 0.02 M sodium acetate solution of ethanol for 1.5 h and degassed for 16 h at 623 K under around 10^{-4} Pa. Scanning electron microscopy (SEM) images were obtained on a JSM-7500F over Pt-coated specimens by operating at 20 kV, while this equipment allowed energy dispersive X-ray (EDX) analyses.

3. Results and discussion

3.1. Crystal phases and structure properties

As illustrated in Fig. 1, XRD patterns of ETS-10 and normal JDF-L1 showed the characteristic reflections associated with the targeted structures, respectively [2, 6]. In light of the reflections differentiated by asterisks, the intergrowth was composed of ETS-10 and JDF-L1 phases. The lamellar JDF-L1 exhibited an intensive diffraction pattern identical to normal JDF-L1 structure. Furthermore, the

intensity ratio of [001] to [002] reflections was remarkably heightened in contrast to those observed on normal JDF-L1 and an analogue reported elsewhere [8]. Structural properties of the space group and unit cell dimensions were decomposed and collected in Table 1. The unit cell parameters associated with tetragonal lattices were found to change slightly for lamellar JDF-L1 with respect to the known crystallographic data of normal JDF-L1 [1], although these crystallographic data have been solved early in light of JDF-L1 aggregates. The results observed in both aspects are likely to signify quite distinct properties in structure and texture, as evidenced by their featured SEM micrographs below.

3.2. Morphological and N_2 -adsorbed features

SEM images in Fig. 2 reveal the phase evolution of a series of titanosilicates. Fig. 2 (a, b) displays the difference in crystal habit between ETS-10 and normal JDF-L1 crystals. The intergrowth (Fig. 2c) identified by XRD was shown to comprise lamellar JDF-L1 and square truncated bipyramidal ETS-10 crystals, accompanied by little quartz formed [10], despite no reflections visible. To focus immediately on the images in Fig. 2 (d, e), lamellar JDF-L1 exhibited the key feature of large single crystals giving rise to square sheets of ca. $15\ \mu\text{m} \times 15\ \mu\text{m}$ along with a mean thickness of ca. $1.5\ \mu\text{m}$. This illustrates that the JDF-L1 might grow preferentially in two-dimensional orientations of [100] and [010] [1]. Meanwhile, the crystallographic symmetries were higher for lamellar JDF-L1 than for normal JDF-L1, evidencing the space group attributable and unit-cell dimensions available in Table 1.

On the desorption behavior of lamellar JDF-L1, the type II isotherms with type H3 hysteresis (Fig. 3) did exhibit a greatly weak N_2 -adsorbed capacity of small framework micropores (ca. 0.3 nm) [2]. In any event, the low BET specific surface area ($14.5\ \text{m}^2/\text{g}$) was almost equivalent to the external surface area ($14.2\ \text{m}^2/\text{g}$) by t -plot method. The BJH pore size distribution (insert in Fig. 3) presented the dispersive

profile of departing from an **expected** normal distribution, probably due to a random stacking of lamellar JDF-L1 crystals. This should be a case in point of the single crystal character of lamellar JDF-L1 with ultra-micropores.

3.3. *Observation on phase transformation*

Crystal phases of the titanosilicates were correlated with their chemical compositions in [Table 1](#). Phase transformation between ETS-10 and JDF-L1 via the intergrowth thereof was shown related factually with the initial K^+/Na^+ and KF/TiO_2 ratios. The occurrence of alkali cations including Na^+ and K^+ ions was required for nucleation and crystal growth of ETS-10 [\[10\]](#), as supported by ETS-10 crystal compositions and also by the empirical formula $(Na, K)_2TiSi_5O_{13} \cdot 4H_2O$ [\[12\]](#). The single phase of either normal or lamellar JDF-L1 was formed in the facile hydrothermal systems of K^+ -free or extremely low K^+/Na^+ ratios. Intergrowth ETS-10/JDF-L1 was obtained from the F^- -containing system of decreased K^+/Na^+ ratios. However, no K atoms were measured to occur in intergrowing JDF-L1 crystals. The correlation between crystal compositions and phases demonstrated the preferential growth of lamellar JDF-L1 crystals due to due to keeping concentrated Na^+ and F^- ions in initial gels. Besides the selective effect of JDF-L1 formation requiring Na^+ ions, high concentrations of concomitant F^- ions in initial gels evoked the large single crystal feature of JDF-L1 with orthogonally lamellar architectures. In addition, JDF-L1 was shown to have a diversity of crystal morphologies, depending on the role of F^- ions.

4. Conclusions

Large single crystals of lamellar JDF-L1 were obtained from F^- -containing hydrothermal systems, giving rise to square sheets of ca. 15, 15 and 1.5 μm in three orthogonal orientations. Unit cell dimensions of typical lamellar JDF-L1 crystals were provided for reference. ETS-10 crystals were shown to grow

preferentially in the presence of K^+ , Na^+ and concomitant F^- ions. K^+ ions were shown not to participate in the crystal growth of lamellar JDF-L1. High concentrations of F^- and Na^+ ions in initial gels facilitated the selective formation of the sizable JDF-L1 crystals.

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Figure 1

Fig. 1. XRD patterns of ETS-10, normal JDF-L1, lamellar JDF-L1 and ETS-10/JDF-L1 intergrowth (asterisks denote the ETS-10 phase in the intergrowth).

Figure 2

Fig. 2. SEM micrographs of microporous layered titanosilicates with different crystal structures: (a) ETS-10, (b) normal JDF-L1, (c) JDF-L1/ETS-10 intergrowth, (d) lamellar JDF-L1, and (e) lamellar JDF-L1 single crystal.

Figure 3

Fig. 3. N₂ adsorption/desorption isotherms and BJH pore-size distribution (insert) of lamellar JDF-L1.

Table 1

Data on crystal phase(s), compositions and crystallographic parameters of various layered titanosilicates synthesized.

Sample	Atomic ratio of crystals by EDX (mol/mol)			Crystallographic parameters	
	Si/Ti	(Na + K)/Ti	K/Na	Space group	Tetragonal unit-cell dimension
ETS-10	4.55 ±0.08	2.09 ±0.08	0.31 ±0.08	P4 ₁ or P4 ₃	a =14.58 Å, c =27.08 Å [10]
ETS-10/JDF-L1	5.17 ±0.15	2.26 ±0.15	0.16 ±0.15 ^a	-	-
intergrowth			(0.32/0.00) ^b		
Normal JDF-L1	4.36 ±0.12	1.91 ±0.12	0.00 ±0.00	P4 ₂ 12	a =7.3673 Å, c =10.6998 Å [1]
Lamellar JDF-L1	4.71 ±0.10	2.10 ±0.10	0.06 ±0.10	P4 ₂ 12	a =7.3867 Å, c =10.6166 Å

^a An average K/Na ratio of the two phases upon all 10-times EDX analyses.

^b Atomic K/Na ratios of respective ETS-10 and JDF-L1 crystals in the intergrowth according to an equal seizing probability.

Graphical abstract