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Facile fabrication of titanosilicate zeolites with unprecedented wide range of Si/Ti ratios by employing transition metal dichalcogenides as metal precursors

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Table of Contents

CONTENTS **Page**
SI-1 Experimental Section **S2-S4**
SI-2 Supplementary Figures **S4-S15**
SI-3 Supplementary References **S16**

SI-1 Experimental Section

Materials: Silicon dioxide (SiO_2, 99.5 %) and Titanium (Ⅳ) sulfide (TiS_2, 99.9 %) were purchased from Aladdin (Shanghai). Sodium oxide (Na_2O, 80.0 %) was provided by Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 30.0 %) was supplied by Kemiou Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH, 96.0 %) and Hydrochloric acid (HCl, 36.0 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of JDF-L1 zeolites from TiS_2 precursor: The synthesis of JDF-L1 zeolites followed the typical route as reported previously with slight modifications.[1] To form an initial gel, SiO_2 (0.33 g) and Na_2O (0.10 g) were mixed under stirring in aqueous sodium hydroxide solution (7.70 wt%, 2.98 g) at room temperature; simultaneously, TiS_2 (0.11 g) was dissolved in hydrochloric acid aqueous solution (8.00 wt%, 2.06 g) under same condition. Then two solutions were mixed together at room temperature. The final gel with a molar composition of 4.5 Na_2O: x SiO_2: TiO_2: 258 H_2O (x =10.0-1.5) was transferred into a 50 ml Teflon-lined autoclave and kept at 200 °C under static condition for 72 h. After cooling down, the resulting solid product was recovered by centrifugation, washed with deionized water and finally dried at 70 °C overnight.

Synthesis of ETS-4 zeolites: The synthesis of ETS-4 zeolites followed typical routes as reported previously with slight modifications.[2] To form an initial gel, TiS_2 (0.06 g) was dissolved in hydrochloric acid aqueous solution (6.00 wt%, 2.98 g) at room temperature; simultaneously, SiO_2 (0.61 g) was dissolved in aqueous sodium hydroxide solution (7.45 wt%, 9.67 g). The resulting Ti-containing solution was dissolved by adding aqueous hydrogen peroxide (0.57g, 30 %). Then two solutions were mixed together and further stirred for 1 h. The final gel with a molar composition of 5 H_2O_2: 0.5 TiO_2: 10 SiO_2: 18 NaOH: 675 H_2O was transferred into a 50 ml Teflon-lined autoclave and kept at 200 °C under static condition for 72 h. After cooling down, the resulting solid product was recovered by centrifugation, washed with deionized water and finally dried at 70 °C overnight.

Characterization: Powder X-ray diffraction (XRD) patterns were collected on a Rigaku SmartLab diffractometer with Cu K_a radiation (λ =0.15418 nm). SEM images were taken on a field mission scanning electron microscope (FlexSEM 1000, HITACHI). The elemental composition and energy distribution of obtained samples were analyzed by energy-dispersive X-ray spectroscopy (EDS). N_2 adsorption-desorption isotherms of JDF-L1 zeolites at 77 K were measured with a Quantachrom Autosorb-iQ instrument. Prior to the measurement, samples were outgassed at 160 °C overnight. Diffuse reflectance (DR) UV−vis spectra were conducted using a JASCO 550 spectrophotometer in the 200-600 nm wavelength range with $BaSO_4$ as the reference. FT-IR spectra were recorded using an EQUINOX55 Fourier transform infrared spectrometer (Bruker, Germany) by means of KBr pellet technique. Thermo gravimetric analysis was performed on a NETZSCH TG 209 unit in air with a heating rate of 10 °C/min from room temperature to 900 °C. Metallic elemental analysis was conducted by ICP over a Perkin Elmer OPTIMA 2000DV apparatus. The pH values of precursor solution during the whole conversion process was measured by PHS-3C tester (INESA, Shanghai).

Calculation methods of Gibbs energies for the side reaction

$$TiS_2 + 2\ H_2O \rightarrow TiO_2 + 2\ H_2S \uparrow \qquad (2)$$

Following the classical thermodynamics, the total molar Gibbs free energy ($\Delta_r G^\theta_m$) for a chemical reaction at a certain temperature (T, this reaction is 473.15K) is defined as the following equation (S1):

$$\begin{aligned}\Delta_r G^\theta_m (T) &= \Delta_r H^\theta_m (T) - T\ \Delta_r S^\theta_m (T)\\ &\approx \Delta_r H^\theta_m (298.15\ K) - T\ \Delta_r S^\theta_m (298.15\ K) \qquad (S1)\end{aligned}$$

Where H and S represent the enthalpy and entropy, respectively. From the Lange's handbook of chemistry (**Table S1**),[3] the total molar Gibbs free energy of side reaction could be calculated as follow:

$$\Delta_r G^\theta_m (T) \approx -187.77\ KJ/mol < 0.$$

Table S1. Enthalpies and Entropies of these compounds of the side reaction.*

Compound	TiS_2	H_2O	TiO_2	H_2S
$\Delta_r H^\theta{}_m$ （KJ / mol）	-334.72	-285.83	-938.72	-20.17
$\Delta_r S^\theta$ （J / k·mol）	78.37	69.91	49.92	205.77

* Lange's handbook of chemistry (298.15 K).[3]

SI-2 Supplementary Figures

1. FT-IR spectrum and TG-DTG curve of JDF-L1 zeolites

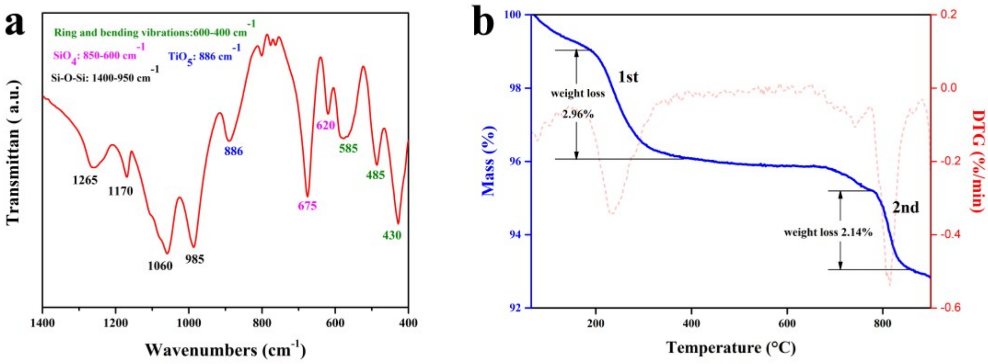

Fig. S1 (a) FT-IR spectrum and (b) TG-DTG curve of JDF-L1 titanosilicate zeolites.

FT-IR spectrum of prepared sample showed typical characteristic vibration peaks of JDF-L1 zeolites. To be specific, the band at 886 cm^{-1} was attributed to asymmetric stretching vibration of one short Ti-O bond pointing to the unshared vertex of the TiO_5 polyhedra which was characteristic of five-coordinate Ti atoms for JDF-L1 zeolites. Several bands at 1265, 1170, 1060, 985, 886, 675, 620, 585, 485 and 430 cm^{-1} appeared, which were related to asymmetric stretching vibrations of Si-O-Si linkages and/or SiO_3 group (1400-950 cm^{-1}), short Ti-O bond (900-800 cm^{-1}), symmetric stretching vibrations of SiO_4 group (850-600 cm^{-1}) and ring/bending vibrations (600-400 cm^{-1}), respectively.

2. Chemical stability of JDF-L1 zeolites

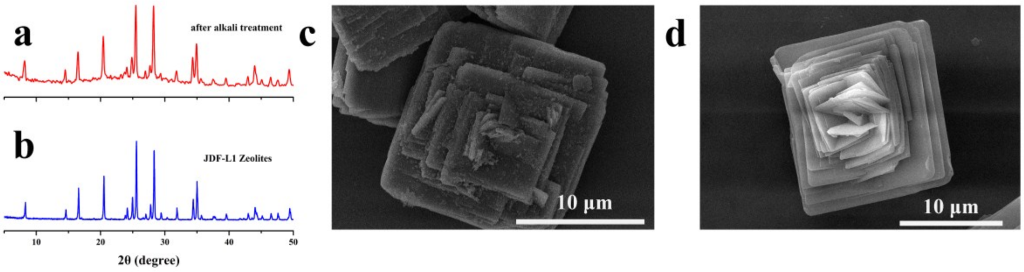

Fig. S2 XRD patterns (a-after, b-before) and SEM images (c-after, d-before) of JDF-L1 titanosilicate zeolites under 2 M NaOH solution treatment (60 °C, 48 h).

3. XRD pattern, SEM image and Diffusion reflectance spectrum of TiS_2 powders

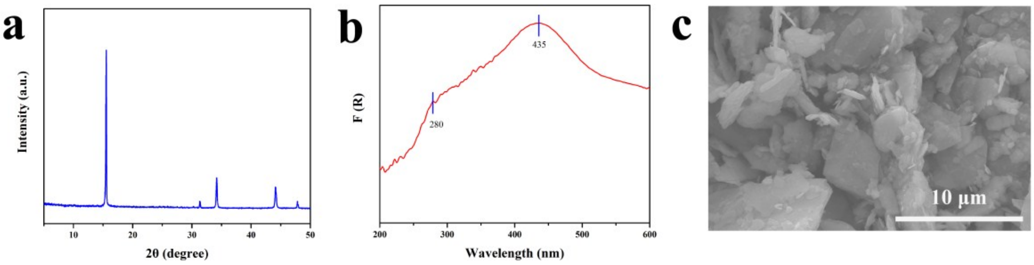

Fig. S3 (a) XRD pattern, (b) UV-vis spectra and (c) SEM image of TiS_2 powders.

4. SEM characterization of JDF-L1 zeolites obtained under different crystallization time

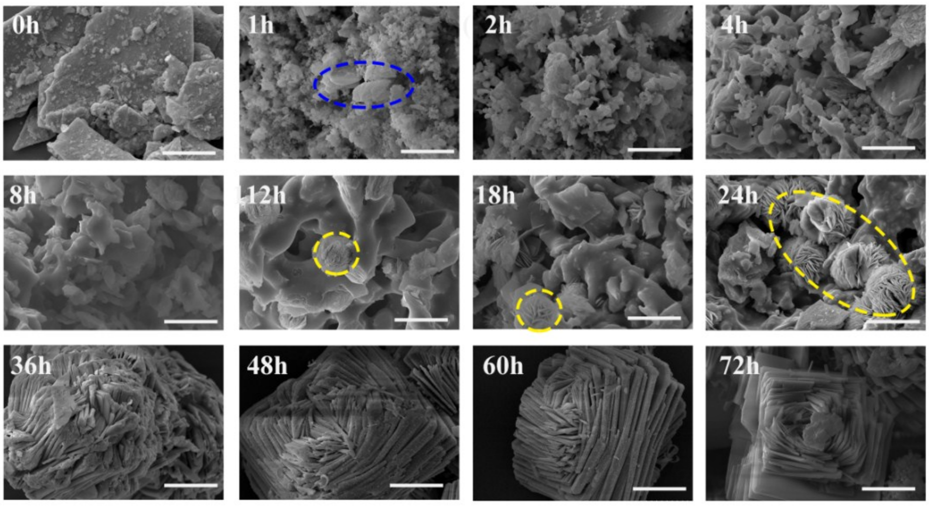

Fig. S4 SEM images (high magnification) of JDF-L1 zeolites prepared under different crystallization time (Scale bar: **10 μm**).

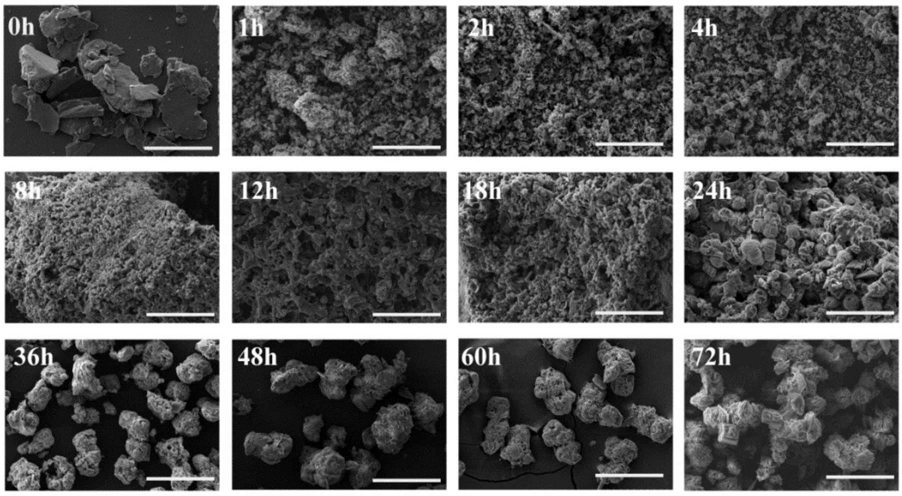

Fig. S5 SEM images (low magnification) of JDF-L1 zeolites prepared under different crystallization time (Scale bar: **100 μm**).

5. Elemental analysis of JDF-L1 zeolites obtained under different crystallization time

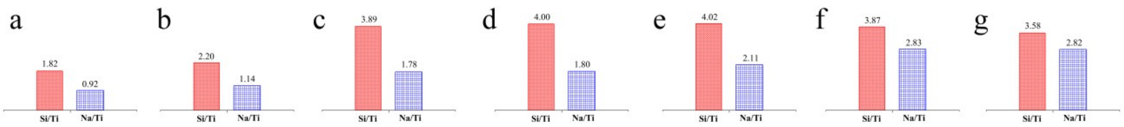

Fig. S6 ICP results of JDF-L1 zeolites prepared under different crystallization time: (a) 0 h, (b) 1 h, (c) 8 h, (d) 24 h, (e) 36 h, (f) 48 h and (g) 72 h.

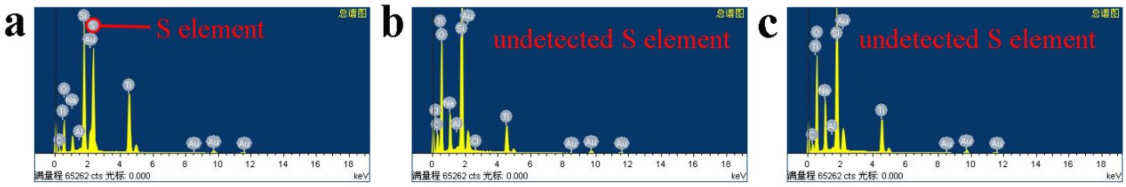

Fig. S7 EDS element distribution of JDF-L1 zeolites obtained under different crystallization time: (a) 0 h, (b) 1 h and (c) 72 h.

Table S2. pH values of JDF-L1 zeolites prepared under different crystallization time.

Time/h	0 h	1 h	8 h	18 h	24 h	36 h	72 h
pH value	11.76	10.77	10.85	11.04	11.15	10.59	10.48

6. Diffusion reflectance analysis of JDF-L1 zeolites obtained under different crystallization time

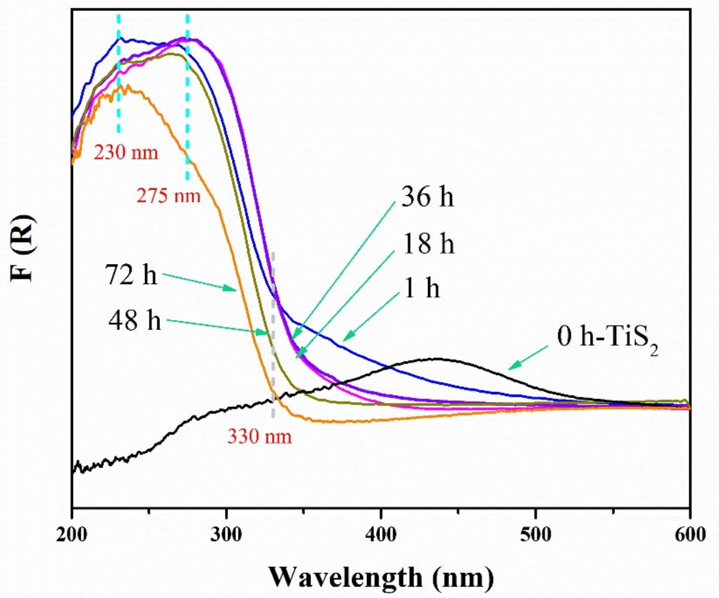

Fig. S8 UV-vis spectra of JDF-L1 zeolites obtained under different crystallization time.

Fig. S8 shows UV-vis spectra of JDF-L1 zeolites obtained under different crystallization time. At the beginning of the reaction, two bands appearing at 230 nm and 275 nm in the UV-vis absorption spectra could be assigned to the dehydrated Ti in the hydrophilic silica surface and incipient oligomerization Ti species. With the crystallization time increasing, the former disappeared gradually while the latter first increased then disappeared. In addition, the appearance of a new band located at 230 nm in UV-vis spectra could be assigned to five-coordinated Ti species of JDF-L1 zeolites, while the absence of the band located at 330 nm further ruled out the formation of other impure phase like TiO_2.

7. FT-IR spectra of JDF-L1 zeolites obtained under different crystallization time

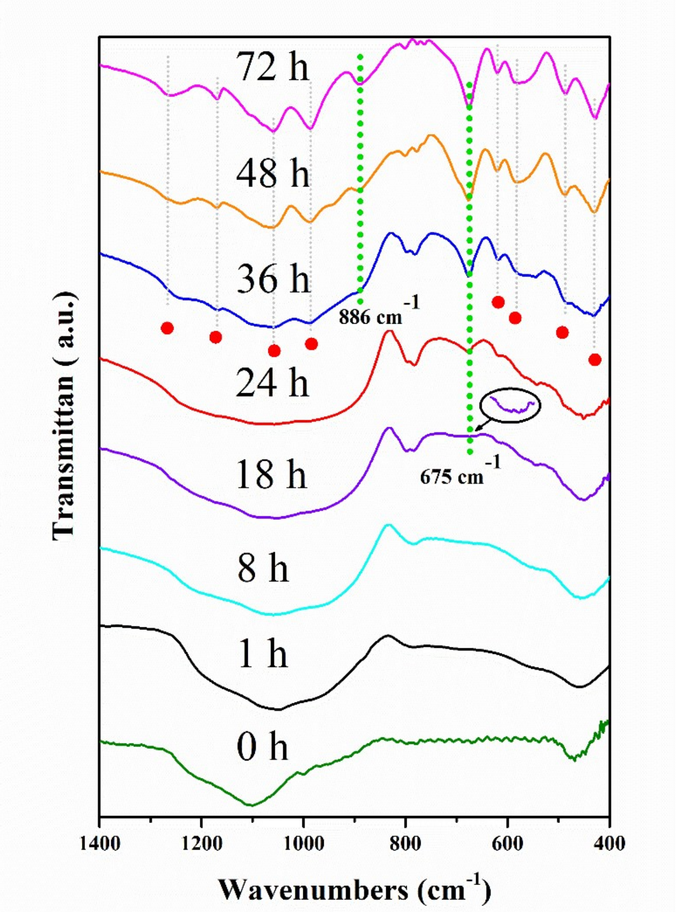

Fig. S9 FT-IR spectra of JDF-L1 zeolites obtained under different crystallization time.

Fig. S9 showed FT-IR spectra of layered TiS_2-derived JDF-L1 samples with different crystallization time. After hydrothermal reaction for 1 h, two broad absorption bands around 1060 cm^{-1} and 460 cm^{-1}, which corresponded to Si-O stretching vibrations and Si-O-Si bending vibrations, were observed. These results indicated that raw materials were transformed to an initial amorphous gel phase. After 36 h, several weak bands (●) at 1265, 1170, 1060, 985, 886, 675, 620, 585, 485 and 430 cm^{-1} appeared, which were associated with asymmetric stretching vibrations of Si-O-Si linkages and/or SiO_3 group (1400-950 cm^{-1}), short Ti-O bond (900-800 cm^{-1}), symmetric stretching vibrations of SiO_4 group (850-600 cm^{-1}) and ring and bending vibrations (600-400 cm^{-1}), respectively. Meanwhile, unique TiO_5 polyhedra (675 cm^{-1}) also verified the presence of five-coordinate Ti species of JDF-L1 zeolites.

8. More SEM images of JDF-L1 titanosilicate zeolites (36 h) with different phase

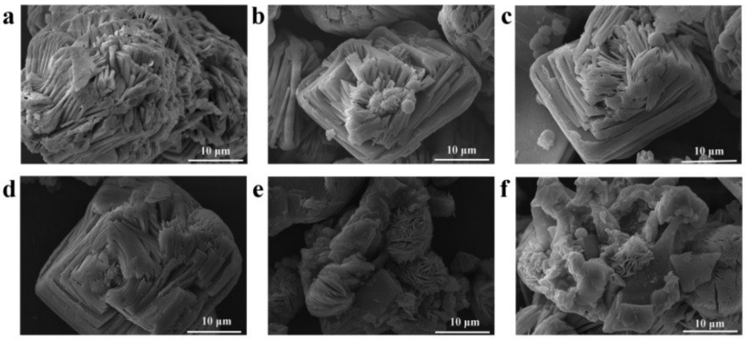

Fig. S10 SEM images of JDF-L1 titanosilicate zeolites obtained at 200 °C under 36 h crystallization time with different phase: (a-d) crystalline phase and (e,f) amorphous phase.

9. FT-IR spectra of JDF-L1 zeolites obtained with different Si/Ti ratios

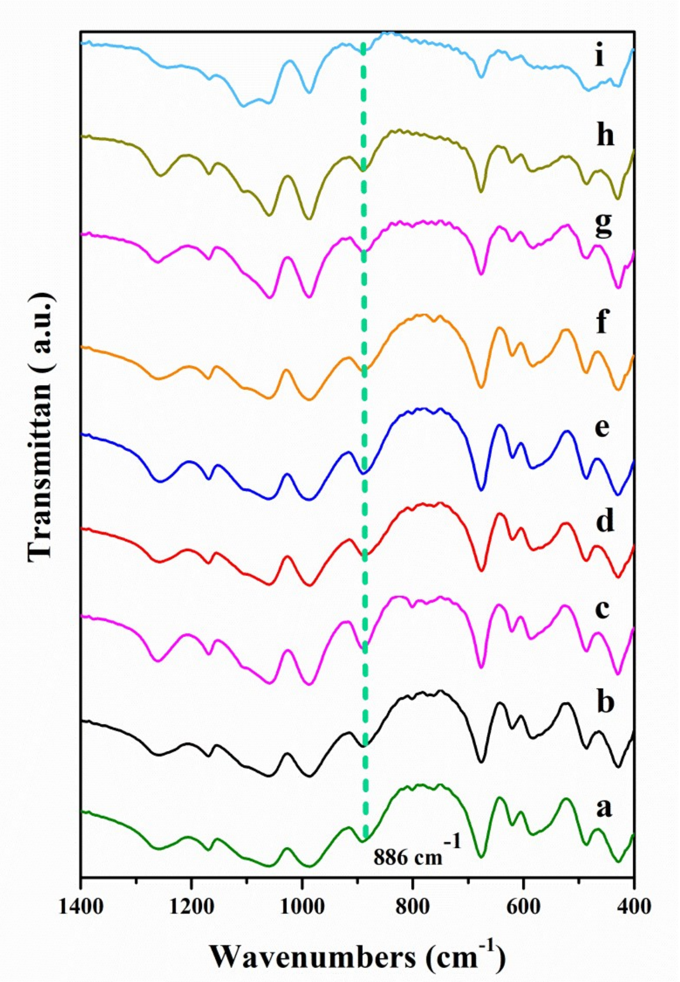

Fig. S11 FT-IR spectra of JDF-L1 zeolites obtained with various Si/Ti gel ratios: (a) 10.0, (b) 8.0, (c) 6.0, (d) 5.5, (e) 5.0, (f) 4.0, (g) 3.0, (h) 2.5 and (i) 2.0, respectively.

A distinct band at 886 cm^{-1} was observed for JDF-L1 zeolites prepared with various Si/Ti ratios in the range of 2.0-10.0, which suggested unique TiO_5 polyhedra had been established in the corresponding zeolite framework.

10. ICP results of JDF-L1 zeolites obtained under different Si/Ti ratios

Table S3. ICP results of JDF-L1 zeolites prepared with various Si/Ti ratios.

Samples	**a-10**	**b-8.0**	**c-6.0**	**d-5.5**	**e-5.0**	**f-4.0**	**g-3.0**	**h-2.5**	**i-2.0**	**j-1.5**
Na/Ti	3.079	3.096	3.038	2.823	2.799	2.740	2.100	1.902	1.429	/
Si/Ti	3.679	3.739	4.243	3.581	3.339	3.171	2.554	2.048	1.860	/

In case the Si/Ti gel ratio further reduced to 1.5 (j), the sample was not pure JDF-L1 phase.

11. Diffusion reflectance analysis of JDF-L1 zeolites obtained with different Si/Ti ratios

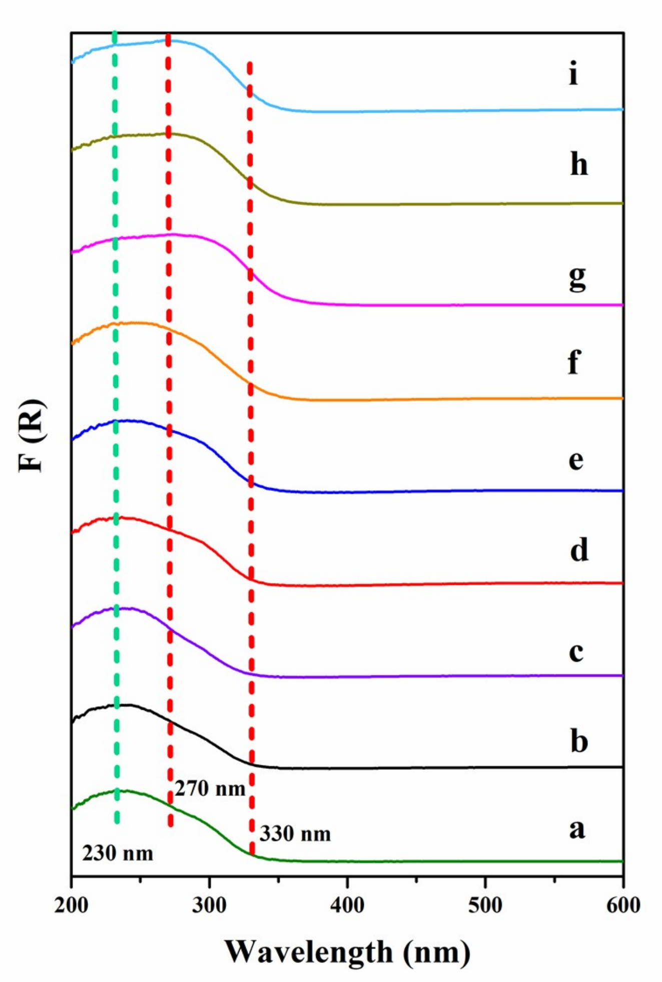

Fig. S12 UV-vis spectra of JDF-L1 zeolites prepared with various Si/Ti gel ratios: (a) 10.0, (b) 8.0, (c) 6.0, (d) 5.5, (e) 5.0, (f) 4.0, (g) 3.0, (h) 2.5 and (i) 2.0, respectively.

SI-3 Supplementary References

1 Y. Sun, F. Zhang, X. Du, X. Liu, G. Chu, S. Zhang and Y. Jin, *Mater. Lett.*, 2013, **97**, 31–33.

2 J. D. Jeon, J. Kim and S. Y. Kwak, *J. Memb. Sci.*, 2012, **415**–**416**, 353–359.

3 J. A. Dean, Lange's handbook of chemistry, McGraw-Hill, Inc., 15th edn, 1999.