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Catalytic carpets: Pt@MIL-101@electrospun PCL, a surprisingly active and robust hydrogenation catalyst

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ABSTRACT

Metal Organic Frameworks (MOFs) have been explored widely to create heterogeneity in a catalytic system. Catalytic applications require the use of stable catalysts with no leaching and easy recovery. In this regard, Pt@MIL-101 is embedded in a poly-ϵ-caprolactone (PCL) matrix by means of electrospinning to create a "catalytic carpet" which is highly efficient and can be recovered within seconds after catalysis. The obtained composite material is completely intact with a homogeneous distribution of the Pt@MIL-101 throughout the electrospun PCL fiber matrix. The catalytic carpet was examined in the hydrogenation of cyclohexene and full conversion was obtained in just 90 min. Remarkably, a very large fraction (>65%) of the total Pt-atoms participate in the reaction. Reusability tests showed that the material could be recycled for at least 4 runs without detectable Cr and Pt leaching displaying the durability of the catalytic carpets. Complete recovery is achieved with zero weight loss while fully preserving the crystalline structure.

1. Introduction

Metal Organic Frameworks (MOFs) are a class of porous crystalline materials constructed by a combination of metal ions/clusters and organic building units. Since their discovery in the late nineties [1], MOFs have been utilized in a variety of applications such as gas storage, gas separation, adsorption and heterogeneous catalysis [2–9], owing to their high surface area, exceptional porosity, chemical tunability and flexibility. In heterogeneous catalysis, these characteristics are examined to obtain novel catalytic systems. Firstly, the careful selection of the inorganic metal clusters and the organic moieties can result into the design of inherent catalytic active sites in the structure [7]. Secondly, as a consequence of their high surface area, porosity and intrinsic functional groups, MOFs have been used as support materials to stabilize catalytic sites [10]. In the past, many metallic complexes have been attached to the organic linkers by coordination chemistry [10,11]. Besides the anchoring of various homogeneous catalysts, several nanoparticles have been deposited onto the inorganic metal clusters, illustrating the versatility of MOFs as support material towards their use in catalysis [8,9]. Despite the interesting properties of MOFs, their practical application has been limited due to issues concerning leaching, low recyclability and material handling. To overcome these issues, MOFs have been deposited onto various types of scaffold materials such as alumina [12], silica [13], graphite oxide [14] and ceramics [15]. However, MOF deposition on "polymer" based scaffolds for catalysis remains rather limited and unexplored [16] in spite of their good mechanical and chemical stability.

Recently, MOF/polymer interfaces have been produced through electrospinning due to the simplicity of processing polymer solutions [17–25]. Electrospinning is a processing technique to form polymer fibers in the micro/nanometer range by stretching a polymer solution with the aid of an electric field. MOFs can be either blended in a polymer solution before electrospinning or they can be synthesized *in situ* with the electrospun fibers to process MOF/polymer composites [26,27]. Such composites have been mostly examined for gas storage, adsorption and anti-microbial properties [17–25]. However, MOF/polymer composites have been rarely investigated for their use in catalysis to synthesize fine chemicals. To the best of our knowledge, they have only been applied for the catalytic degradation of chemical warfare agents [28–30]. A "MOF-cloth" was formed using a rapid assembly of presynthesized UiO-66-NH_2 crystals onto nonwoven polypropylene fibrous mats which incredibly improved the application effectiveness [30].

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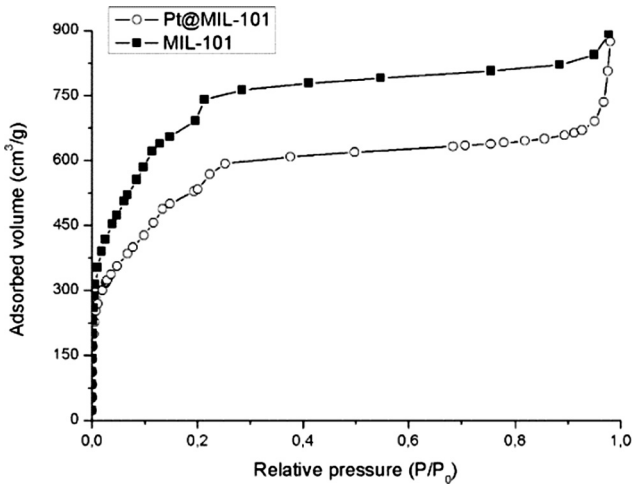

Fig. 1. Nitrogen adsorption isotherms of MIL-101 and Pt@MIL-101.

As a rational extension, in this work, we present a MOF/polymer composite system produced through electrospinning which is utilized for room temperature catalytic hydrogenation. The chromium-based MIL-101 [31] (Materials Institute Lavoisier) was chosen as MOF host due to its high chemical and thermal stability [32]. Inside the cages of MIL-101, Pt nanoparticles were deposited by means of Atomic Layer Deposition as reported in our earlier work [33]. Poly-ϵ-caprolactone (PCL) was used as a polymer scaffold material to produce the composite material as it is one of the most commonly used polymers in the field of electrospinning and has the required mechanical and thermal stability [34–36]. The resulting "catalytic carpet" was used for the hydrogenation of cyclohexene and the activity of the catalytic carpet was compared to that of the pure Pt@MIL-101 powder.

2. Experimental

2.1. Chemicals and characterization

All chemicals were purchased from Sigma Aldrich and used without further purification. Nitrogen adsorption experiments were carried out at −196 °C using a Belsorp-mini II gas analyser. Prior to analysis the samples were dried under vacuum at 90 °C overnight to remove adsorbed water. X-ray Powder Diffraction (XRPD) patterns were collected on ARL X'TRA X-ray diffractometer with Cu Kα radiation of 0.15418 nm wavelength and a solid state detector. Elemental analyses were conducted using a Vista-MPX CCD Simultaneous Inductively Coupled Plasma Emission Spectrometer (ICP-OES). Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 FEG microscope with 4 nm resolution operating at 30 kV. SEM-EDX measurements were performed at room temperature using a Hitachi (Hitachi High-technologies Co. Ltd. Tokyo, Japan) S-3400 N SEM equipped with a Thermo Scientific Noran System 7 energy-dispersive X-ray detector (EDX) for elemental analysis. Chemisorption was performed using an Autosorb-iQ instrument with H_2 analysis gas on Pt metal.

2.2. Synthesis of MIL-101 and Pt@MIL-101

MIL-101 was synthesized according to an adapted procedure reported by Edler et al. [37]. In a typical reaction, 0.665 g terephthalic acid (4 mmol) and 1.608 g $Cr(NO_3)_3{\cdot}9H_2O$ (4 mmol) were added to 20 mL of deionized water in a Teflon-lined autoclave. The autoclave was gradually heated to 210 °C during 2 h in a Nabertherm muffle furnace and kept at this temperature for 8 h. In the following step, the suspension was filtered and stirred in DMF for 24 h at 60 °C to remove unreacted terephthalic acid. Finally, MIL-101 was stirred in 1 M HCl overnight at RT, filtered and dried under vacuum at 90 °C to obtain the pure MIL-101 powder.

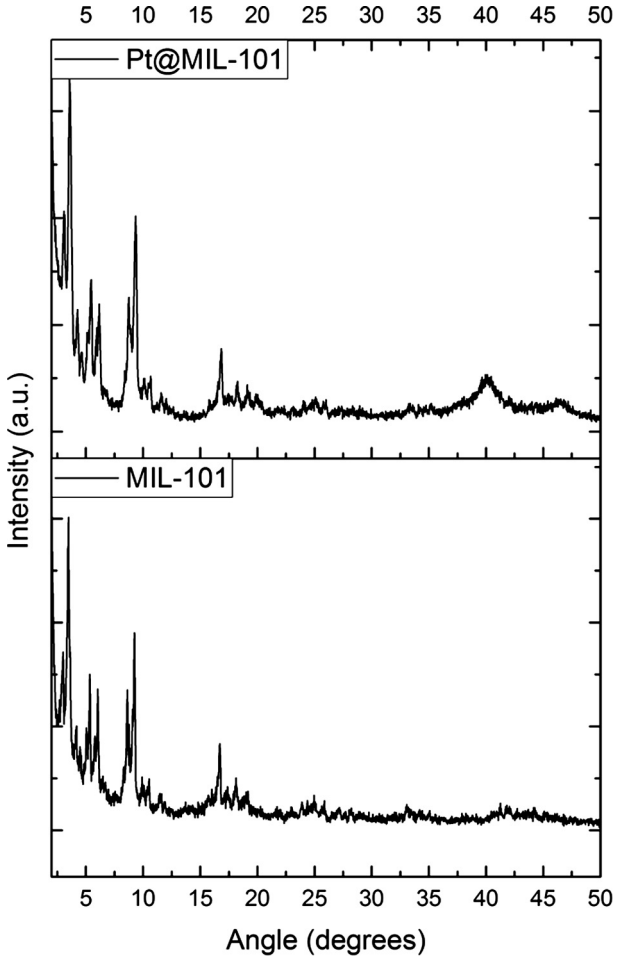

Fig. 2. XRPD patterns of MIL-101 and Pt@MIL-101.

The deposition of Pt nanoparticles inside the cages of MIL-101 was performed by ALD using (methylcyclopentadienyl)-trimethyl platinum ($MeCpPtMe_3$) as Pt source and O_3 as reactant at 200 °C [38]. The depositions were performed in a home built experimental cold-wall ALD chamber. MIL-101 was loaded in a molybdenum sample cup which was then transferred into the ALD reactor. After loading, MIL-101 was allowed to outgas and thermally equilibrate for at least 1 h under vacuum. The solid $MeCpPtMe_3$ precursor (99% Strem Chemicals), kept in a stainless steel container, was heated above its melting point (30 °C), and the delivery line to the chamber was heated to 60 °C. Argon was used as a carrier gas for the Pt precursor. O_3 was produced from a 99% O_2/N_2 mixture with an AC-2025 (USA Inc.) generator, resulting in an O_3 concentration of 200 μg/mL. A static exposure mode was applied during both ALD half-cycles. The pulse time of the $MeCpPtMe_3$ precursor was 10 s, after which the valves to the pumping system were kept closed for another 20 s, resulting in a total exposure time of 30 s. The same pulse time and exposure time was also used for the O_3 [33,38]. Pt@MIL-101 was obtained after 120 cycles of ALD.

2.3. Preparation of the polymer solution

The preparation of the PCL solution was adapted according to the examined solvent. The DCM/DMF polymer solutions were stirred during 12 h before electrospinning. Prior to electrospinning,