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Photocatalysis by morphologically tailored mesoporous silica (SBA-15) embedded with SnO_2 nanoparticles: Experiments and model

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ABSTRACT

Commonly obtained SBA-15 particles (fiber-like morphology), if used as a catalyst-host, has limitations in diffusion of reactant molecules (e.g. of a dye) inside the pores of the SBA-15 particle. The systematic synthetic approach developed here provides an easy control of SBA-15 particle morphology over a wide range (fiber, rod, and sphere), by only varying the HCl concentration. To assess its effect on molecular diffusion and reaction inside pores, SnO_2 nanoparticles of 3.5 nm diameter were synthesized *in situ*, inside the 6.3 nm diameter pores of SBA-15. These hybrids were tested for photocatalytic degradation of rhodamine B dye. Sphere-like morphology of SBA-15 with SnO_2 nanoparticle loading of 17.7 wt% showed the highest first-order degradation rate constant of 0.54 h^{-1}, compared to other morphologies (rod—0.51 h^{-1}, fiber—0.33 h^{-1}). On incorporating rates of diffusion, adsorption, and degradation-reaction of the dye in a single pore-level mathematical model of the SBA-15 particle, we have predicted the experimentally measured temporal variation of dye concentration for different SBA-15 morphologies and SnO_2-catalyst loadings. Therefore, the present work identifies the best SBA-15 particle morphology (sphere-like) for such reactions and provides a validated model to optimize such coupled problems of chemical transport and reaction.

1. Introduction

Water pollution caused by organic dyes is a serious global problem [1,2]. Discharge of effluents with dyes is undesirable, not only in terms of the persisting nature of color, but also harmful to human beings because some of the dyes are reported to be toxic, carcinogenic, and mutagenic [3–5]. Most common techniques to remove dyes from wastewater are adsorption on activated carbon, reverse osmosis, coagulation by chemical agents, and ultrafiltration [6–11]. However, these techniques transfer organic dyes to intermediate products, and do not completely convert to harmless substances [5,12,13]. So, it is necessary to develop a method for complete degradation of such compounds. Photocatalysis by semiconductor nanoparticles upon UV-ray irradiation involves generation of holes and electrons, and their migration to the external surface of the particle. Subsequently, these react on the particle-surface with contaminants. Photocatalytic performance of these semiconductor particles is strongly dependent on their size, location, and available specific surface area. Semiconductor particles such as TiO_2, SnO_2, ZnO, and WO_3 have been identified as potential photocatalysts in removal of organic contaminants, synthetic dyes, etc. However, these semiconductor nanoparticles when used directly in a solution without any catalyst-host tend to agglomerate, resulting in reduction in photocatalytic activity [13]. To overcome these difficulties, nanoparticles can be embedded within the conventionally synthesized, fiber-like mesoporous silica (SBA-15) host-particles, so as to increase the effective utilization of nanoparticle surface [14]. For example, Pt metal nanoparticles were embedded inside the pores of SBA-15 to increase the catalytic activity for CO oxidation [15]. Similarly, semiconductor nanoparticles (SnO_2, TiO_2, etc.) were embedded within the porous host-particles (zeolite, SBA-15, activated carbon, etc.), for a potentially higher photocatalytic activity against an organic dye [16,17].

Among the various ordered mesoporous silica materials, SBA-15 has a high thermal and hydrothermal stability due to its large wall-thickness [18]. It is the most preferable host for loading various guest species. The morphology of conventionally synthesized SBA-15 is a fiber-like particle, which consists of many micron-sized rods aligned unidirectionally, having a few tens of micrometers length and a few micrometers diameter. This however, results in a large diffusion-path length for any reactant, like a dye-molecule, impacting the overall degradation rate.

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Therefore, it is necessary to decrease the external particle size to shorten the diffusion path-length, requiring morphological changes during SBA-15 synthesis. There have been some investigations to understand how mass transport efficiency changes with various SBA-15 morphologies and pore diameters [19,20]. Since controlling parameters for particle morphology and size are related to surface energy and cooperative organization between the block co-polymer micellar-template and the inorganic precursor, many different synthetic strategies for SBA-15 have been attempted in the literature. These are, addition of co-solvent and salt, variation of synthesis temperature and stirring rate, etc., which however, result in non-uniformity of pore-size distribution, and uncontrolled particle size and shape. Since the structural attributes are very critical for high adsorption, diffusion, and reaction rates, the above are not preferred routes for uniform uptake and release of molecules [21,22].

Considering all the problems in loosing structural order due to the use of additives and alteration of parameters during the synthesis of SBA-15, the present study for the first time aims to demonstrate continuous morphological transition of SBA-15 from fiber to rod to sphere, which could be achieved by systematic tuning of only one variable, namely HCl concentration. All the other reactant concentrations are kept constant, without the addition of any external agent. Following that, in order to assess performance of these morphologically tailored SBA-15 hybrids on molecular diffusion and reaction, SnO_2 nanoparticles with a mean diameter of 3.5 nm were synthesized and embedded in three different SBA-15 morphologies (fiber, rod, and sphere) of pore diameter 6.3 nm. The focus is to study their photocatalytic activity against rhodamine B dye degradation. Finally, the present work also attempts a single pore-level mathematical model, incorporating diffusion, adsorption, and reaction leading to dye degradation. The overall objective is to predict our own experimental dye degradation data and suggest the best possible morphology of SBA-15, for such applications in water treatment.

2. Experimental

2.1. Preparation of different morphologies of SBA-15

SBA-15 particles in the form of fiber were synthesized with a slight modification in the molar ratio of reactants [17]. 1 g of Pluronic 123 was dissolved in 145 ml of distilled water at 35 °C, followed by the addition of 15 ml HCl (35%). 3 g of TEOS was added to the above mixture and stirred at 200 rpm for 24 h. Then, the above mixture was transferred to a Teflon-coated closed vessel and heated at 100 °C for 24 h, without stirring. The solid product was filtered, washed thoroughly with water and ethanol, and dried at 100 °C for drying. The dried solid powder was calcined in the presence of air at 550 °C for 6 h to decompose Pluronic 123 from the SBA-15 matrix. Mole ratio of the reactants for fiber-like SBA-15 was P123: HCl: H_2O: TEOS = 1:83.5:50,000:835.

Gradual morphological transitions (fiber to rod to sphere) are seen in SBA-15 particles with further increase in HCl concentration. The molar ratio for these SBA-15 particles is shown in Table 1.

Table 1
Molar compositions and morphology of SBA-15 samples synthesized with different HCl concentrations.

Samples	P123	TEOS	H_2O	HCl	Morphology
S1	1	83.5	50,000	835	Fiber
S2	1	83.5	50,000	1135	Mostly rod, some fiber
S3	1	83.5	50,000	1435	Rod
S4	1	83.5	50,000	1735	Mostly sphere
S5	1	83.5	50,000	2035	Sphere

2.2. Preparation of SnO_2 nanoparticles inside mesopores of different morphologies of SBA-15

Next, SnO_2 nanoparticles were formed inside the pores of all three morphologies of SBA-15, following our previous work [17]. Briefly, $SnCl_4$ was allowed to diffuse inside the pore of calcined SBA-15, with subsequent reduction by aqueous $NaBH_4$. For this, 50 ml of 1 mM $SnCl_4$ aqueous solution was added to 50 mg of calcined SBA-15 and stirred for 12 h. After $SnCl_4$ impregnation, 50 ml of 5 mM aqueous solution of $NaBH_4$ was added drop by drop to the above mixture and stirred for 30 min. The resultant solid product was filtered, washed thoroughly with water, and kept at 100 °C for oxidation of Sn in presence of air. The synthesized samples were denoted by $SnO_2(x)$–y SBA-15 (where x represents the weight percentage of SnO_2 nanoparticles in the hybrid and y represents the morphology of SBA-15 particle).

2.3. Photocatalytic activity measurement

Photocatalytic activity measurements of three different morphologies of SBA-15 embedded with SnO_2 nanoparticles were studied by measuring the temporal evolution in concentration of rhodamine B in a photochemical reactor. In case of SnO_2(5.8%)–fiber-like SBA-15, 50 mg of hybrid was taken in a quartz tube containing 100 ml of 50 μM rhodamine B solution. The hybrid in the dye solution was stirred for 30 min to achieve adsorption equilibrium. Then, the mixture was irradiated using a 250 W high-pressure mercury vapor lamp. The quartz tube was equipped with a jacketed tube, in which water was circulated to prevent overheating of the dispersion. After every 2 h, 3 ml of aliquots were withdrawn from the reactor and centrifuged for 10 min at 10,000 rpm to avoid scattering during absorbance measurement in the UV–vis spectrophotometer. The concentration of rhodamine B dye was measured by the characteristic absorption peak of rhodamine B at 554 nm with a UV–vis spectrophotometer.

2.4. Characterization techniques

Small-angle X-ray scattering experiments were performed in line-collimation, in a SAXSess instrument (Anton Paar), using Cu Kα as incident radiation (wavelength, λ = 0.1542 nm). The scattering intensities were collected on a sensitive imaging plate, and integrated over a linear profile to convert into one-dimensional scattering data of scattering intensity $I(q)$ vs scattering wave vector, q The scattering data was collected over a period of 30 min at 25 °C. Anton Paar TC50 Peltier temperature controller was used to maintain the temperature. Nitrogen adsorption measurements were conducted at liquid nitrogen temperature (77 K) using micrometrics ASAP 2020 apparatus. Samples were degassed at 130 °C for 4 h before measurement. Surface area was calculated using the BET model. Scanning electron micrographs of the samples were taken on Hitachi SEM-OIM (FEI quanta 200 HV SEM with TSL-EDX), operated at 10–15 kV. The samples were spread uniformly on the carbon tape for SEM imaging, which was attached on the flat surface of a brass stub. Transmission electron micrographs were taken on Philips CM200 at 200 kV. The samples (3 mg) were dispersed in 20 ml of isopropanol and a small amount of the mixture (10 μl) was placed on a holey, carbon-coated copper grid for TEM imaging. UV–vis spectrophotometer (PerkinElmer Lambda 35) was used to measure absorbance spectra of Rhodamine B dye.

3. Mathematical Model

To understand the importance of diffusion and reaction in a SBA-15 particle of any morphology, a single pore-level model has been developed in this work. The system modeled is schematically