ORGANIC-FREE COLLOIDAL TITANIA AS THE IMPREGNATION MEDIA OF MESOPOROUS SILICA IN INDOOR AIR-CLEANING APPLICATIONS

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ABSTRACT

Different types of TiO_2-SiO_2 composites in the form of powder or thin layers have been reported as efficient photocatalysts for decomposition of organic compounds in liquid and gas phase. Herein, we report for the first time on the formation of efficient TiO_2-SiO_2 thin layers made from acidic organic-free colloidal solution of TiO_2 anatase nanoparticles (AS) and mesoporous SiO_2 (SBA-15) with 100 % loading (TiO_2 : SiO_2 molar ratio 1:1) under simple and low cost procedure. AS was prepared from metatitanic acid precursor using a novel, environmentally friendly approach of TiO_2 nanoparticles precipitation with NaOH and peptization with HCl. The colloidal form of titania has proven suitable for impregnation of mesoporous silica and resulted in AS/SBA-15 thin layers, immobilized by brush deposition on glass carriers, which showed total decomposition of toluene and 92 % decomposition of formaldehyde as model VOCs in gas phase, at room temperature under UVA irradiation in lab-made batch photoreactor. Turnover frequencies (TOF) were used to compare the catalysts with their commercial analogues and AS/SBA-15 sample was found to have the highest TOF values for formaldehyde decomposition.

Keywords: photocatalysis, titanium dioxide (TiO_2), mesoporous silica, volatile organic compounds (VOC).

INTRODUCTION

UV-photocatalysis is a well known technique aimed at total and no-selective oxidation of organic compounds [1], [2] and in this respect the most studied material is titania (TiO_2). However, because TiO_2 photocatalysis is a surface reaction the intrinsic activity of material is limited by its surface area. This can be conveniently solved by introducing titania in nanometer scale, having a porous structure or providing a porous substrate to which TiO_2 is deposited. Still, the accessibility of the pores becomes a vital problem in providing the pollutant to the active sites (TiO_2), hence avoiding mass transfer being the limiting factor in the kinetics of the reaction. Then, the properties of titania can be studied from the optoelectronic point of view. TiO_2 in anatase phase has an energy band gap (E_g) of 3.2 eV, which corresponds to excitation wavelength of 388 nm. However, many factors affect the E_g value including the extent of structural disorder [3]. Therefore, many factors should be taken into account during the preparation of highly active titania catalysts. However, from the application point of view usage of TiO_2 in powder form is not practical due to the need for post-separation of the catalyst. Hence, the usage of catalyst in form of thin layers or coatings is highly desirable. The problem of this type of reactor design is in providing a stable-enough layer to prevent the leaching of the catalyst from the surface. Hence, mixed binary oxides can be prepared in order to solve this problem. The most usual choice for binary oxide is silica (SiO_2), due to its UV-transparency,

pore size tunability and structural stability. Furthermore, it has been proven that the addition of SiO_2 can promote the crystallization of TiO_2 and can delay the anatase to rutile transformation to higher temperatures during the synthesis [4]. Especially, the use of ordered mesoporous silica is interesting, because it can improve the distribution of titania nanoparticles, hence decresing the shadding effect. Because most catalysts on the marked are available in the powder form, with particle sizes in range of few tents of nm, this can promote pulmonary response upon inhalation or via skin exposure [5]. Hence, a great care should be taken when handling these materials. The alternative would be the usage of TiO_2 in colloidal form, therefore avoiding the possible hazardous dust formation.

In this report we developed the low-cost process of immobilization of active TiO_2 nanoparticles in colloidal form into porous silicate support (SBA-15) with high surface area with the molar ratio $TiO_2 : SiO_2 = 1 : 1$ (100 % loading). AS/SBA-15 composite was deposited via brush deposition method in the form of thin layer on glass carriers. Finally, the catalytic activity of AS/SBA-15 composite was compared with AS and also different commercially-available pure TiO_2 (P-25, PC500), used for benchmarking.

EXPERIMENTAL

A stable acidic colloidal solution of TiO_2 anatase nanoparticles was prepared for this work from metatitanic acid. The metatitanic acid was prepared in Cinkarna Inc. using a well-established sulphate process in which ilmenite is dissolved with concentrated H_2SO_4 and then hydrolysed in the presence of anatase seeds [6]. The anatase seeds were prepared separately by hydrolysing a titanyl sulphate solution at 80 ^{o}C and were added into the dissolved ilmenite solution. It was then converted into an anatase nanoparticulate suspension by NaOH for precipitation and HCl for peptization. P25 (Degussa) and PC500 (Millennium) powders were used as received. Ordered mesoporous silica SBA-15 powder was synthesized according to the slightly modified well-known procedure [7]. To 1.250 mL AS suspension (239.7 gL^{-1}) 0.2253 g SBA-15 silica was added and the resulting mixture was diluted with 2.500 mL 1-Propanol (99 %, Fluka) Samples were immobilized on glass slides using brush technique and baked on 150 ^{o}C for 1 h. Photocatalytic tests were conducted in a lab-made photoreactor system [8].

RESULTS AND DISCUSSION

N_2 adsorption isotherms for materials are shown in Figure 1a. Samples SBA-15, AS/SBA-15, AS and PC500 exhibit type IV sorption isotherms, while sample P25 shows isotherm type II [9]. SBA-15 sample exhibits sorption isotherm with relatively narrow hysteresis loop of H1 type, typical for ordered mesoporous silicas with hexagonal pore arrangement [9]. Additional hysteresis loop at relative pressure above 0.97 on sorption isotherm is present in this sample, evidencing the presence of an interparticle or textural porosity [10]. It can clearly be observed that AS titania impregnation of SBA-15 (AS/SBA-15) leads to a marked change in the shape of the hysteresis loop, showing on partial collapse of ordered pore arrangement into disordered pore arrangement, which finds some evidence in SEM, TEM and XRD analyses. The loading of titania nanoparticles into SBA-15 support led to a decreased specific surface area, pore volume and multimodal porosity. It can be concluded that titania nanoparticles have been dispersed inside of the support, which is in agreement with TEM. Furthermore, titania nanoparticles are present also on the external surface of the support, which is evident by the decrease of the textural porosity due to TiO_2 nanoparticles filling of the voids between SBA-15 particles. For AS sample, titania nanoparticles are less uniform and their agglomeration leads

to irregular mesoporous structure with broader pore size distribution. The latter is reflected by H2 hysteresis, often attributed to porous inorganic oxides [11]. Sorption isotherms of samples P25 and PC500 indicate the presence of mesopores [9].
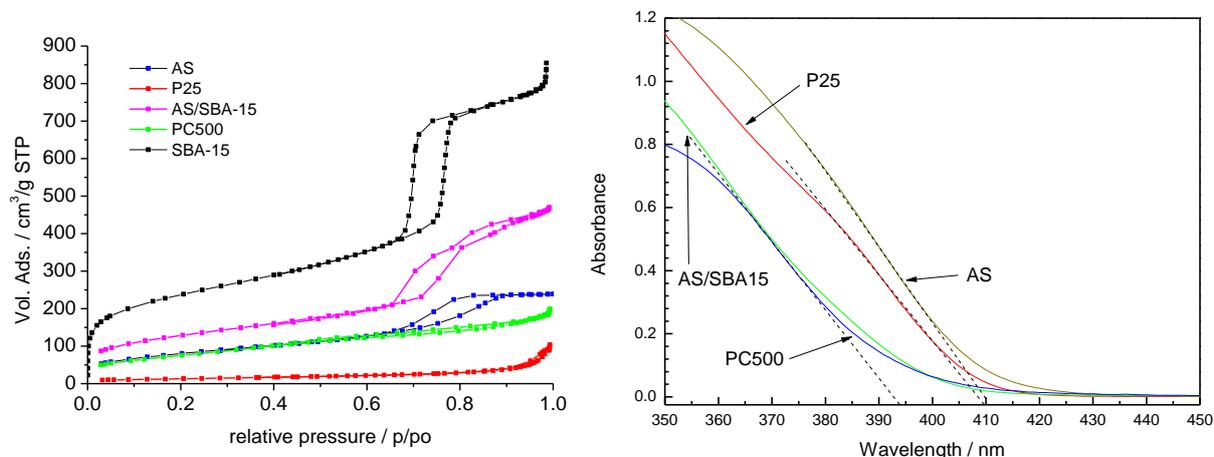

Figure 1. (a) N_2-sorption isotherms, showing different porosities and surface areas of the samples and (b) UV-Vis diffuse reflectance measurements of the catalysts.

UV-Vis diffuse reflectance spectra shown in Figure 1b indicate an increase in band-gap energy (E_g) of titania in the case of SBA-15 impregnation with AS titania. A number of studies have linked higher band-gap values to decreased number of surface defects in titania nanocrystals [12], [13]. These defects are probably in the form of oxygen vacancy or Ti^{3+} defects, as these have been found to be the main source of defect states in titania [13]. On the other hand, increased band gap can be associated with well-known quantum size effect [14]. The increase in this case is probably a result of both phenomena. Hence, the increased energy band-gap could result in the lower recombination of the charge carriers (h^+ and e^-) and higher oxidative potential, which would be beneficial for the photocatalytic process. Interestingly, the band-gap value of AS/SBA-15 is very similar as in the PC500 sample which contains amorphous phase, and it is known that amorphous materials show higher band-gap values, even exceeding 3.5 eV [15].
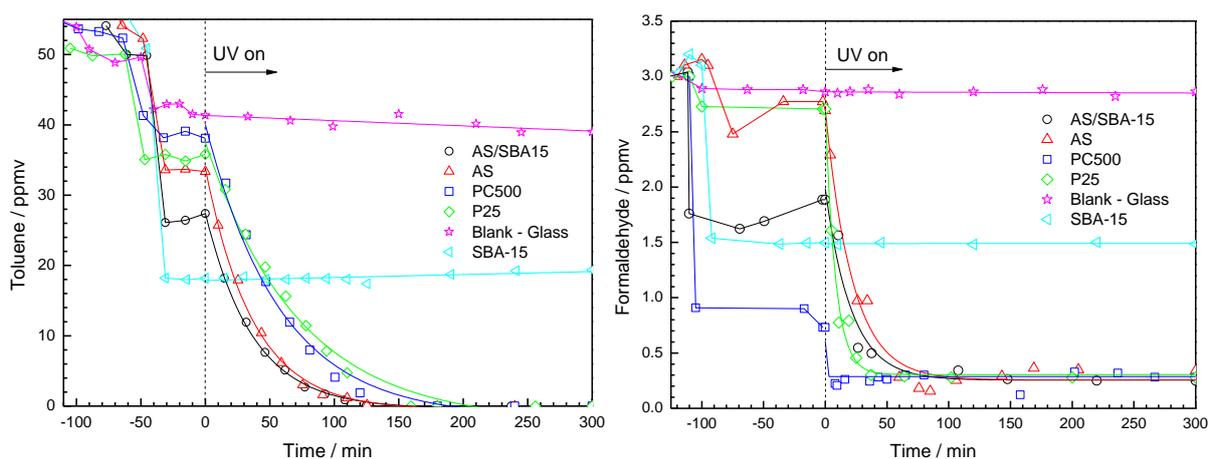

Figure 2. (a) Degradation kinetics of toluene and formaldehyde in the presence of the catalysts.

Toluene is generally a member of VOCs having the highest concentration found in the indoor environment and formaldehyde is a major indoor air contaminant [16], [17]. From Figure 2 it can be seen, that the catalysts were able to completely decompose toluene, while formaldehyde was not totally degraded, which is in accordance with other researches [17]. In case of toluene,

faster kinetics when AS was incorporated into SBA-15 is mainly a consequence of increased surface area and preserved pore structure of pure titania (see Fig. 1a). In case of formaldehyde, improved degradation efficiency in AS/SBA-15 (91.7 %) compared to AS (88.3 %) is a result of better crystallinity and increased Eg (see Fig. 1b) due to structure-directing role of mesoporous SiO_2. Hence, titania in colloidal form, with size of nanoparticles small enough to be encapsulated into mesopores of silica is appropriate for the impregnation of such SiO_2. Accordingly, the sample AS/SBA-15 has proven to be the most suitable for toluene as well as formaldehyde decomposition and the addition of mesoporous silica SBA-15 is a purposeful way of improving the properties of photocatalytic materials.

CONCLUSIONS

Titania in colloidal form, with size of nanoparticles small enough to be encapsulated into mesopores of silica is appropriate for the impregnation of such SiO_2. Accordingly, the sample AS/SBA-15 has proven to be the most suitable for toluene as well as formaldehyde decomposition and the addition of mesoporous silica SBA-15 is a purposeful way of improving the properties of photocatalytic materials. The beneficial effects of mesoporous silica were explained by the increase in band gap energy and increase in the surface area of the composite.

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