



## VOCs abatement using thick eggshell Pt/SBA-15 pellets with hierarchical porosity

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### ABSTRACT

Mechanically stable 3-D pellets made of mesoporous SBA-15 silica fibers containing highly dispersed platinum nanoparticles have been successfully synthesized with the aid of a sacrificial polyacrylamide network using a gel-casting deposition technique. The pellets exhibit a hierarchical porosity, with spaces of 3 microns among the silica fibers, and a core-shell distribution of Pt, with an outer Pt-rich layer of 450 microns accounting for over 73% of the Pt. Both factors (hierarchical structure and concentration of the catalyst on the outer pellet surface) facilitated reactant access to the catalyst centers, and as a consequence an excellent catalytic activity toward the total oxidation of n-hexane, used as a VOC model. There was no measurable loss of activity after 70 h on stream and the subsequent examination of the catalyst revealed that interparticle coalescence of Pt nanoparticles was largely prevented due to the encapsulation of the noble-metal particles within the silica mesochannels.

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### 1. Introduction

Many efforts are currently paid to design and engineer efficient microsystems featuring internal structures with sizes ranging from a few micrometers to a few tens of millimeters such as microstructured multichannel reactors [1,2], or macroporous monolithic and pellet structures with multimodal porosity [3–5]. In contrast with millimetric parallel multichannel reactors, macroporous monoliths and pellets are characterized by a higher surface-to-volume ratio and an efficient mixing of reactants thanks to their interconnected macroporous network [6]. They show low pressure drops and elevated mass and heat transfers as compared to classical fixed-bed reactors where the catalyst is in its powdered form.

Mesoporous silica materials, with highly ordered pore structures and uniform pore sizes, are considered as suitable host materials for active catalysts, on account of their large surface areas (up to  $\sim 1800 \text{ m}^2/\text{g}$  for SBA-15 mesoporous silicas [7]), high surface to volume ratios, large pore volumes (reaching values as high as  $1.7 \text{ cm}^3/\text{g}$  for bimodal mesoporous silica-based spheres [8] and  $2.48 \text{ cm}^3/\text{g}$  for SBA-15 [7]), tailorable and uniform pore sizes, and infinite possibilities of pore-wall functionalization allow-

ing them to host in their interior many active catalysts. SBA-15, in particular, shows an ordered hexagonal ( $p6mm$  symmetry) array of pores, high surface area, pore volume, and higher hydrothermal and mechanical stability than other mesoporous silicas such as MCM-41 [9]. In this way, Vinu et al. [10] demonstrated by using  $\text{N}_2$  adsorption-desorption measurements together with XRD diffraction that upon mechanical compression the pore structure of SBA-15 still remains intact even after loads up to 260 MPa.

Pelletizing mesoporous silicas facilitates handling of mesoporous silica powders and reduces the pressure drop in packed bed applications, while maintaining a consistent mesostructure and the oriented pore channels characteristic of the constituting silica particles. In fact, these pellets can be considered as hierarchical bimodal pore structures due to the co-existence of inner mesopores and inter-particle macropores. Compared to conventional packed-bed reactors with powdered catalysts, pellets greatly reduce pressure drops (up to two orders of magnitude) [11]. However, a common problem regarding mesoporous pellet preparation is that they tend to be mechanically unstable unless they were encapsulated or embedded within a polymeric network (i.e., monoliths tend to crack upon calcination and un-molding, yielding irregular pieces and coarse powders, especially as the diameter of the monolith decreases) [12].

In view of these problems and due to the numerous potential applications, various techniques for synthesizing silica pellets with an ordered macro/mesoporous structure have been investigated.

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Bimodal macro/mesoporous silica-based monoliths can be prepared in two ways: by direct-templating in a mold that holds up the desired shape of the monolith (dual-templating techniques) [13], and by using as-synthesized or modified mesoporous silica within a polymeric network acting as binder and holding the desired shape [5,14,15]. Additional binders such as colloidal silica, activated carbon or calcium titanate have been also successfully tested [5,15]. Another preparation method involves controlled fusion of mesoporous spherical silica particles [16] yielding mechanically stable pellets with tunable open macropores and surfactant-templated ordered mesopores.

Volatile organic compounds (VOCs) are known as one of the major contributors to air pollution. They may cause short and long term adverse health effects, act as greenhouse gases and constitute the major source of ground-level ozone, which is the primary constituent of the photochemical smog [17]. Total oxidation by catalytic combustion is commonly used for VOCs abatement because it can be carried out at relatively low temperatures, allows VOC handling at low concentrations and greatly reduces the formation of toxic by-products [18] and the need of post-processing the product gas. Compared to non-catalytic thermal incineration which is usually carried out at temperatures higher than 900 °C catalytic oxidation takes place at much lower temperatures (below 500 °C) and is therefore regarded as an efficient, cost-effective and environmentally friendly way to treat VOCs emissions.

Mesoporous silicas are limited in their use as catalysts due to their lack of ion-exchange capability and acid sites. Therefore, they are frequently used as catalytic supports after being doped with an active catalyst or after being modified by the introduction of Al or other transition-metal elements on the amorphous silica walls. Commonly used VOCs oxidation catalysts are based on supported noble metals or transition metal oxides. Metal oxides, mainly of Co, Cu, Ni and Mn, have the advantage of being economically viable and resistant to deactivation by poisoning [13,19–23]. Noble metal catalysts are generally preferred because of their high activity, excellent stability and good selectivity to CO<sub>2</sub> [24,25].

Different Pt-based catalysts have been used in n-hexane abatement. Anic et al. [26] used Pt (0.12 wt.%) / Mn catalysts deposited on Al<sub>2</sub>O<sub>3</sub> reaching a 50% n-hexane (1500 ppm) conversion at 198 °C. Pt on Al<sub>2</sub>O<sub>3</sub> was also used for the same catalytic reaction in fixed bed reactors achieving a 50% n-hexane (1500 ppm) conversion at ~160 °C [27]. Our group [28] has used zeolite-coated microreactors for n-hexane (200 ppm) removal using Pt (0.8 wt.%) / ZSM-5 and Pt (0.6 wt.%) / ZY as catalysts, obtaining a 50% conversion at 191 and 162 °C, respectively. Radic et al. [29] used 0.12 wt.% Pt / Al<sub>2</sub>O<sub>3</sub> catalysts in the oxidation of n-hexane (1500 ppm) reaching a 50% conversion at 220 °C.

In this work, we report on the preparation and use of hierarchically structured pellets made of ordered mesoporous silica, with a Pt-rich layer on the outside. Unlike conventional eggshell catalysts in which a very thin catalytic layer is used (which serves the purpose of attaining a high effectiveness factor but reduces the useful catalyst load per pellet), we have prepared thick-shell catalyst by gel-casting the hierarchical silica structure and then introducing Pt active sites via grafting of electrostatically assembled organic precursors. The catalysts prepared were highly active in the combustion of hexane as a model VOC compound.

## 2. Experimental

### 2.1. Catalyst preparation

Fibrous SBA-15 was synthesized following the protocol described by Katiyar et al. [30] using Pluronic® (P123, PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub>), tetraethyl orthosilicate (TEOS, 98%) and

hydrochloric acid (HCl, 37%) as a structure directing agent, silica precursor and catalyst, respectively. In a typical synthesis, 4 g of P123 were dissolved at 37 °C in 121 mL of distilled water with 3.2 mL HCl under stirring (350 rpm). After a complete dissolution, 9.2 mL of TEOS were added drop-wise and left under stirring and heating for 24 h. The aged precursor mixture was hydrothermally heated at 100 °C for 3 days in a Teflon-lined autoclave. The solid product was then filtered, washed three times with distilled water and dried for 24 h at room temperature. The removal of the organic template was achieved by calcination in a furnace with a heating ramp of 1 °C min<sup>-1</sup> up to 550 °C and a dwell time of 6 h at that temperature. A fibrous shape for the catalyst support was deliberately selected in order to favor the appearance of macropores during the packing of the fibers to form the catalyst pellet.

Mesoporous silica pellets based on the former fibrous SBA-15 with a bimodal pore structure (mesopores and macropores) were prepared using gel-casting procedures. SBA-15 fibers were entrapped in a crosslinked polyacrylamide macromolecular network; the polymer/particle composition replicates the shape of the mold used (Fig. 1) and the shape remains after the removal of the polymeric template. The elastic hydrogel/particle network was formed using acrylamide (Ac, 99%) as monomer, N-N'-methylene-bisacrylamide (BisAc, 99%) as cross linker and ammonium persulfate as initiator of the polymerization following the experimental procedure described by Liang et al. [14]. All the chemicals were purchased from Sigma-Aldrich and used as received. The weight ratio of monomer, cross-linker, initiator and water was 5/0.5/0.05/100; with 2 wt.% of SBA-15 added as filler. Reagents were mixed in a vial and sonicated for 10 min to assure homogeneity. The resulting suspension was then transferred into a 4 mm internal diameter glass tube (since it was going to be used as external template to shape the pellet) placed inside the conical centrifugation tube, and centrifuged at 3500 rpm for 5 min. The mesoporous silica particles were packed at the bottom of the tube by centrifugal force and the supernatant was replaced with fresh suspension before repeating the centrifugation (see Fig. 1). This protocol was repeated until the desired pellet height was achieved. Tubes were capped and cured in an oven at 50 °C for 1 h to allow monomer and cross-linker polymerization and hydrogel formation and then uncapped and left overnight at this temperature for hydrogel hardening. The hard pellets were then dried thoroughly in a vacuum oven at 60 °C and 100 mbar for 48 h, and the glass tubes were removed from inside the microcentrifuge tubes and calcined in a ceramic crucible at 700 °C. After calcination, hard silica pellets of 4 mm × 6 mm could be easily removed from the glass-tube templates without significant shrinkage. The resulting pellets were amino-grafted by using (3-aminopropyl)triethoxysilane (APTES, ≥98% Sigma-Aldrich) following a previously described experimental protocol [31].

Pt-loading was carried out by wet impregnation and in situ reduction of a Pt precursor. Pt nanoparticles were prepared at room temperature using a protocol previously published by our group [32]. In this protocol the organophosphorus salt tetrakis-(hydroxymethyl)-phosphonium chloride (THPC) (80 wt.%, Sigma-Aldrich) acts as simultaneous reductor and stabilizing agent. THPC generates formaldehyde and hydrogen, both of which act as active reducing agents. Then, 100 μL of HPTClO<sub>4</sub> (8 wt.%) in 15 mL of DDI water containing 6.67 mg of NaOH were added to 50 mg of the pelletized amino-functionalized SBA-15. After stirring, 333 μL of a 65 mM THPC solution were added and left under stirring for 4 days. The resulting product was thoroughly washed with DDI water, dried and stored for further use. The nanoparticles generated are strongly attached to the mesoporous silica walls due to the electrostatic attraction between the electron-rich nitrogen present in the amino groups of the SBA-15 and the metal orbitals via their lone pairs [33].

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