

TiO₂-2D mordenite nanocomposites for photocatalytic applications

Saint-Petersburg State University, St. Petersburg, Russia

M.G. Shelyapina

Centro de Nanociencias y Nanotecnología, UNAM, Ensenada, Mexico

R. Yocupicio-Gaxiola
U. Caudillo-Flores, A. Urtaza
V. Petranovskii

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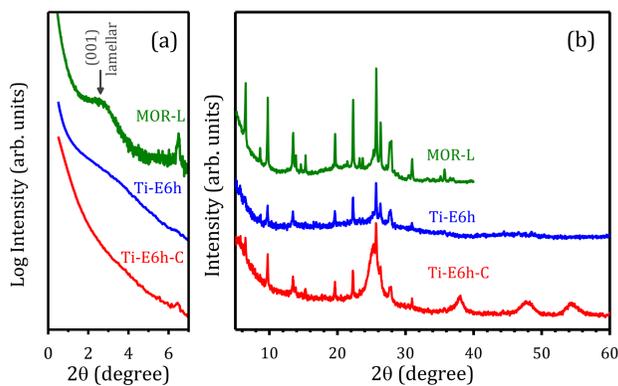
Development of environmentally friendly water treatment technologies is one of the global goals for sustainability. Photocatalytic decomposition of organic pollutants is an important strategy for water treatment. TiO₂ is an n-type semiconductor with a wide energy band gap. Its photocatalytic effectiveness is governed by the crystal phase, particle size and crystallinity. Anatase is generally considered as the most active phase of TiO₂. Nanoparticles due to their high surface area-to-volume ratio normally exhibit better efficiency than bulk TiO₂. The band gap of TiO₂ particles less than 10 nm strongly depends on their size that is attributed to the quantum size effect [1]. One of the drawbacks of such photocatalysts is the mass transfer limitation between solid and liquid phases. Combining TiO₂ and zeolites helps overcome it, enhancing the degradation of organics in water [2]. In this contribution we report on the new TiO₂-2D mordenite nanocomposites perspective for photocatalytic applications.

PREPARATION METHOD

TiO₂-2D mordenite nanocomposites were synthesized from layered mordenite grown by self-organization method in the presence of cetyltrimethylammonium bromide (CTAB) as an organic structure-directing agent [3]. The synthesis included several steps- (i) synthesis of the lamellar mordenite (the sample is labelled as MOR-L); (ii) introduction of titanium tetraoxide (TEOT) into the interlamellar space of 2D mordenite; (iii) subsequent hydrolysis in water (Ti-W6h) or ethanol (Ti-E6h) for 6 h; and (iv) annealing for 4 h at 550 °C to remove the organic molecules (the samples are labelled as Ti-W6h-C and Ti-E6h-C).

XRD STUDIES

Powder X-ray diffraction (XRD) analysis was done on a Bruker D8 DISCOVER diffractometer (CuK α). Diffractograms were recorded in the 2 θ range of 5–40°, step width 0.0302° for the initial layered zeolite (after Step i), where the main characteristic peaks of the mordenite appear, and in the 2 θ range of 5–60° for synthesized nanocomposites (after Steps iii and iv) to identify formation of TiO₂ nanoparticles. Small angle X-ray scattering (SAXS) patterns were recorded in a scan range from 0.2 to 7.0 2 θ degree, step width 0.01°.



The sample MOR-L exhibits typical features of the mordenite structure with an amorphous halo (range 2 θ between 17-30 degrees). This amorphous halo vanishes after calcination process.

SAXS patterns shown in Figures 1(a) unambiguously indicate the formation of lamellar mesophases in MOR-L [3].

For the lamellar sample, the peak at 2 θ = 2.7° corresponds to the (001) reflections with interplanar distances d = 3.2 nm. However, the introduction of TEOT with further hydrolysis leads to smoothing this peak and disappearing after calcination. For the calcinated sample additional large peaks that corresponds to the TiO₂ anatase nanoparticles appear. The average size of the TiO₂ nanoparticles as determined by Scherrer formula from single diffraction peaks of the experimental patterns is about 10 nm. The nanocomposites, obtained by using hydrolysis in water exhibit the very similar XRD patterns.

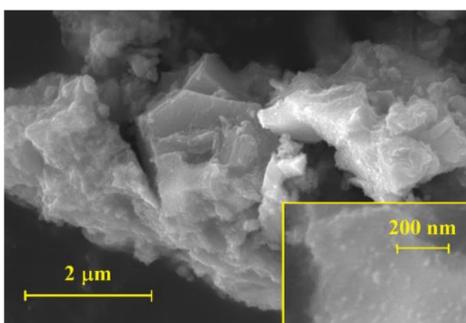
ELEMENTAL ANALYSIS AND MORPHOLOGY

Sample	Si/Al	Na/Al	Ti/Al
MOR-L	8.4 ± 0.3	1.14 ± 0.03	–
Ti-W6h-C	10.3 ± 0.4	0.3 ± 0.1	25 ± 1
Ti-E6h-C	10.5 ± 0.6	0.3 ± 0.2	15 ± 2

The morphology and elemental analysis of the samples was studied by an optical system integrated into D8 DISCOVER Bruker spectrometer and by scanning electron microscopy (SEM) applying Zeiss Merlin equipped with an Energy Dispersive X-rays (EDX) Oxford Instruments INCAx-act

The results of the EDX elemental analysis of the lamellar mordenite and the titania loaded and calcinated samples are summarized in Table 1. As one can see for the as synthesized lamellar sample the Si/Al ratios is 8.4; an excess of positive charge (Na/Al > 1) is balanced by Br anions (Br/Al = 0.24). This means that CTAB is present only in its cationic forms, CTA⁺ balancing the dangling bonds of the zeolite layers.

The pillaring results in a significant dealumination with a simultaneous decrease in the Na content. Despite the rather similar Al content, the Ti loading is very sensitive to the media in which the TEOT hydrolysis occurs: the hydrolysis in water results to an essentially higher Ti content. In addition, it should be noted that all the materials are characterized by a certain inhomogeneity in the distribution of elements: there are regions with higher and lower Si/Al and Ti/Al ratios, which is reflected in a rather large experimental error.



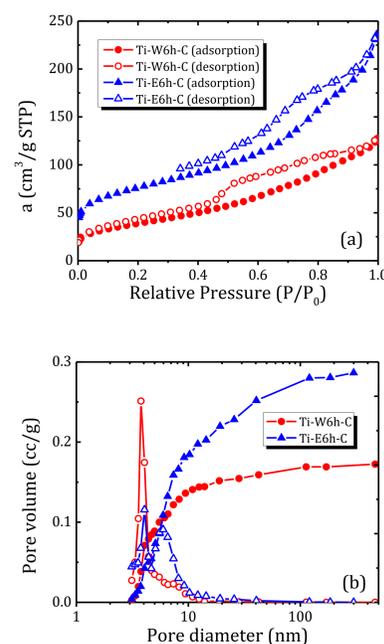
The morphology of the samples was studied by SEM. The TiO₂-2D mordenite nanocomposites represent thin plates up to 1-2 μm in size, combined in stacks, see Figure 2. Nanoparticles of about 8-10 nm dispersed on the surface of the zeolite plates are, presumably, TiO₂, that leaks out from interlamellar space.

SEM image of the Ti-W6h-C sample.

ACKNOWLEDGEMENTS

The samples were synthesized at CNYN-UNAM and studied at the Research Park of Saint Petersburg State University (Centre for X-ray Diffraction Studies, Interdisciplinary Resource Centre for Nanotechnology, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Centre for Optical and Laser Materials Research).

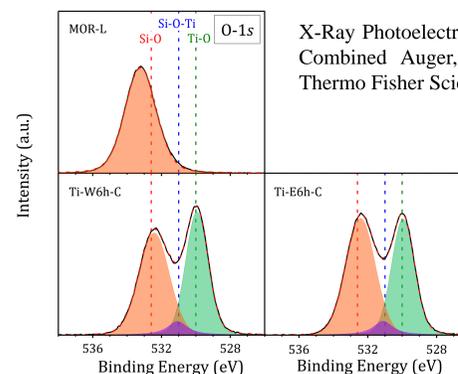
TEXTURAL ANALYSIS



N₂ physisorption isotherms were recorded at 77 K using a QuadraSorb SI instrument. Surface areas were obtained by applying the Brunauer–Emmett–Teller (BET) equation on the linear zone of the BET plot.

N₂ adsorption/desorption isotherms of calcined samples exhibit feature typical for hierarchically porous structures with both micro- and mesopores: firstly, a sharp uptake of a gas at low pressure (isotherm I, as classified by IUPAC) and, secondly, another uptake at higher pressures, accompanied with a hysteresis loop (isotherm IV, as classified by IUPAC). The hysteresis loop for the Ti-W6h-C sample corresponds to predominantly ink-bottle-shaped pores (type H2) with presence of slit-shaped pores (type H3); the inflection point visible in the desorption curves appears around P/P₀ = 0.5, followed by wide hysteresis loop. The N₂ adsorption isotherm of Ti-E6h-C shows a characteristic loop for a lower ordered arrangement of mesopores. The determined surface area is 139.547 and 149.368 m²/g for the Ti-W6h-C and Ti-E6h-C samples, respectively. The hydrolysis in water leads to the formation of mesopores of about 3.8 nm in size with a total mesopore volume of 0.172 cc/g. Hydrolysis in ethanol leads to a bimodal pore size distribution: 4 and 6 nm, with a predominance of the 6 nm diameter fraction. The volume of mesopores is 0.266 cm³/g.

XPS STUDY



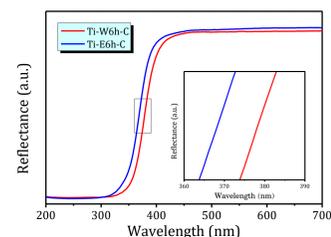
X-Ray Photoelectron Spectroscopy measurements were done by using a Combined Auger, X-ray and Ultraviolet Photoelectron spectrometer Thermo Fisher Scientific ESCALab 250Xi.

The O-1s spectra for the TiO₂ containing samples besides peaks at shows a peak at 532.2 and 529.9 eV, that corresponds to zeolitic Si-O and anatase Ti-O bonds, respectively, exhibit a peak at about 531.0 eV that could be related to the presence of a Si-O-Ti bond due to good interaction between TiO₂ and the zeolitic phase.

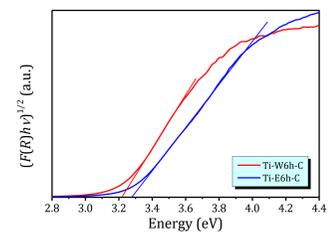
UV-vis STUDY

Energy gaps were determined by diffusive reflectance spectroscopy (DRS) using a spectrophotometer Lambda 1050 (Perkin Elmer) equipped with an integrating sphere in the spectral range 200–700 nm.

To determine the energy bandgap E_g the Kubelka–Munk method was applied. Both the samples exhibit absorption edges near 400 nm due to the anatase TiO₂ band gap absorption. A steep linear increase of light absorption (see reflectance spectra) with increasing energy is characteristic for semiconductor materials. The band gap energy can be estimated from the x -axis intersection point of the linear fit of the Tauc plot. The sample obtained by hydrolysis in water exhibit E_g values close to the bulk anatase 3.22 eV. The hydrolysis in ethanol results to higher E_g values, about 3.28 eV, that is typical for anatase nanoparticle and is known as a blue shift as compared to bulk TiO₂.



Sample	E _g (eV)	Ref.
Ti-W6h-C	3.22	This work
Ti-E6h-C	3.28	This work
TiO ₂ - anatase nano	3.25	[4]
TiO ₂ - anatase bulk	3.21	[4]
	3.0-3.2	[5]



CONCLUSION

New TiO₂-2D mordenite nanocomposites were successfully synthesized from a lamellar mordenite. Anatase nanoparticles of 10 nm in size are immobilized at zeolite surface and form pillars separating mordenite layers, creating mesoporosity. The textural properties depend on the media in which hydrolysis of TEOT occurs. The band gap width of the synthesized nanocomposites is close to that one in bulk TiO₂ but slightly affected by preparation procedure. Altogether it suggests that these new nanocomposites will be effective photocatalysts for degradation of organics in water with high mass transfer.

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