



# Selective removal of external Ni nanoparticles on Ni@silicalite-1 single crystal nanoboxes: Application to size-selective arene hydrogenation



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## ABSTRACT

Undesired metal nanoparticles located outside zeolite nanoboxes (hollow zeolites) can be formed during the preparation of zeolite-embedded metal nanoparticles. The present work demonstrates that it is possible to use citric acid to selectively leach out most of the external Ni nanoparticles from a Ni@silicalite-1 material. The leached sample exhibited an improved selectivity in the hydrogenation of toluene as compared to that of the bulkier mesitylene.

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## 1. Introduction

Size-selective membranes and catalysts find important applications in separation, sensing and catalytic technologies. Catalytic hydrogenation is an ubiquitous reaction and is used for instance in the synthesis of fine chemicals and fuel upgrading [1–5], with substrate sizes that are similar to that of zeolite pores. The possibility to prepare nanoparticles of metals embedded inside zeolite single crystal nanoboxes was recently reported by our group [6–12] and others [13–15]. The total size exclusion of mesitylene (kinetic diameter = 0.87 nm) from the silicalite-1 (purely siliceous zeolite with MFI topology) hollow nanocrystals was demonstrated and led to a Pt-based catalyst that was highly active for the hydrogenation of toluene (kinetic diameter = 0.58 nm) and totally inactive for that of mesitylene [6]. In addition, we also have reported that these nanoboxes act as nanoreactors [8,9] in which the nanoparticles are encapsulated and protected from sintering by coalescence [10]. We recently reported during an investigation of the effect of tars on methane steam reforming that these silicalite-1-based nanoboxes can retain their structural integrity up to 900 °C [16].

The use of noble metals typically led to single nanoparticles with a well-defined size embedded in silicalite-1 nanoboxes [11,12]. In contrast, the method applied to base metals led in most cases to a large number of nanoparticles present in each nanobox [7]. In the present work dealing with Ni, we show that metal nanoparti-

cles can also be formed outside of the silicalite-1 nanoboxes when attempting to prepare high metal loadings, leading to less size-selective catalysts. The presence of metal nanoparticles outside the nanoboxes can be particularly detrimental if the reactants are converted into deactivating molecules that can poison or block the nanobox surface or pores, as when dealing with reforming or dehydrogenation reactions.

Obuchi and co-workers have previously reported a method to selectively remove Pt nanoparticles located outside ZSM-5 (aluminosilicate zeolite with MFI-type framework) crystals based on a complex procedure involving the use of tetraethylammonium halide salts and halogens [17]. We demonstrate here that a simple citric acid-based treatment can selectively leach out most external Ni nanoparticles, while leaving a significant amount of nanoparticles located inside the nanoboxes. The leached sample exhibited an improved selectivity in the hydrogenation of toluene as compared to that of the bulkier mesitylene.

## 2. Experimental section

### 2.1. Sample synthesis

Silicalite-1 was prepared using tetraethylorthosilicate (TEOS, Aldrich, 98%) and 1 M TPAOH (tetrapropyl ammonium hydroxide) solutions obtained from aqueous TPABr (tetrapropyl ammonium bromide) by exchange with Ag<sub>2</sub>O. The gel of composition SiO<sub>2</sub>-0.4TPAOH-35H<sub>2</sub>O was stirred at room temperature overnight to fully hydrolyze the TEOS, then transferred into a Teflon-lined autoclave and heated at 170 °C under static conditions for 3 days.

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The autoclave was then cooled to room temperature and the solid was centrifuged, washed with water until pH=7 and dried overnight at 90 °C. Finally, the resulting solid was calcined for 12 h at 525 °C in air yielding silicalite-1 crystals of approximately 200 nm × 150 nm × 140 nm in size.

Ni@silicalite-1 materials were synthesized following the previously described generic method for the encapsulation of transition metal nanoparticles in hollow silicalite-1 single crystals [7,10,18,19]. In brief, the 5%Ni@sil-1 was prepared by wet impregnation: 2 mL of an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6(H<sub>2</sub>O) (99.999%, Sigma-Aldrich) with a concentration of 426 mmol/L was added to 1 g of silicalite-1, which had been outgassed at 300 °C overnight. The mixture was stirred at 50 °C until complete evaporation of water to obtain a Ni(NO<sub>3</sub>)<sub>2</sub>/sil-1. The hollow structure was then obtained by treating 1 g of this material in a TPAOH aqueous solution (7.5 mL; 0.55 M) in a Teflon-lined autoclave at 170 °C under rotating conditions for 24 h. The solution was then cooled down, washed with water until pH=7, dried overnight at 90 °C and calcined in air at 450 °C for 6 h to obtain a NiO@silicalite-1. Finally the solid was reduced at 750 °C under H<sub>2</sub> for 3 h with a heating rate of 2.5 °C min<sup>-1</sup> to yield the sample referred to as 5%Ni@sil-1.

The citric acid post-treatment was carried out as follows. 0.5 g of NiO@silicalite-1 was added to 50 mL of a 0.5 mol/L aqueous solution of citric acid (≥99.0%, Sigma-Aldrich). The mixture was stirred vigorously at 80 °C for 2 h. The solution was then centrifuged and washed with water until pH=7 and dried overnight at 90 °C. Finally the solid was reduced at 750 °C under H<sub>2</sub> for 2 h to yield a sample referred to as CitAc Ni@sil-1. This sample was further calcined in air at 550 °C for 6 h to obtain the calc-CitAc Ni@sil-1. A reference catalyst named 5%Ni/sil-1 was produced by direct calcination and reduction of Ni(NO<sub>3</sub>)<sub>2</sub>/sil-1 under the same conditions as 5%Ni@sil-1.

## 2.2. Sample characterization

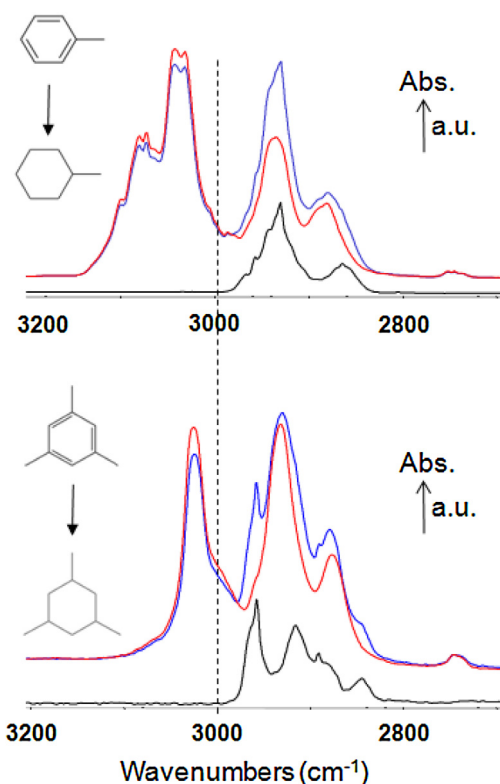
Powder X-ray diffraction patterns (XRD) were recorded to assess the crystallinity of the samples. Diffractograms were collected between 4 and 90° (2θ) with steps of 0.02° and 1 s per step with a Bruker D5005 diffractometer using CuKα radiation at λ = 1.5418 Å.

Elemental analysis of the catalysts was performed using an ICP-OES ACTIVA from HORIBA Jobin Yvon equipped with a CCD detector for the determination of metal loadings. Nitrogen adsorption isotherms were measured at 77 K on a Belsorp-mini from BEL-Japan. Samples were first outgassed under vacuum at 300 °C for 4 h. The *t*-plot analysis was not considered here, in view of the debate on the validity of the *t*-plot method to assess microporosity in hierarchical materials [20].

TEM pictures were obtained using a Jeol 2010 LaB6 microscope operating at 200 kV. Nanoparticle size distributions of zeolite-based materials were obtained by counting 500 nanoparticles using Image J software [21]. Both number-weighted ( $d_{NW} = \sum n_i d_i / \sum n_i$ ) and surface-weighted ( $d_{SW} = \sum n_i d_i^2 / \sum n_i d_i^3$ ) mean diameters were calculated from the nanoparticle size distributions. Each distribution was then modeled using a normal law centered on the corresponding  $d_{NW}$ . Metal dispersions were deduced from the corresponding  $d_{SW}$  considering a cuboctahedral model and a calculation method described by Van Hardeveld and Hartog [22]. EDX measurements were performed using an EDX Link ISIS analyzer from Oxford Instruments to identify the elements present in the samples.

## 2.3. Catalytic tests

Toluene and mesitylene (i.e. 1,3,5-trimethylbenzene) hydrogenation tests were carried out using a fixed-bed continuous-flow reactor consisting of a quartz tube (length 400 mm, 4 mm ID, 6 mm



**Fig. 1.** FT-IR transmission spectra recorded in the 10 cm pathlength gas-cell during the hydrogenation of (top) toluene and (bottom) mesitylene. The spectra in red are those of the reactants. The blue spectra were collected after the reactor at a conversion level of about 9%. The spectra in black are obtained from removing the contribution of the reactant (red) from that of the reactor effluent (blue) and corresponded to (top) methylcyclohexane and (bottom) the two stereoisomers of 1,3,5-trimethylcyclohexane. The area of the bands between 3200 and 3000 cm<sup>-1</sup> were used to quantify arene concentrations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

OD) containing the powdered catalyst held between quartz wool plugs. The system was operated at atmospheric pressure and the samples were reduced *in situ* at 500 °C in pure H<sub>2</sub> for 60 min before the catalytic tests. Aromatic reactants were fed individually using a saturator kept at 0 °C, leading to partial pressures of 912 and 62 Pa for toluene and mesitylene, respectively. A flow of 20 mL/min of pure H<sub>2</sub> was used as reactant carrier gas and fed through one saturator at a time. The catalyst powders were crushed and sieved and the fraction 100–200 μm was selected. Between 60–180 mg of catalyst was used, depending on the activity of the sample, to remain under differential conditions. The gas hourly space velocity was so varied between 6700 and 20000 h<sup>-1</sup>, approximating the catalyst density as being unity.

The reactor effluent was then analyzed using a 10 cm pathlength FT-IR gas cell fitted in a Tensor 27 FT-IR spectrophotometer from Bruker. Typically 32 scans were collected at a resolution of 4 cm<sup>-1</sup> and averaged. The conversion of the arene reactants was determined through integration of spectral regions corresponding to the C–H stretching vibration modes [6,23,24]. Note that FT-IR spectroscopy is commonly used as an analytical technique to investigate complex reaction mixtures as found during alkane dehydrogenation [25] and NO<sub>x</sub> reduction [26]. The IR spectra of toluene and mesitylene are shown in Fig. 1 (spectra in red). The spectra in blue are those of the corresponding reactor effluents at a conversion of ca. 9%. The spectra of the reaction products (black spectra) could be obtained by removing the contribution of the reactants and corresponded to that of methylcyclohexane in the case of toluene (Fig. 1, top) and to that of the two stereoisomers

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