



Platinum nanoparticles entrapped in zeolite nanoshells as active and sintering-resistant arene hydrogenation catalysts



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ABSTRACT

Pt nanoparticles supported on ZSM-5 nanoshells have been prepared by a mild desilication method. The zeolite support is a ZSM-5 crystal with extremely thin walls (ca. 15 nm) that contain meso/microporous defects. The 2–3 nm diameter Pt nanoparticles are entrapped and highly dispersed in these ZSM-5 nanoshells. The particles are stable up to 750 °C in H₂ owing to this immobilization. Catalytic activities for toluene hydrogenation were compared with those of reference Pt-based catalysts. The reaction rates obtained on the novel Pt-ZSM-5 nanoshells catalyst were about 100 times higher than those measured over conventional Pt-ZSM-5 catalysts. The highly defective zeolite nanoshell allowed even bulky molecules such as mesitylene to access all the Pt particles. This was in contrast to Pt nanoparticles encapsulated in ZSM-5 hollow single crystals, which were totally inactive due to molecular sieving. This novel Pt-ZSM-5 nanoshell catalyst shows outstanding sintering-resistance and mass transfer properties owing to its hierarchical design.

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1. Introduction

Supported nanoparticles have been used for several decades as catalysts, the sample activity and stability being due to the combination of mono-dispersed particles with a high fraction of surface atoms and the textural properties of the supports. However, these materials are often thermally unstable, as particles tend to sinter at high temperature, which is a serious drawback particularly in the case of expensive noble metals. Recent attention has been paid to addressing the sintering problem of supported catalysts by covering or encapsulating metal particles into porous inorganic materials [1,2]. Yolk-shell catalysts in which nanoparticles are encapsulated into a thin hollow shell are particularly attractive because of the minor diffusion resistance toward reactants introduced by the nanoporous shell, which is yet able to maintain particles isolated from each other [3–10]. Particles are very accessible to reactants through the porosity of the thin shell, which is generally made of mesoporous oxides (ZrO₂, [3–5] SiO₂, [6,7] TiO₂ [8]) or amorphous carbon [9,10]. However, these elegant synthesis methods are yet complicated, usually requiring many condensation/calcination/dissolution steps. Attempts to develop

general synthesis methods of yolk-shell materials with thin microporous hollow zeolitic shells are still lacking. Such shells would be of great interest since zeolites are microporous aluminosilicates widely used in refinery industry, adsorption and separation. Several strategies have been reported to prepare metal nanoparticles encapsulated in zeolites [11–20] or coated by polycrystalline zeolite layers with a thickness more than hundreds of nanometers, some of those acting as shape- or size-selective catalysts [16–20]. To the best of our knowledge the reported thicknesses of the shell are always larger than 100 nm, which should lead to diffusion limitations of reactants and/or products throughout the zeolite layer. We have recently reported that diffusional limitation is observed even in yolk-shell materials with 30 nm thick silicalite-1 shell [21–23]. It is acknowledged that major enhancement of mass transport in zeolitic systems can be achieved by appropriate design of porous structures such as hierarchical micro-meso systems or ultra-thin zeolite nanosheets [24]. Here, we report on the synthesis of Pt nanoparticles of 2–3 nm in size supported in ZSM-5 nanoshells (hereafter called Pt@nanoshell) highly stable with respect to high temperatures. Markedly higher hydrogenation rates are obtained over this Pt@nanoshell as compared to conventional bulk Pt-ZSM-5 (hereafter called Pt/bulk). Adsorption and hydrogenation measurements over Pt@nanoshell and a series of reference Pt catalysts clearly indicate that the higher reaction rates result from the absence of transport limitations.

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2. Experimental section

2.1. Catalyst preparation

ZSM-5 was synthesized from the crystallization of gels containing tetraethyl orthosilicate (TEOS, Aldrich, 98%), 1 M tetrapropylammonium hydroxide (TPAOH) solutions (prepared from TPABr by exchange with Ag_2O) and NaAlO_2 (Strem Chemicals, 99.9%). The gel, with composition $140\text{SiO}_2\text{-Al}_2\text{O}_3\text{-30TPAOH-1240H}_2\text{O}$ was stirred at room temperature for 7 h, and transferred into a Teflon-lined autoclave and heated under static conditions at 180°C for 7 days. The autoclave was then cooled and the solid was centrifuged, washed with water and dried overnight at 110°C . After that, the as-made zeolite was washed with a 5 M HCl solution at 90°C for 5 h to remove the non-framework aluminum species, then centrifuged, washed with water until $\text{pH} = 7$ and dried at 110°C . Finally the zeolite was calcined for 12 h at 525°C in air.

2 ml $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ aqueous solution with a concentration of 2.5 mM/L was added to 1 g ZSM-5 zeolite, preliminary desorbed under vacuum at 200°C for 3 h. The corresponding Pt^{2+} ZSM-5 was obtained after stirring the mixture at 50°C overnight until complete evaporation of the liquid. Desilication of the zeolite was carried out by dispersing 0.5 g calcined Pt^{2+} ZSM-5 into 25 ml Na_2CO_3 solution which concentration was in the range of 0.6–1 M. The mixture was stirred for 12 h at 80°C , and then the solid was centrifuged, washed with water until $\text{pH} = 7$ and dried at 110°C . Finally the solid was reduced at 500°C under H_2 for 2 h with a heating rate of $1^\circ\text{C}/\text{min}$ to yield the Pt@nanoshell.

Pt@hollow zeolite was obtained by treating Pt^{2+} ZSM-5 crystals (1 g) in TPAOH (7.5 ml; 0.55 M) in a Teflon-lined autoclave at 170°C under static conditions for 24 h. The zeolite was then washed with water, dried and calcined in air at 450°C for 6 h. The obtained Pt@hollow zeolite was then reduced under H_2 under the same conditions as the Pt@nanoshell material.

A reference catalyst Pt/bulk was produced by direct reduction of Pt^{2+} ZSM-5 under the same condition as the Pt@nanoshell. The sintering tests have been carried out over Pt@nanoshell and a commercial available Pt/SiO₂ material. Both of those were reduced at 750°C under H_2 for 10 h with a heating rate of $1^\circ\text{C}/\text{min}$, and the resulting materials were further characterized by TEM. The obtained Pt@nanoshell after this sintering test was then evaluated in the hydrogenation reactions.

2.2. Hydrogenation tests

Toluene and mesitylene hydrogenations were carried out in a diffuse reflectance FT-IR spectroscopy (DRIFTS) reaction cell. The reaction bed of the DRIFTS cell was made of a ceramic crucible. A catalyst layer was deposited on top of a SiC layer filling up the crucible. The catalyst mass was adjusted to get a Pt loading about 0.1 mg (see Table S2, ESI†). A flow of 50 mL/min of pure hydrogen was used as carrier gas and fed through a saturator, which contained either toluene or mesitylene. During the experimental process, the saturator was kept at 0°C . The values of toluene and mesitylene flows were 0.1265 and 0.00847 micromol/s, respectively. The effluent was then diluted with 380 mL/min of Ar before reaching a 2 m path-length gas cell fitted in a Thermo FTIR spectrophotometer. The proportion of the reactant and the corresponding saturated product were determined through integration of two areas in the C-H stretching spectral region. In our tests methylcyclohexane and trimethylcyclohexane were the only products obtained in the hydrogenation of toluene and mesitylene, respectively.

3. Results and discussion

The synthesis of the original Pt@nanoshell material requires a specific preparation of ZSM-5 nanocrystals. First, ZSM-5 was prepared in order to obtain nanocrystals with pronounced Al zoning [25]. It is known that this condition is necessary to get hollow structures upon preferential desilication of the silica-rich core with respect to the Al-rich outer surface [26]. The calcined ZSM-5 was then added to a $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ aqueous solution, and the suspension was continuously stirred until the solvent was totally evaporated. At this step, no significant changes of the shape of zeolite were observed (not shown here). Hollow ZSM-5 nanoshells are formed by a desilication process with an aqueous solution of Na_2CO_3 following a procedure published elsewhere [25]. During this step the Si-rich core of the crystal was preferentially dissolved under the alkaline pH of the solution.

Treatment conditions were optimized to get hollow ZSM-5 with very thin nanoshells. The effect of the concentration of the Na_2CO_3 solution was studied from 0.6 M to 1 M. The shell thickness and Si/Al ratio of the resulting zeolites were tunable from 50 nm to 10 nm and 84 to 24, respectively (see Fig. S1, Table S1, ESI†). Meanwhile, X-ray diffraction peaks became broader (see Fig. S2 ESI†), consistent with small coherent domains within the shell, as already observed in the case of MFI nanosheets [24]. For low Na_2CO_3 concentrations, N_2 adsorption/desorption isotherms showed a hysteresis loop with closure at $P/P_0 = 0.45$, characteristic of fully closed shells accessible by pores smaller than 4 nm (see Fig. S3 ESI†).

At higher concentration (1 M), the hysteresis disappeared, indicating that the shells contain mesoporous/macroporous holes allowing gases to easily penetrate in the cavities (Fig. 1). The departure of the isotherm from the plateau further confirms the presence of a large amount of mesopores. TEM pictures (see Fig. S1 ESI†) confirmed that many of the crystals were broken due to the fragility of the sample made of extremely thin shells. After treatment with 1 M Na_2CO_3 solution, the mesoporous volume increases from 0.11 to $0.61\text{ cm}^3/\text{g}$, which indicates defects in the porous structure of the ZSM-5 nanoshells and/or inter-particle porosity (Table 1).

When not mentioned, zeolites were further treated with 1 M Na_2CO_3 for 12 h. After the Na_2CO_3 treatment, Pt species are located in the Al-rich outer region of the ZSM-5 nanoshells. TEM images (Fig. 2a) show that Pt particles around 1 nm in size are formed in an approximately 15 nm thick ZSM-5 shells. After reduction at

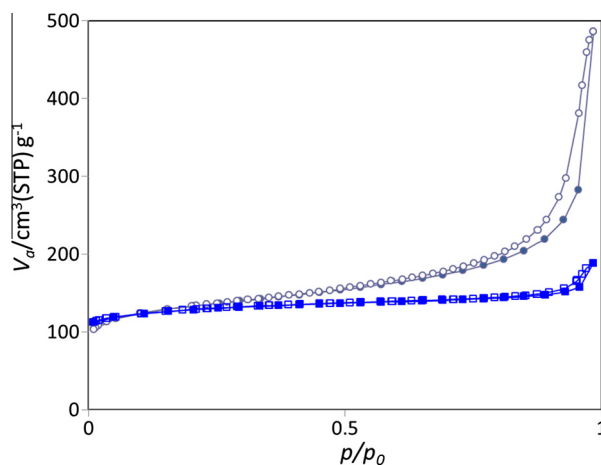


Fig. 1. N_2 adsorption/desorption isotherms at 77 K of parent ZSM-5 (square) and ZSM-5 nanoshell (circle) obtained by treating parent ZSM-5 with 1 M Na_2CO_3 solutions.

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