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Facile encapsulation of P25 (TiO_2) in spherical silica with hierarchical porosity with enhanced photocatalytic properties for gas-phase propene oxidation

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ABSTRACT

In this work, we have performed the encapsulation of a reference TiO_2 material (P25) in spherical silica with hierarchical porosity using a sol-gel methodology. The same P25 material has been encapsulated within a "classical" MCM-41 mesoporous silica and a precipitated silica. The materials synthesized in this work were characterized by ICP-OES, SEM, TEM, EDX, XRD, UV–VIS, TG, and nitrogen adsorption. It has been observed that the P25 samples encapsulated in silica present improved CO_2 production rates per mol of P25 in the photo-oxidation of propene, compared to P25 alone as well as the physical mixture of the two components. Moreover, the sample with a low content of P25 encapsulated in silica with hierarchical porosity presents the highest CO_2 production rates per mol of P25 with respect to the other P25/silica samples, due to a better accessibility of the titania phase and improved illumination of the active phase. Furthermore, the hierarchical porosity of the silica shell material favours mass transport and an increased concentration of reagents by adsorption near the titania phase. This improvement in photocatalytic activity is obtained by following a simple and reproducible synthesis methodology that employs an established silica preparation protocol. Thus, the choice of a silica with an adequate porosity for this application is proven to be a promising advancement in the development of efficient photocatalysts.

1. Introduction

One of the most extensively researched photocatalysts over the past decades up to date is titanium dioxide (TiO_2), due to its unique properties including high photocatalytic efficiency, physical and chemical stability, and relatively low cost and toxicity [1–3]. Moreover, this semiconductor is an important industrial product in many applications such as inorganic pigment, photocatalysis, sunscreen and energy storage, among others [4–10]. An interesting commercially available TiO_2 powder is P25 (EVONIK), which consists approximately of 80% anatase and 20% rutile titanium dioxide [11]. This commercial TiO_2 is widely used as photocatalyst in photochemical reactions due to its high activity both in aqueous phase and in gas phase [12]. In many cases P25 is used as benchmark material to compare the potential of different photocatalysts in both mediums [13,14].

Many factors influence the photocatalytic properties of TiO_2, such as particle size, morphology, exposed lattice planes, and crystalline phase [9,15,16]. Despite the fine-tuning through which P25 has already undergone, this material presents low surface area (it is essentially a non-porous material) and low concentration of active surface groups, such as hydroxyl groups, as main drawbacks [17].

In the last years, many efforts have been made to increase the porosity of TiO_2 by synthesis of new nanoporous TiO_2 materials [18–20]. Many works have also focused on the fabrication of Ti/Adsorbent composites or supported TiO_2 on the surface of adsorbents to improve the aforementioned factors, with the aim of enhancing the photocatalytic activity of TiO_2. The most interesting materials used as adsorbents in these composites are carbon materials, zeolites, mesoporous materials, and polymers, among others [17,21–23].

TiO_2/SiO_2 materials have attracted a great deal of attention due to the advantages of SiO_2 as support or as component of composites, due to its tunable surface area and pore size, as well as interconnectivity of the pore network facilitating mass transport, high surface acidity (presence of Ti-O-Si) species, abundant surface hydroxyl groups and transparency in a wide wavelength range in the UV/Vis region [17,24].

Some studies have pointed out that the photocatalytic activity of TiO_2/SiO_2 composites is worse than that of the pure TiO_2 due to a blocking effect exerted by the silica on the active phase. For example,

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K.J. Nakamura et al. showed a decreased rate of photocatalytic degradation of methylene blue when using TiO_2 encapsulated in SiO_2 [25]. Another report by M. Nussbaum et al. demonstrated that as the thickness of the SiO_2 shell (measured in SiO_2 layers prepared by chemisorption-oxidation cycles according to the authors) around the TiO_2 photocatalyst decreased the activity of the active phase [26].

On the other hand, many studies show that the presence of SiO_2 with TiO_2 particles is not deleterious. In fact, several reports point out that silica favours the photoactivity of TiO_2 [27–30]. In the last years, many efforts have been made to synthesize a nanostructured photocatalyst with enhanced adsorption and molecular-sieving properties, with tunable conformations, as well as improved mass transfer in order to optimize the activity of the photocatalyst. In this aspect, S. Wang et al. synthesised Core(TiO_2)@shell(SiO_2) nanoparticles, with a void interlayer [31]. Another approach was carried out by Y. Kuwahara et al. where they developed yolk–shell nanostructured photocatalysts, consisting of TiO_2 nanoparticles in the core of spherical hollow silica shells [32]. Also, X. Chen et al. synthesised TiO_2/SiO_2 and TiO_2/ZrO_2 nanocomposites with hierarchical macro/mesopores [29]. In all cases the authors intended the preparation of well-defined porous textures of their composites in order to favour mass transport and the selective concentration of reagents on the photoactive surface so as to optimize the photocatalytic activity. Some authors used this type of composites for the selective degradation of molecules due to the textural properties that silica brings forth to the composite [31,33].

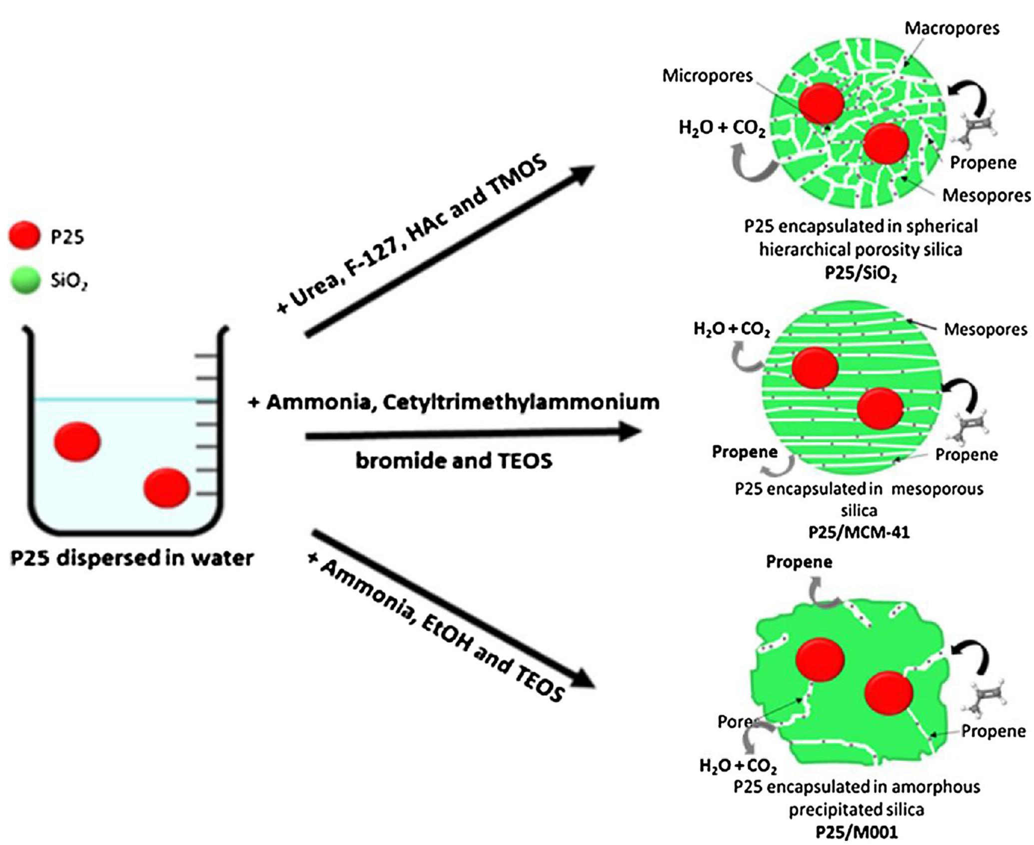
Considering the extensive background, this work approach consists of a facile and reproducible synthesis of TiO_2/SiO_2 composites through the encapsulation of commercial P25 in silica materials with markedly different porous textures (combining micro, meso, and macro-porosity in the best case scenario) in order to improve the photocatalytic activity by enhancing the adsorption characteristics of the composites (see Scheme 1). In this respect, the use of a silica shell displaying hierarchical porosity favours the aspects commented previously. Also, this work studies the effect of the percentage of P25 encapsulated in the silica with hierarchical porous texture in order to test the illumination efficiency and optimize the photocatalytic activity. This type of study, has not been undertaken through this approach to the best of our knowledge.

The materials studied in this work will be tested in the elimination of propene since this type of composites (TiO_2/SiO_2) can improve the photooxidation of VOCs as reported in the literature [17,21]. Moreover, these compounds are known to be very harmful to the environment and human health [34,35]. In particular, this work deals with the removal of propene al low concentration because this molecule might be taken as a representative example of low molecular weight VOCs [36]. These results are compared to the benchmark P25 and other related materials [37,38], in order to study the effect of the porous texture of the silica on the photocatalytic performance.

2. Experimental section

2.1. Materials

Titanium Tetramethyl orthosilicate (TMOS, 99%, Sigma-Aldrich), Tetraethyl orthosilicate (TEOS, 99%, Sigma-Aldrich), glacial acetic acid (HAc, 99%, Sigma-Aldrich), Pluronic F-127 (F-127, Sigma-Aldrich), Cetyltrimethylammonium bromidedeionized (Sigma-Aldrich), urea (99%, Merck), ammonium hydroxide (NH_4OH, 30%, Panreac), absolute ethanol (EtOH, 99.8%, Fisher Scientific), TiO_2 (P25, Rutile: Anatase/ 85:15, 99.9%, 20 nm, Degussa) and deionized water were used in the present work. All reactants were used as received, without further purification. The ultrasonic probe equipment SONOPULS HD 2200 (BANDELIN electronic GmbH & Co. KG) was used to disperse the P25 powder in water.



Scheme 1. Schematic representation of the synthetic procedure followed for the preparation of silica samples with different porous textures.