

## COMBINING TITANIA WITH MESOPOROUS SILICA – A STEP TOWARDS HIGHER CATALYTIC PERFORMANCE?

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### ABSTRACT

Efforts for increasing the applicability of titanium dioxide in industrial scale have led to studies of introduction of other oxides, i.e. mixed  $\text{TiO}_2\text{-M}_x\text{O}_x$  oxides, where M stands for metal, usually Si, W, Cu, Fe, etc. However, the effects of such modification can be seen on the macroscopic, i.e. structural level as well as on the electronic level. It is therefore critical to understand both aspects of such modifications in order to exploit the full potential of such systems. Herein we, present the efforts and effects of including silica phase to titania one. The changes are discussed on the electronic and on the structural level, with studies of nitrogen adsorption, electron microscopy as well as on the aspect to which such modifications affect the photocatalytic performance in gas- and liquid-solid interface. We additionally discuss the role of ordered mesopores in the pollutant abatements.

Keywords: mesoporous silica, photocatalysis, mixed metal oxides, gas-phase.

### INTRODUCTION

With the estimate of the annual production of nanomaterials worldwide [1] being led by  $\text{SiO}_2$  (median = 5500 t/year) and followed by  $\text{TiO}_2$  (median = 3000 t/year), the inclusion of  $\text{SiO}_2$  phase to the  $\text{TiO}_2$  phase is not only scientifically feasible but also economical. However, the relationships between the amounts of mesoporous silica in the catalyst, its structure (pore sizes, surface area, etc.) and the photocatalytic performance remains hard to elucidate. Works have been done regarding the role of ordered pores [2], optimum amount of silica needed for improvement in the activity [3].

In this work, we studied the relationship between the addition of mesoporous silica and the mechanical properties and photocatalytic activity towards aqueous and gaseous model pollutants. The results confirm the beneficial role of silica addition and the fact that ordered structure of  $\text{SiO}_2$  does not play an important role.

### EXPERIMENTAL

The materials used were P25- $\text{TiO}_2$  from Degussa (Germany), CCA100AS and CC-40  $\text{TiO}_2$  from Cinkarna (Slovenia), PC500  $\text{TiO}_2$  powder (Cristal Global, France), hydrochloric acid (37 %, Sigma-Aldrich, USA), Tetraethylorthosilicate (TEOS from Acros Organics) Colloidal silica Levasil 200/30% from Obermeier (Germany), 1-Propanol from Sigma-Aldrich (USA), terephthalic acid (TPA) from Alfa Aesar, hydroxyethyl cellulose (HEC) from Fluka, glycerol (99.5% from Sigma-Aldrich) and ethanol (96%) from Itrij. SBA-15 ordered mesoporous silica SBA-15 powder was synthesized according to the slightly modified well-known procedure [4], while disordered mesoporous silica was prepared by a hydrothermal method published elsewhere [5].

Gas-phase toluene oxidation were conducted in a lab-made batch-circulated photoreactor with 1.4 L capacity, where the photocatalytic cell volume is 500 mL. In each test, 65 mg of catalyst was employed under UV-light irradiation (broad maximum at 365 nm), while for solid-solid interface, photocatalysts were put in form of films (brush deposition) on

glass and the pollutant were thick layers of either terephthalic acid or resazurin dye trapped in a polymer matrix of HEC or glycerol, respectively.

## RESULTS AND DISCUSSION

In order to study the effect of pore order in mesoporous silica, ordered SBA-15 and disordered KIL-2 silica sources were employed. The results towards gas-phase toluene oxidation show that both disordered and ordered silica improved adsorption substantially (Figure 1a). However, composites with ordered mesoporous silica (TiO<sub>2</sub>-SBA15) showed higher improvements in adsorption while also showing slightly better improvements in reaction rate constants. It was thus inferred that silica adds adsorption sites, while the intimate contact between TiO<sub>2</sub> and SiO<sub>2</sub> particles is still necessary for fast transfer of photoinduced electrons or holes to target pollutants.

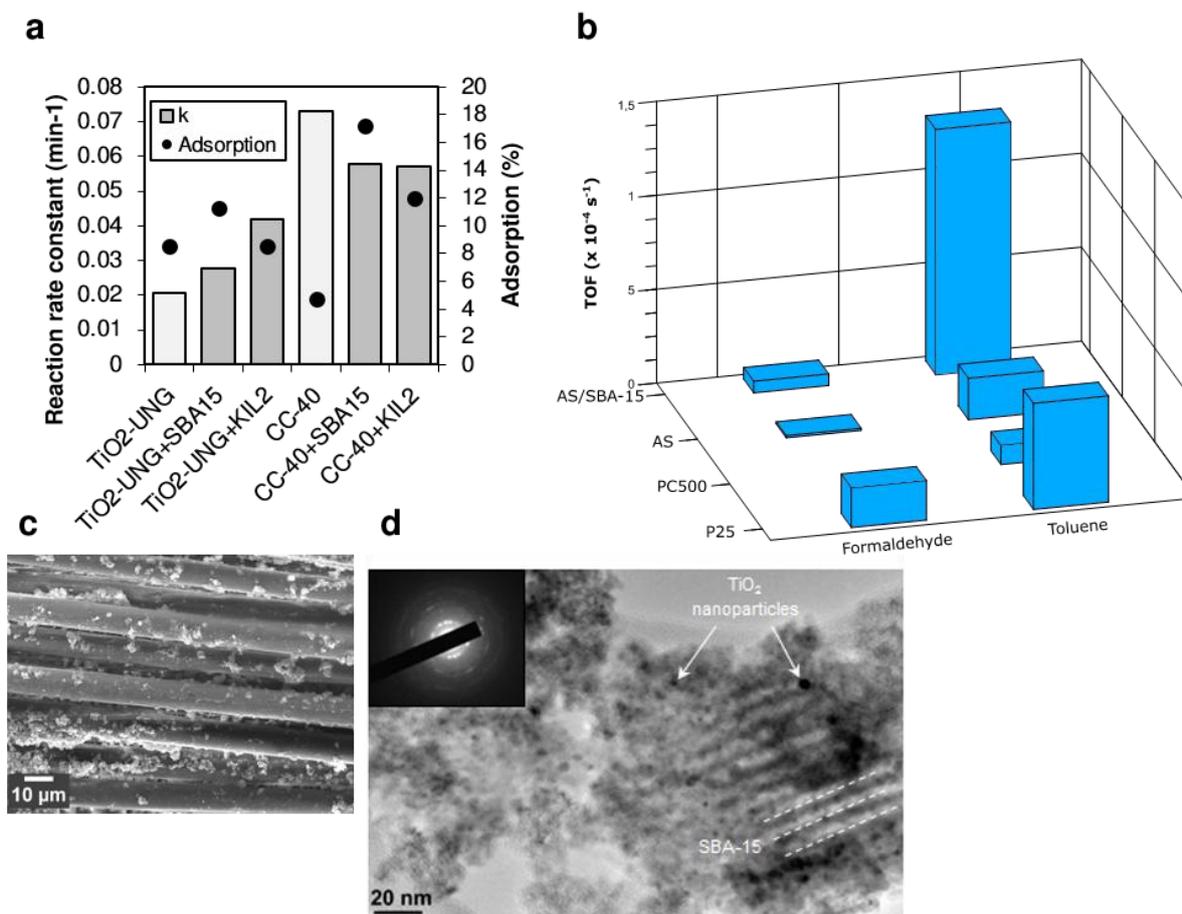


Figure 1. Photocatalytic degradation of toluene (a), and toluene and formaldehyde (b) with different TiO<sub>2</sub>-SiO<sub>2</sub> catalysts. In (c) SEM image of successful binding of TiO<sub>2</sub>-SiO<sub>2</sub> catalyst to fiberglass is shown; (d) a TEM image of TiO<sub>2</sub> nanoparticles incorporated into mesoporous SBA-15 silica.

However, the specific surface area of the ordered silica composites was higher (460 m<sup>2</sup>/g) compared to composites with disordered SiO<sub>2</sub> (336 m<sup>2</sup>/g). Since SSA of pure silica decreased more in the ordered SiO<sub>2</sub> source (SBA-15) than in disordered one and the pore order was substantially reduced (Figure 1d) we then studied whether pore order is crucial for obtaining good photocatalytic activities. It was shown that this is not the case. TiO<sub>2</sub>/SBA15 composite, despite having the pores now disordered showed substantial gains in photocatalytic activity. This meant we could proceed with synthesis of wider range of mesoporous silicas, including a large family of disordered ones, such as KIL-2.

Novel sources of silica was then tested for gas-phase reactions in catalysts immobilized on glass fiber cloths [6]. In this case, the silica source was a mixture of sol-gel-derived amorphous SiO<sub>2</sub> and colloidal silica particles (diameter = 30 nm, Figure 1c). Samples showed improved adsorption and degradation kinetics as well as greatly improved mechanical stability of the coatings on fiberglass [6,7].

Surface acidity of such disordered silica-titania composites was given a look (Figure 2b,c) and results showed that such samples showed higher hydrophobic character, which was the reason for higher adsorption (airborne pollutants commonly show a hydrophobic character). Additionally, the presence of silanol groups was studied for their accessibility. It was shown that a portion of Si–OH groups was inaccessible in these mixed oxides, which implied that some pores are hydrophilic but inaccessible for pollutants (Figure 2a). However, since <sup>•</sup>OH and O<sub>2</sub><sup>•-</sup> derived photoexcitation can travel relatively far (up to 500 nm), this means the pores show good connectivity which coincided with pore structure and SEM/TEM analysis.

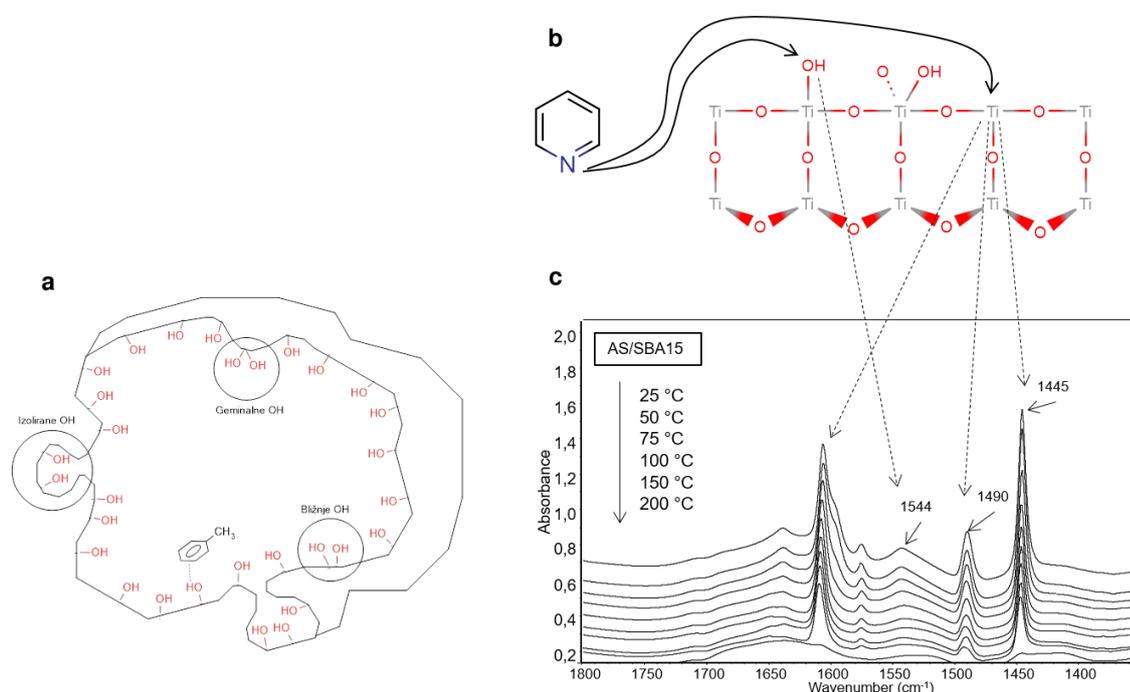


Figure 2. Schematic representation of a SiO<sub>2</sub> pore (a) with different surface Si–OH; binding sites of pyridine (b) and their respective FT-IR absorption responses (c).

## CONCLUSION

Despite some reports in the past showing the addition of silica reduces the reaction rate of photocatalytic oxidation [8], we have shown that by inclusion of mesoporous silica with a more acidic character, it is possible to obtain higher reaction rates with such modifications. It is crucial, however, that the properties of silica are chosen wisely. Most importantly, the amount of surface silanol groups, pore sizes and distributions shape, surface acidity and size of silica particles have to be chosen in a way that preserves the pore morphology of the original TiO<sub>2</sub> material and allows for easy diffusion of reactants to the

active sites or photo-produced radicals. Lastly, such composite materials offer big advantages in the mechanical stability of material and offer wider shaping possibilities.

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