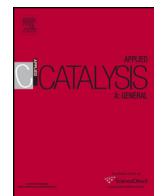




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Improving the catalytic performances of metal nanoparticles by combining shape control and encapsulation

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ABSTRACT

Shape-controlled palladium nanocubes embedded in a mesoporous silica shell were synthesized via successive colloidal and aerosol techniques, and tested in the catalytic hydrogenation of 1,3-butadiene. Encapsulation using the evaporation-induced self-assembly (EISA) process preserves the high activity and selectivity of the nanocubes while inhibiting their agglomeration and shape modification.

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1. Introduction

Heterogeneous catalysis plays a key role in the current energetic and environmental contexts, and sustainable solutions are more and more requested in many research fields, particularly in the area of nanomaterials used as heterogeneous catalysts [1]. The catalyst preparation methods, such as the well-known incipient wetness impregnation, are mostly based on the interactions of a mineral or organic molecular precursor with an oxide surface [2]. However, impregnation techniques suffer different drawbacks such as: (i) the precursor solubility limit, which controls the loading of the active phase; (ii) the instability of concentrated colloidal solutions in the porous media, making difficult the impregnation of high metal contents; (iii) the various post-synthesis steps (drying, calcination, activation) which hardly enable a good control of the metal–support interactions [2]. Moreover, these techniques are also limited as far as complex structures are targeted, such as core (yolk)@shell nanostructures, which appear as potential

alternatives to conventional supported systems for many applications in heterogeneous catalysis [3,4]. These new solids consist of metal cores surrounded by either full or hollowed mesoporous oxide shells, protecting and stabilizing the active nanoparticles (NPs), in particular by inhibiting NP thermal sintering [5–8]. In the specific case of Pd, NPs encapsulated in silica shells have been shown as active and much more stable than traditional impregnated Pd catalysts [9,10]. Furthermore, the catalytic performances of Pd NPs are strongly sensitive to the surface structure [11]. Thus, it appears interesting to explore the silica encapsulation route to stabilize both the size and the *shape* of Pd nanocatalysts.

Many new techniques have been developed in the last decades to synthesize such embedded systems. In particular, the aerosol process combines sol–gel chemistry with evaporation-induced self-assembly (EISA) mechanism. This upscalable and continuous method allows manufacturing mesostructured materials using soft matter chemistry in one-pot synthesis [12]. For instance, using the spray-drying technique, ceria NPs were successfully embedded in mesostructured silica spheres, showing the role of surface functional groups on the NP distribution [13]. In another work, Pd NPs were encapsulated in several types of silica mesostructures (lamellar, cubic or hexagonal) through the use of different surfactants, and exhibited high catalytic activity and ethylene selectivity in the hydrodechlorination of 1,2-dichloroethane [14].

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Table 1
Physicochemical characteristics and catalytic performances of the samples.

	Pd load. ^a (wt.%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Porous volume ($\text{cm}^3 \text{g}^{-1}$)	Desorption pore width ^b (nm)	Pd particle size ^c (nm)	Pd disp. ^d (%)	TOF ^e (s^{-1})
Unsupported Pd	100	–	–	–	10.7 ± 3.6	12.0	0.03
Pd@SiO ₂	6.88 ± 0.03	254	0.24	2.9	13.7 ± 3.7	9.7	0.30
Pd/SiO ₂	1.94 ± 0.05	520	0.81	6.3	3.1 ± 0.9	37.2	0.36

^a Measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

^b Determined by the Barrett–Joyner–Halenda (BJH) method.

^c Obtained from transmission electron microscopy (TEM). The Pd NP size distribution was determined by counting more than 200 particles over ca. 15 micrographs for each sample.

^d Estimated using the Pd particle sizes and shapes established from TEM.

^e Initial turnover frequency of butadiene conversion per surface Pd atom for stationary reaction runs: $\text{TOF}(t=0) = [V/(m_{\text{Pd}}d_{\text{Pd}}kT)][dP_{\text{C}_4\text{H}_6}/dt]_{t=0}$ where V is the reactor volume (120 cm^3), m_{Pd} is the mass of Pd in the catalyst ($m_{\text{Pd}} = m_{\text{catalyst}} \times \text{Pd loading}$), d_{Pd} is the Pd dispersion, k is the Boltzmann constant, T is the temperature and $P_{\text{C}_4\text{H}_6}$ is the partial pressure of butadiene.

In this study, we combined the synthesis of catalytically active and selective shape-controlled Pd NPs with a cubic morphology and the encapsulation into a mesoporous silica matrix using the aerosol technique. The NP shape/morphology is known to have a dramatic influence on catalytic properties [15], but retaining the morphology under catalytic operating conditions remains challenging. Embedding the shape-controlled NPs in a porous matrix could be a way to achieve that goal.

Our method involves a colloidal homogeneous solution containing metallic NPs as well as an oxide precursor and a surfactant to form an aerosol spray of fine colloidal liquid droplets, which are quickly evaporated [16,17]. The catalytic properties were studied using the selective hydrogenation of 1,3-butadiene as model reaction. For this important petrochemical reaction, the challenge consists in enhancing the olefins selectivity by removing butadiene impurities present in the C₄ stream-cracker cut. Hence, the over-hydrogenation leading to the loss of the desired product into butane must be avoided [11,18–21].

2. Experimental

2.1. Preparation methods

Pd nanocubes were firstly synthesized in aqueous solution under Ar atmosphere, following the procedure detailed elsewhere [22]. Using K₂PdCl₄ salt as active metal precursor, hexadecyltrimethylammonium bromide (CTAB) as NPs stabilizer, and sodium ascorbate as reducing agent, a colloidal solution of well-dispersed NPs was obtained. Practically, 180 mL of a K₂PdCl₄ 2.8 mM solution were firstly added to 150 mL of a CTAB 60 mM solution under moderate magnetic stirring at 80 °C under Ar atmosphere. Then, 3 mL of a sodium ascorbate 185 mM solution were added, and the resulting solution was left under stirring at 80 °C for 3 h under Ar. After centrifugation, washing and drying at room temperature, the colloidal solution of Pd NPs was cooled down to 4 °C in order to remove the excess of CTAB by crystallization. The residual amount of CTAB was used as mesoporosity agent. For the atomization step, tetraethylorthosilicate (TEOS) was used as silica precursor and pre-hydrolyzed in an aqueous solution (pH = 2) under vigorous magnetic stirring at room temperature. Then, this solution and the colloidal solution of Pd NPs were mixed together and sprayed using a Büchi B-290 spray drier. After drying and treatment at 350 °C under hydrogen flow, a powder was obtained.

The new Pd@SiO₂ catalyst (6.9 wt.% Pd loading, Table 1) was compared to a conventionally prepared Pd/SiO₂ reference catalyst obtained by incipient wetness impregnation of a Pd(NO₃)₂ solution on a Grace Davison X254 silica support (1.9 wt.% Pd loading). The solid was dried in an oven at 100 °C overnight, then calcined under dry air flow at 450 °C for 2 h.

2.2. Characterization techniques

Nitrogen physisorption isotherms were recorded using a Micromeritics ASAP 2000 apparatus. The samples were outgassed at room temperature for 24 h before the measurements. Specific surface area calculations were carried out using the conventional BET method. Pore size distributions were deduced using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherm. Transmission electron microscopy (TEM) measurements were performed on a F20 Tecnai microscope operating at 200 kV. Samples for TEM were prepared by depositing a drop of an ultrasonically dispersed solution on a standard amorphous carbon-coated copper grid.

2.3. Catalytic testing

The gas-phase catalytic tests were performed with a surface-science setup used for low-surface-area materials. It consisted of an ultrahigh-vacuum (UHV) preparation chamber coupled to a 120 cm³ static stainless-steel reaction cell [23]. As testing conditions, 0.4–2.1 mg of catalyst (weighted using a Sartorius MC5 microbalance accurate within 0.02 mg) were used at near room temperature (24 ± 1 °C) and for initial pressures of reactants equal to 0.5 and 5 Torr for C₄H₆ and H₂, respectively (1 Torr = 133 Pa). The samples were pre-reduced at ca. 200 °C under UHV prior to catalytic measurements. The evolution of hydrocarbon partial pressures during the reaction was followed by continuous sampling and mass spectroscopy analysis. Several reaction runs, separated by evacuation stages down to secondary vacuum, were performed in order to assess the catalyst stability. Finally, the selectivity toward butenes was taken as the ratio of butenes formation rate to butadiene consumption rate, and plotted in function of the amount of consumed butadiene.

3. Results

3.1. Materials structure

The reference catalyst presented roughly spherical NPs of 3.1 nm in mean size (Figs. 1a and 1e, and Table 1). Before atomization, the material prepared by colloidal synthesis exhibited homogeneously distributed nanocubes of 11 nm in size (corresponding to 12% metallic dispersion) (Figs. 1b and 1e, and Table 1), exhibiting a majority of (100) facets. Encapsulation from the aerosol technique produced spherical silica particles with diameter ranging between 100 nm and 20 μm (Fig. 1c), with collections of Pd NPs dispersed inside. Figs. 1c and 1d show the Pd nanocubes located in the outer shell of the silica particles and cores with large pores, ascribed to the competition between hydrolysis/condensation and solvents

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