NATURE OF CORONA IN TiO₂-SBA-15-LIKE MESOPOROUS NANOCOMPOSITE

S. Perathoner\textsuperscript{a,c}, P. Lanzafame\textsuperscript{a,c}, G. Centi\textsuperscript{a,c}, F.C. Jentoft\textsuperscript{b,c}, Tz.V. Venkov\textsuperscript{b,c}, R. Schlögl\textsuperscript{b,c}

\textsuperscript{a} Dept. of Ind. Chemistry and Eng of Materials, Univ. of Messina, UdR INSTM Salita Sperone 31, 98166 Messina. Tel: +39-090-676.5609, Fax: +39-090-391518, e-mail: perathon@unime.it

\textsuperscript{b} Dept. Inorg. Chem., Fritz Haber Inst. of the Max Planck Soc., Faradayweg 4-6,D-14195 Berlin, Germany.

\textsuperscript{c} ELCASS (European Laboratory for Catalysis and Surface Science)

Summary

TiO₂@SBA-15 mesoporous nanocomposite are of increasing interest as materials for photocatalytic applications. We report here an investigation on the characteristics of TiO₂@SBA-15 prepared by introducing titanium by a grafting technique. The samples, having TiO₂ loadings of 10\%, have been characterized by XRF, XRD, FT-IR (CO adsorption), porosimetry, SEM, HRTEM, and UV-Visible diffuse reflectance. Three different titanium species were evidenced to be present. The first two derive from the reaction of titanium with silanol groups in the corona area of inner SBA-15 walls leading to the formation of either TiO₄ tetrahedral sites (by reaction by hydroxyl nests of surface defect sites) and/or pseudo-octahedral surface sites anchored by two (or more) Si or Ti ions through bridging oxygen. The third species derives from the reaction of titanium in the regions with high sylanol density, e.g. in the micropores located in the corona of SBA-15 channels, leading to the formation of TiO₂-like nanoareas with dimensions of around 1-2 nm maximum, but having characteristics different from those of crystalline titania as shown by FTIR data.

Introduction

There is an increasing interest to develop TiO₂@SBA-15 nanocomposite for their use as novel photoactive materials for gas and liquid streams purification, H₂ production by water splitting and methane direct conversion to higher hydrocarbons. Ti ions incorporated in the silica walls also provide anchoring sites to stabilize well dispersed metal nanoparticles and develop interesting catalysts for a number of applications.

Ti ions may be incorporated either during the synthesis of the mesoporous material, or added later typically by grafting or related methods. However, in the second case, the nature of the titanium species which form is still not well understood. We noted earlier that upon introduction of titanium by grafting in SBA-15 a structural reorganization of the inner walls (corona region) in SBA-15 channels occurs [1].

The nature of the “corona” in SBA-15, e.g. the region with low silica density and microporosity which form upon calcination due to the partial occlusion of the PEO (poly-(ethylene oxide)) chains in the silica matrix, is not well understood, but it is of critical relevance for the reactivity properties of these mesoporous materials. The possibility of controlling its characteristics by secondary reaction with Ti ions is quite important, not only for introducing catalytically active sites, but also for a tuning of the acidity and reactivity properties of the mesoporous material itself.

Experimental

SBA-15 was synthesized by self assembly on triblock copolymer PEO-PPO-PEO using tetraethyl orthosilicate. Titanium was introduced by a grafting technique using titanium isopropoxide in absolute ethanol. The samples have been characterized by XRF, XRD, FT-IR (CO adsorption), porosimetry, SEM, HRTEM, and UV-Visible diffuse reflectance.
Result and Discussion

Low-angle XRD showed the characteristic peaks of hexagonal mesoporous SBA-15, indicating that the samples consist of well-ordered channels which are maintained during all the reaction procedures. An increase in the intensity of the (10), (11) and (20) diffraction lines was noted due to the structural reorganization of the corona region of the mesopores after the introduction of titanium. TiO$_2$ particles were instead not detected.

β-plots of the N$_2$ adsorption-desorption isotherms confirm the reorganization of the microporous region. For the SBA-15 the micropore volume is about 7-8% of the overall pore volume. In TiO$_2$-SBA-15 samples this microporosity disappears.

HRTEM images and diffuse reflectance UV-Vis spectra provide further indication on the nature of modification of corona region by grafting with Ti ions. The results are summarized in the nearby cartoon model. Introducing by grafting, titanium reacts with the silanol groups in the corona area of inner SBA-15 walls forming either TiO$_4$ tetrahedral sites (by reaction by hydroxyl nests of surface defect sites) and/or pseudo-octahedral surface sites anchored by two (or more) Si or Ti ions through bridging oxygens. In the regions of high silanol density, where the micropores are located in the corona of SBA-15 channels, this reaction leads to the formation of TiO$_2$-like nanoareas with dimensions of around 1-2 nm. The reaction of Ti with the silica leads to the elimination of surface defects and of the regions with high hydroxyl density, with a better ordering and an intensification of the XRD reflections at small angles.

DRIFTS spectra show that for TiO$_2$-SBA-15 the intensity of the band of the silanol groups is smaller compared to the respective band of the pure support. FTIR spectra after low temp. CO adsorption on TiO$_2$-SBA-15 show a band at 2180 cm$^{-1}$, which is not detected for pure SBA-15. This band is assigned to CO coordinated to Ti$^{4+}$, evidencing that Ti ions are present at the surface of the SBA-15 matrix, but in an environment different to typical crystalline titania.