Electronic Supplementary Information (ESI)

Enhancement of the visible light absorption intensity of microporous

vanadosilicate AM-6

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A. Materials and Methods

AM-6 materials. A series of samples were prepared as follow.¹ Mixture A was prepared by mixing sodium silicate solution (3.72 g, 20 wt% SiO₂ and 6.9 wt% Na₂O), NaOH (0.84 g) and potassium salt in 15 mL deionized water by stirring for 30 min. Vanadate solution (2.44 mL, 1M VOSO₄) was slowly added to H₂SO₄ (0.33 mL in 10 mL H₂O) solution to obtain the mixture B. Mixtures A and B were combined under stirring for 30 min to obtain the final gel. A series of AM-6 samples were adjusted from K₂SO₄ (0.9 g), KF (0.28 g), KF (0.57 g), to KF (0.85 g) for F/V molar ratio 0, 2, 4 and 6, respectively. A small amount of ETS-10 (10 mg) was added to the final gel as seeds for AM-6 crystallization. Finally, the gel was transferred into a Teflon-lined stainless steel autoclave and placed in an oven for 12 h at 230 °C. Samples synthesized with KF (0.85 g) were taken from autoclaves at different crystallization time, collected by filtration, washed with distilled water, and dried at 80 °C.

Characterization methods. XRD patterns were recorded on a Rigaku D/Max-2500/PC powder diffractometer. Each sample powder was scanned using Cu-K α radiation with an operating voltage of 40 kV and an operating current of 200 mA. 2 θ angles from 5 ° to 40 ° were measured with the speed of 5 °/min. UV-vis diffuse reflectance spectra were recorded on a JASCO V-550 UV-vis spectrophotometer. Raman spectra were collected on a home-made Raman spectrograph system using CCD detector. The scattered photons were collected by the ellipse collecting mirror in a back-scattering geometry and focused into the entrance

of the Raman spectrograph. The Raman spectra were recorded with a spectral resolution of 2 cm^{-1} with the laser excitation at 325, 457, 532 and 671 nm.

B. Theoretical Methods

DFT calculations were performed using Gaussian 03² program. The simulated vanadium substituted cluster model was constructed by a single O-V-O chain with three V atoms encapsulated in the supporting SiO₂ framework. The initial cluster was cut from ETS-10 lattice unit reported by Anderson et al³. The locations of charge compensating Na⁺ ions were according to Grillo's result⁴. The dangling Si-O bonds at the periphery of the cluster were saturated by hydrogen atoms which were kept fixed to orient in the direction of the next Si site during all calculations. The 1996 functional of Perdew, Burke, and Ernzerhof⁵ was employed to describe the exchange and correlation energies. A CEP-121G basis set was used for all types of atoms.⁶ Time-dependent DFT⁷⁻¹⁰ calculation was carried out using the same functional and basis set to evaluate the excitation energies. The number of excited states used to simulate the spectra was 80, which was enough to include the excitations observed above 400 nm in the experiment. The relevant excitation energies have been assigned to the transitions having the largest coefficient in the CI expansion.

C. Supplementary Figures



Fig. S1. XRD of the AM-6 with different F/V ratios.



Fig. S2 XRD patterns of the AM-6(6) for the different crystallization stages.



Fig. S3. Raman spectra of AM-6 samples with different F/V molar ratio excited at 325

nm.

References

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