

Titanium dioxide phases in mesostructured silica matrices for cyclohexene oxidation

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Introduction

Studies on the photocatalytic properties of TiO₂ nanoparticles (NPs) have gained prominence in green chemistry. The catalytic properties of TiO₂ NPs have been found to primarily depend on the crystalline phase and particle size [1] and can be tuned by controlling the preparation method [2]. Despite recent advances in the preparation of TiO₂ NPs, a remaining challenge is to produce NPs with tailored catalytic properties. The photocatalytic properties can be controlled and the low adsorption ability of TiO₂ NPs can be improved by surface augmentation by using inert supports.

Experimental

The TiO₂-SiO₂ hybrid material is synthesized by using an acid catalyzed sol-gel process with tetraethyl orthosilicate (TEOS) as the silica precursor [3]. The method includes hydrolysis, condensation, aging, and drying. As a derivative of imidazole, I16IL forms complexes with the chloride salts of metals (M-I16IL). The IL metal chloride complex forms a mesophase in solution, allowing these compounds to be employed as templates for porous silica. Hydrolysis and condensation steps begin to form interconnected regions of Si-O-Si that form a sol. The casting step of the sol-gel process is accomplished by use of mesophase molecular templates, as the silica precursor interacts with the hydrophilic phase and does not enter the hydrophobic phase. Metal chlorides complex with the hydrophilic imidazole-ring structure and, during the sol-gel process, the casting of metal chlorides into the silica may leave aggregated metal NPs embedded in the channels of the porous material after removal of the template by calcination. This TiO₂-SiO₂ hybrid material exhibited very-high surface areas with predominantly mesoporous-sized pore diameters, though the specific surface areas were not as high as the acid-catalyzed materials. This is likely due to the metal oxide occupying or occluding some available surface area.

Results/Discussion

The diffraction line in the XRD patterns confirmed the crystalline structures of TiO₂, Figure 1,

with particle size about 20 nm when the calcinations of material was done at 750°C, Figure 2.

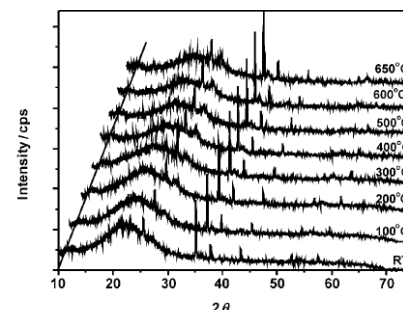


Figure 1. XRD patterns of nanocrystalline TiO₂ on silica calcined in the range of 30-650°C

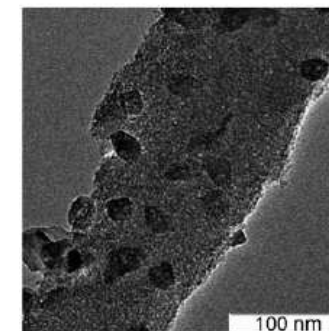


Figure 2. TEM images of nanocrystalline TiO₂ on silica calcined at 750°C

The photocatalytic oxidation of cyclohexene catalyzed by the as synthesized TiO₂-SiO₂ hybrid led to conversions of approximately 4.7%. Under the same experimental conditions the photooxidation of cyclohexene by using the reference titania Degussa P25 resulted in a conversion of only 0.7 %. Between the two investigated systems there are important differences in terms of crystallinity, composition of phases and size of the oxide particles. However, compared with previous data [4] the enhancement in the activity is much higher than those typically obtained when the phase composition is modified. It is also higher than for the cases titania is impregnated on silica in different loadings. On this basis, we assign the differences between the selectivity on these catalysts and on the new TiO₂-SiO₂ materials to the size of the anatase particles in the silica matrix. This behaviour is also confirmed by liquid-phase oxidation tests on the TiO₂-SiO₂ catalyst in dioxane, where very high oxidant capabilities were detected at low temperatures. The major products at 25°C were the mono and diketone, while at 50°C the diketone and adipic acid. Changing dioxane for acetonitrile led to similar conversions, but with major differences in selectivity. At 50°C, the epoxide and adipic acid were the main reaction products.

References

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