SYNTHESIS AND BANDGAP ENGINEERING OF VANADOSILICATE AM-6 FOR PHOTOCATALYTIC APPLICATIONS

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Vanadosilicate AM-6 is a large-pore microporous material, isostructural with titanosilicate ETS-10. This material contains in its structure semiconducting monatomic …V-O-V-O-V… chains that are embedded in a silica matrix. Microporosity, pore regularity, and the presence of stoichiometric amounts of vanadium in the silicate framework make AM-6 a promising material in both traditional and advanced zeolite-type materials applications. AM-6 has recently been demonstrated to exhibit photocatalytic activity in the visible light range. These diverse applications require AM-6 crystals with controlled characteristics such as purity, size, morphology, topography, and defect concentration. However, to date, AM-6 has only been synthesized using seeds of ETS-10, and no control of the crystal characteristics has been reported. The use of titanosilicate ETS-10 crystals in the synthesis of vanadosilicate AM-6 limits the ability to control product characteristics without also influencing the AM-6 product titanium content.

In this investigation, a novel method for synthesizing AM-6 crystals without the use of seeds was developed. The use of a structure-directing agent facilitated the synthesis of pure (i.e., Ti-free) AM-6 products with various sizes, morphologies/topographies, and defect concentrations. AM-6 crystals appeared to grow via a two-dimensional nucleation crystal growth mechanism. UV-vis, FTIR, and Raman spectroscopic analyses suggested the presence of two oxidation states of vanadium (V^{4+} and V^{5+}) in AM-6. The optical properties of AM-6 were modified by varying the supersaturation levels in the synthesis mixtures and consequently the rate of surface nucleation relative to the rate of layer lateral spreading. Structural spectroscopic analyses were carried out to elucidate the effect of varying these supersaturation levels on the …V-O-V-O-V… chains. “High quality” crystals with less interrupted (i.e., more continuous) chains in their bulk as determined from XRD and UV-vis analyses were found to be more effective towards the photodegradation of methylene blue under visible light irradiation than “low quality” crystals with more discontinuous chains in their bulk. These findings were attributed to the presence of more V^{5+} species in the “outer surface region” of “high quality” crystals than the “low quality” crystals as determined from Raman analysis using different laser excitation lines.

In situ isomorphous framework substitutions of transition metals were carried out in efforts to enhance the photocatalytic activity of AM-6 by introducing new ligand-to-metal charge-transfer transitions and separating the V^{4+} and V^{5+} oxidation states along the …V-O-V-O-V… chains. The proximity of these vanadium oxidation states has been reported to promote electron-hole recombination. Successful incorporation of Cr^{3+}, Fe^{3+}, and Co^{2+/3+} in the AM-6 framework was established by EDX, XRD, UV-vis, Raman and FTIR spectroscopic analyses. All transition metal ions-incorporated AM-6 products showed a red shift of their bandgap energies (3.62-3.78 eV) compared to unmodified AM-6 (3.82 eV), and new low energy charge-transfer transitions. Chromium-substituted AM-6 showed a substantial improvement in the photodegradation of methylene blue under UV and visible light irradiation compared to unmodified AM-6.