



Highly dispersed platinum in metal organic framework NH₂-MIL-101(Al) containing phosphotungstic acid – Characterization and catalytic performance

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ABSTRACT

The synthesis, characterization (FT-IR, XPS, NMR, UV-Vis), and catalytic performance of Pt supported on phosphotungstic acid (PTA) encapsulated in a metal organic framework (MOF) are reported. The highly dispersed Keggin units of PTA in NH₂-MIL-101(Al), synthesized in one step, act as anchoring sites for the Pt precursor species. After different post-treatments, the resulting catalysts have been tested in the oxidation of CO, the preferential oxidation of CO in the presence of H₂, and the hydrogenation of toluene. Reduction at 473 K results in the formation of small Pt⁰ clusters and Pt²⁺ species. Reduction at 573 K induces the formation of intermetallic Pt–W⁵⁺ species, which exhibit the best CO oxidation activity and a higher selectivity toward CO₂ than alumina supported Pt, resembling the combination of a noble metal on a reducible support. In toluene hydrogenation, the MOF catalysts perform worse than Pt on alumina, ascribed to the too small size of the Pt clusters in the MOF catalysts.

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1. Introduction

During the last few decades, polyoxometalates (POMs) have received a great deal of attention in the catalysis field. The combination of outstanding redox properties, high acidity, and good thermal and chemical stability makes POMs excellent candidates for a wide variety of catalytic applications. Among the different topologies that POMs may present, the most studied are those displaying the well-known Keggin structure [XM₁₂O₄₀]ⁿ⁻ (X = P, Si, Al, ..., and M = W, Mo) [1–3]. The specific surface area of these solid materials is, however, very low, in the range of 1–5 m²/g, making dispersion on a good support crucial for eventual application. Several attempts to support Keggin POMs on materials like silicas, activated carbons, or zeolites have been reported [4–6]. Nevertheless, low POM loadings, agglomeration of POM particles and POM leaching are still unresolved drawbacks. Recently, several studies of Keggin-type POM-based MOFs have been reported. Sun et al. presented the direct encapsulation of POMs in HKUST-1 [7]. At the same time, we reported the successful one-pot encapsulation of a similar POMs in the large and medium mesoporous cavities of MIL-101(Cr), achieving a highly dispersed material with outstanding catalytic performance in different Knoevenagel condensa-

tions and in the dehydration of methanol to dimethyl ether (DME) [8]. The same one-pot procedure was later used for the application of POM-MIL-101 in the dehydration of sugars and the use of POM-NENU in methanol dehydration to DME and the formation of ethyl acetate from acetic acid and ethylene [9,10]. Bajpe et al. studied the acidity of encapsulated POMs in HKUST-1, while templating effects of POM were described for the one-step POM-MOF synthesis [11,12]. These POM templating effects have lately been monitored by *in situ* time-resolved X-ray scattering [13]. Recently, Ma et al. made use of one-pot encapsulation for the adsorption and further hydrolysis of dimethyl methylphosphonate in the so-called NENU-11 (POM-HKUST) [14], and Canioni et al. successfully incorporated different POMs in MIL-100(Fe) through microwave heating [15].

POMs redox chemistry allows for stepwise, multi-electron redox reactions, while the structure remains intact. They participate in catalytic redox processes as electron relays [16]. POMs can be reduced and oxidized very easily. Thus, POMs are used as efficient oxidation catalysts in many oxidation reactions [2,17] or electrocatalytic processes such as methanol oxidation [18] or oxygen reduction [19]. Troupis et al. used the redox properties to reduce noble metal precursors to produce well-dispersed nanoparticles [20]. Furthermore, other authors have proposed polyoxometalate anions as good stabilizers of metal nanoparticles [18,21–25]. For instance, Legagneux et al. grafted platinum complexes on Keggin structures, demonstrating ionic interaction between the polyoxometalate and the platinum complex, with the charge being on

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the platinum atom [26,27]. Similar findings were reported by Kuznetsova et al. where Pt(II) and Pd(II) complexes were immobilized on different Keggin heteropolyanions [2,17].

In this paper, we report the incorporation of Pt species on the polyoxometalatephosphotungstic acid, which is highly dispersed in the MOF NH₂-MIL-101(Al) and the application of the resulting composites in hydrogenation and oxidation reactions. In this way, sintering and leaching of the POM is eliminated and its properties for supporting active species are preserved. These results demonstrate that POM-MOF composites offer excellent possibilities for nanoparticle engineering.

2. Experimental

2.1. Materials

All the chemicals were purchased from Sigma–Aldrich and used without further purification: N,N-dimethylformamide (DMF, >99.9%), ethanol (98%), methanol (99%) aluminum trichloride (AlCl₃·6H₂O > 98%) aminoterephthalic acid (95%), phosphotungstic acid hydrate (POM, H₃PW₁₂O₄₀·xH₂O, reagent grade), and hexachloroplatinic acid (H₂PtCl₆ 37.4 wt.% Pt basis).

A 1 wt.% Pt/Al₂O₃ catalyst (Sigma–Aldrich) was used as a reference in the catalytic performance.

2.2. Catalyst synthesis

For the microwave synthesis of PTA-NH₂-MIL-101(Al), 0.507 g of AlCl₃·6H₂O are dissolved in 15 mL DMF. In addition, 0.564 g of 2-aminoterephthalic acid are dissolved in 15 mL DMF and mixed with the previous solution. Finally, 0.34 mmol of PTA are added to the resulting synthesis mixture. The solution is placed in a Teflon insert, which is subsequently placed in a microwave oven. The temperature is ramped in 5 min from room temperature to 403 K and subsequently maintained for one hour. The microwave oven is operated at 400 W, with 50 RPM and 50% stirring rate. The product is filtered off and washed with methanol under reflux overnight. Finally, the sample is filtered off and dried at 442 K during 8 h in air in a static oven.

Pt impregnation procedure: 1 g of NH₂-MIL-101(Al) or PTA-NH₂-MIL-101(Al) is dispersed in 30 ml of ethanol. A second solution containing 206 mg (0.40 mmol) of hexachloroplatinic acid in 20 ml of ethanol is prepared. The platinum solution is added drop wise to the MOF slurry and stirred for 1 day at room temperature. The resulting material is recovered by filtration and washed twice with methanol and dried in air at 333 K.

2.3. Characterization

2.3.1. Nitrogen adsorption at 77 K

A Quantachrome Autosorb-6B unit gas adsorption analyzer was used to determine the textural properties like specific BET surface area (calculated from data between 0.05 and 0.15 relative pressure) and nitrogen uptake volume at 0.5 relative pressure.

2.3.2. X-ray diffraction

The crystalline structures were analyzed using a Bruker-AXS D5005 with CoK α radiation in the region between 5 and 60 2 θ (°).

2.3.3. Icp-oes

For elemental analysis, the samples were digested in a mixture of 1% HF and 1.25% H₂SO₄ and were analyzed with an ICP-OES Perkin Elmer Optima 3000 dv.

2.3.4. Diffuse reflectance IR spectroscopy

DRIFT spectra were recorded on a Nicolet model 8700 spectrometer, equipped with a high-temperature DRIFT flow cell, DTGS-TEC detector, and a 633-nm laser. The spectra were registered from 4000 to 600 cm⁻¹ after accumulation of 128 scans and a resolution of 4 cm⁻¹. A flow of helium at 20 mL min⁻¹ was maintained during the measurements. Before collecting the spectra, the different samples were pretreated in the same helium flow at 393 K for 30 min KBr was used to perform background experiments.

2.3.5. UV–Vis/NIR diffuse reflectance

Spectra were measured with a Perkin–Elmer Lambda 900 spectrophotometer equipped with an integrating sphere (“Labsphere”) in the 200–800 nm range. The Kubelka–Munk function was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of BaSO₄ as a reference and to obtain absorption edge energies directly from the curves.

2.3.6. FT-IR transmission spectroscopy combined with CO adsorption

Brønsted and Lewis acidities of the samples were determined by CO adsorption at low temperature. To this purpose, 7.5 mg of MOF were pressed (1 ton, 60 s) into self-supporting wafers. The pellets were placed in an IR quartz cell equipped with CaF₂ windows. A movable sample holder allows the sample to be placed in the infrared beam for the measurements or into the furnace for thermal treatments. The cell is connected to a vacuum line for pretreatment. The specimen is activated in vacuum at 453 K for two hours to remove adsorbed species. After this step, the samples were cooled down to 143 K and CO was dosed up to 2 mbar. Transmission spectra were recorded in the 400–4000 cm⁻¹ range at 4 cm⁻¹ resolution on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitting and a mercury cadmium telluride (MCT) cryodetector.

The CO chemisorption experiments were done in the same setup at room temperature, but the pretreatment was done under hydrogen atmosphere (1.5 bar) at two different reduction temperatures, 473 and 573 K.

2.3.7. ³¹P MAS-NMR spectroscopy

³¹P NMR spectra were measured on a Bruker Avance-400 spectrometer at 161.98 MHz using a solid-state probe and zirconium sample holders with inner diameter of 3 mm, spinning at the magic angle with a rate of 11 kHz. The spectral width is 617.76 ppm, acquisition time of 12.5 ms, and acquisition delay of 10 s. Chemical shifts (δ) are reported in ppm referring to an external standard: 0.1 M aqueous solution of H₃PO₄ (0 ppm).

2.3.8. XPS analysis

XPS spectra were recorded on a Kratos AXIS Ultra spectrometer, equipped with a monochromatic X-ray source and a delay-line detector (DLD). Spectra were obtained using the aluminum anode (Al K α = 1486.6 eV) operating at 150 W. Survey scans were measured at a constant pass energy of 160 eV and region scans at 40 eV. The background pressure was 2 × 10⁻⁹ mbar. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) shaped peaks. All binding energies (BE) were referenced to the C 1s line at 284.6 eV, which provided binding energy values with an accuracy of ± 0.2 eV.

The surface atomic ratios were estimated from the integrated intensities corrected by the atomic sensitivity factors [28].

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