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Metal organic framework derived magnetic porous carbon composites supported
gold and palladium nanoparticles as highly efficient and recyclable catalysts for
reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol

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Abstract

The development of low cost noble metal nanocatalysts with high activity and
selectivity, high catalytic performance, convenient separation, and reusability is a
significant challenge. Herein, the magnetic porous carbon (MPC) composite,
synthesized from metal organic framework (MOF) was used as catalyst support to
fabricate gold (Au) and palladium (Pd) nanoparticles (NPs) based nanocatalysts. The
MPC not only provided a large surface area and mesopores on which the active
centers (Au and Pd NPs) were finely dispersed, but also exhibited superparamagnetic
behaviour that enabled the magnetic separation and convenient recovery of the
nanocatalysts from the reaction mixture. Thus, the nanocatalysts were repeatedly used
without loss of catalytic efficiency. Both the Au/MPC and Pd/MPC nanocatalysts
showed excellent catalytic activity for the reduction of 4-nitrophenol. Moreover, the
Pd/MPC nanocatalyst exhibited higher efficiency toward hydrodechlorination of
4-chlorophenol compared to the other reported catalysts. This study indicated that the
noble metal NPs (NMNPs) supported on MOF-derived MPC materials could act as
promising catalysts exhibiting potential applications in numerous NMNPs based
catalytic reactions.
Introduction

Recently, noble metal nanoparticles (NMNPs) based heterogeneous catalysts have attracted significant attention in catalysis science due to their high efficiency in numerous liquid-phase catalytic processes. In particular, gold (Au) and palladium (Pd) nanoparticles (NPs) based catalysts have been extensively studied in many organic catalytic reactions, including C–C cross-coupling, hydrogenation, and methanol oxidation. However, the surface energy of NMNPs increases with decrease in the particle size; therefore, NMNPs with smaller particle size have the tendency of inter-particle aggregation, which eventually reduces the catalytic efficiency of the catalysts. Thus, stability of the NMNPs is another crucial issue for their further application. The emergence of new nanomaterials like mesoporous silica, graphene, MoS$_x$, and metal organic frameworks (MOFs) are promising supports to fabricate composite catalysts to solve this problem. Therefore, carbonaceous materials, such as active carbons, carbon nanotubes, and graphene have been conventionally used as efficient support materials for preparing heterogeneous NMNPs catalysts, due to their excellent mechanical strength, chemical stability, and large surface area. However, the micropores of the active carbons are blocked easily by NMNPs, which further hinders the diffusion of reactants and products into their pore texture. Moreover, NMNPs which are physically attached to carbon nanotubes and graphene always undergo easy leaching during the catalytic process, and leaching is a detrimental factor that induces significant loss of catalytic activity. Only functionalized with N- and O-containing functional groups, the NMNPs on these carbon materials could not be easily leaching and subsequently enhance the catalytic activity. Further, high cost and limited resources of noble metals also hinder their practical application. Therefore, to overcome the above mentioned issues, design of heterogeneous NMNPs catalysts that preserve high metal dispersion and stability during the catalytic reactions and easily separate from the reaction mixture, is of significant importance. In recent years, utilization of MOFs as templates or precursor materials for the production of porous carbon materials has been effectively
demonstrated by taking advantage of the fact that MOFs are porous materials and possess a significant amount of carbon source. Recently reported magnetic porous carbon (MPC) composites, derived from MOF, exhibiting mesoporous structure, magnetic separability, and recyclability act as excellent candidates for the NMNPs catalysts support. However, related work has rarely been reported.

Green chemistry has attracted considerable attention to overcome the problem pertaining to the environmental pollution being encountered by the global population. 4-nitrophenol (4-NP) and 4-chlorophenol (4-CP) are useful industrial chemicals to synthesize numerous chemical products. However, as industrial pollutants they exhibit high toxicity and poor biological degradability. In this aspect, disposal of 4-NP and 4-CP is an area of intensive research. Among most of the reported methods, reduction of 4-NP and hydrodechlorination (HDC) of 4-CP are considered to be the most effective methods because the reduction product 4-aminophenol (4-AP) is an extremely useful organic compound employed in various applications, and the HDC product (phenol) can also be subsequently recycled. Therefore, design of catalysts with high catalytic activity and potential practical application for reduction of 4-NP and HDC of 4-CP is of significant importance. A rapid, efficient, and green approach to the fabrication of efficient catalysts for reduction of 4-NP and HDC of 4-CP is highly desirable.

Based on the abovementioned perspective, in this study, two NMNPs (Au and Pd) were successfully immobilized on the magnetic mesoporous carbon matrices derived from MOFs to fabricate Au/MPC and Pd/MPC nanocatalysts. In both the synthesized nanocatalysts, the MPC provided a large surface area and mesopores on which the active centers (Au and Pd NPs) were finely dispersed. The nanocatalysts could be easily recovered from the reaction mixture by a magnet because of the magnetic NPs encapsulated in the porous carbon, and conveniently reused. Both the Au/MPC and Pd/MPC nanocatalysts exhibited excellent catalytic activity toward the reduction of 4-NP than most of the other reported catalysts. Moreover, the Pd/MPC nanocatalyst showed high efficiency toward HDC of chlorophenols. Thus, this study involving Au/MPC and Pd/MPC nanocatalysts provided a useful platform for exploring
environmentally friendly NMNPs based catalysts with superior activity, convenient recovery, and reusability.

**Experimental**

**Materials**

HPLC grade ethyl acetate (CH$_3$COOC$_2$H$_3$), chloroauric acid (HAuCl$_4$· 4H$_2$O), and palladium chloride (PdCl$_2$) were purchased from Sigma Aldrich and used as received. Fumaric acid, Fe(NO$_3$)$_3$ · 9H$_2$O, N,N-dimethylformamide (DMF), Sodium borohydride (NaBH$_4$), 4-NP, and CPs were purchased from Shanghai Chemical Reagent Co., Ltd. All other chemicals were of reagent grade purchased from Tianjin Guangfu Chemical Company and used as supplied.

**Synthesis of MPC composites**

MPC composites were synthesized according to a similar route reported by Moonhyun Oh. The MOF composite, namely, iron(III) dicarboxylate MOFs of the MIL-88 structure type (Fe-MIL-88A), were first prepared according to the reported solvothermal method using Fe(NO$_3$)$_3$ and fumaric acid. Fumaric acid (1.68 g, 14.4 mmol) and Fe(NO$_3$)$_3$ · 9H$_2$O (6.4 g, 16 mmol) were dissolved in DMF (300 mL). The resulting mixture was then heated to 110 °C and allowed to stand for 1 h. The resulting Fe-MIL-88A was obtained by successively washing with DMF and methanol via centrifugation redispersion cycles. Subsequently, the as-prepared Fe-MIL-88A (2 g) was placed in a tube furnace and calcined up to 700 °C under a nitrogen gas flow at a heating rate of 5 °C min$^{-1}$ and held at 700 °C for 1 h. The resulting MPC composites were cooled to room temperature.

**Preparation of Au/MPC nanocatalyst**

The Au/MPC nanocatalyst was prepared by the method similar to the preparation of Au/C catalyst. Briefly, MPC (500 mg) was dispersed in water (H$_2$O, 20 mL) by ultrasonication. This was followed by the addition of HAuCl$_4$ (10 mL, C$_{Au}$ = 2.5 mg mL$^{-1}$) to the aqueous solution by ultrasonic agitation for 30 min. Subsequently, the
mixture was adjusted to alkalescence using ammonia and freshly prepared NaBH₄ solution was rapidly added to the mixture under vigorous stirring, followed by further stirring for 12 h and ageing for 24 h. The contents were filtered to afford Au/MPC nanocatalyst. The as-prepared nanocatalyst was washed adequately with distilled water and dried in an oven at 60 °C for 5 h.

**Fabrication of Pd/MPC nanocatalyst**

The Pd/MPC nanocatalyst was prepared by the following method: First, PdCl₂ was dissolved in the solution of KCl to form [PdCl₄]²⁻ complex. Second, MPC (800 mg) was dispersed in H₂O (20 mL), and the as-prepared K₂PdCl₄ solution (45 mL, C_Pd = 1 mg mL⁻¹) was added to the dispersion. Third, the reaction mixture was heated to 95 °C and five-fold excess amount of formaldehyde solution (28 wt%) was added dropwise. Subsequently, the mixture was allowed to stir mildly for 1 h at 95 °C. Finally, the Pd/MPC nanocatalyst was separated by filtration, washed with KCl solution (0.5 wt%), and dried over night in an oven at room temperature.

**Characterization**

The morphology of the samples was characterized by transmission electron microscopy (TEM) performed on a Tecnai G² F₃₀ instrument operated at an accelerating voltage of 200 kV. The samples were prepared by dispersing the composites and nanocatalysts in C₂H₅OH deposited on a Cu-based TEM grid. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 20–85°. The electronic states of the surface of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-5702). The values of binding energy were calibrated by using C1s = 284.6 eV as a reference. N₂ adsorption–desorption isotherms were recorded at 77 K in a micromeritics ASAP 2010 (USA). Specific surface areas (SBET) and average pore diameters (DP) were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models, respectively. Magnetic measurements on MPC composites, Au/MPC, and Pd/MPC
nanocatalysts were investigated by a quantum design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 kOe. The Au and Pd content of the prepared nanocatalysts were obtained by the inductively coupled plasma atomic emission spectroscopy (ICP–AES). Ultraviolet–Visible (UV–Vis) spectrophotometer (Varian UV-Cary100) was utilized to obtain the absorption spectra. The conversions of the HDC reactions were estimated by gas chromatography–mass spectrometry (GC–MS, Shimadzu QP2010S).

**General procedure for the reduction of 4-NP**

First, 4-NP aqueous solution (0.01M, 30 µL) was mixed with H₂O (2.5 mL), then freshly prepared aqueous NaBH₄ solution (0.5 M, 0.15 mL) was added, which resulted in the formation of a deep yellow solution. Then, Au/MPC nanocatalyst (0.3 mL, 1 mg mL⁻¹) was added to the yellow solution and the reaction was continued until the solution became colorless. For the reduction reaction catalyzed by Pd/MPC nanocatalyst, the amounts of reactants used were 30 µL of 4-NP solution (0.01M), 2.8 mL of H₂O, 0.15 mL of NaBH₄ solution (0.5M), and 30 µL of Pd/MPC nanocatalyst (concentration 1 mg mL⁻¹). The progress of the reduction process was monitored by measuring the UV–Vis absorption spectra. In order to investigate the reusability of the nanocatalysts, a magnet was used to recover the nanocatalysts for the next catalytic run.

**General procedure for the HDC of 4-CP**

The experiments involving HDC of 4-CP were performed in a 50 mL two-necked flask. The H₂ flow rate was 30 mL min⁻¹ and a stirring speed of 600 rpm were set. In general, catalyst (10 mL, 1 mg mL⁻¹), sodium hydroxide (NaOH) solution (10 mL, 0.05 M), and chlorophenol (10 mL, 0.05 M) were mixed in a 50 mL two-necked flask, followed by bubbling H₂ into the reaction mixture and the reaction was timed immediately. The sample was collected with a glass syringe at an interval of 10 min, and then filtered through a 0.45 µm membrane filter. The filtrate was extracted by CH₃COOC₂H₅, then the reaction conversion of the HDC reaction was estimated by
To evaluate the reusability of the Pd/MPC nanocatalyst in the HDC reaction, the nanocatalyst was recovered using a magnet, washed with water, and dried in vacuo at room temperature for the subsequent catalytic run. Moreover, the catalytic procedure was repeated six times.

Results and discussion

The MPC nanorods were derived from the Fe-MIL-88A MOFs by a pyrolysis method. In this study, mesoporous MPC composites consisting of pores with diameters of about 10.9 nm, and surface area of about 138.74 m² g⁻¹, exhibited excellent magnetic property. Therefore, MPC was employed to fabricate highly efficient catalysts (Au/MPC and Pd/MPC) exhibiting high catalytic activities and performance, and convenient magnetic recovery.

Characterization of the catalysts

![TEM images of MPC, Au/MPC, and Pd/MPC](image)

The morphology and particle size of the MPC are displayed in Fig. 1a, which clearly shows that MPC consists of magnetic iron oxide wrapped in the carbon (C) framework. Moreover, the Figure exhibits that MPC has a diameter and length of
about 400 and 1,000 nm, respectively. The nanocatalysts Au/MPC and Pd/MPC were prepared by impregnation–reduction method. Fig. 1b and 1c present the morphologies of the Au/MPC and Pd/MPC nanocatalysts, respectively. Compared to Fig. 1a, the TEM images exhibit tiny black dots without aggregation for both Au NPs (Fig. 1b) and Pd NPs (Fig. 1c). Fig. 1d and 1e show high angle annular dark field–scanning transmission electron microscopy (HAADF-STEM) images displaying a more detailed elemental distribution of the nanocatalysts. The Figures clearly demonstrate that the MPC support is mainly composed of C and Fe elements. As the catalytic activity center, Au NPs (Fig. 1d) and Pd NPs (Fig. 1e) are dispersed in the MPC, indicating the immobilization of Au NPs and Pd NPs in the pores of the mesoporous MPC. From the HAADF-STEM image and the Au mapping image (Au-L), it can be seen that the particle size of the Au NPs was mainly located in 5-8 nm. The particle size of Pd NPs measured from Pd/MPC was about 5 nm.

Fig. 2. PXRD patterns of MPC, Au/MPC and Pd/MPC (Fe$_2$O$_3$ (JCPDS No. 39-1346), Fe$_3$C (JCPDS No. 35-0772)).

PXRD analysis provided evidence for the composition of the as-synthesized samples. Fig. 2 shows the PXRD patterns of MPC, revealing that γ-Fe$_2$O$_3$ and iron carbide (Fe$_3$C) are the major products of the pyrolysis of Fe-MIL-88A at 700 °C. In fact, both γ-Fe$_2$O$_3$ and magnetite (Fe$_3$O$_4$) have almost similar PXRD patterns; therefore, they could not be easily distinguished by using only PXRD data. The formation of γ-Fe$_2$O$_3$ rather than Fe$_3$O$_4$ is confirmed from the XPS spectrum (Fig. 3), the characteristic satellite peak for γ-Fe$_2$O$_3$ was observed at 719.9 eV.$^{24}$ The PXRD patterns of Au/MPC
and Pd/MPC (Fig. 2) also show the characteristic peaks of $\gamma$-Fe$_2$O$_3$ and Fe$_3$C.

However, compared to MPC, the PXRD patterns of Au/MPC show three characteristic peaks located at $2\theta = 38.4$, 64.9, and 77.8° corresponding to the (111), (220), and (311) lattice planes of Au (JCPDS, No. 4-0784), respectively. The PXRD patterns of Pd/MPC also exhibit characteristic Pd NPs diffraction peaks ($2\theta = 39.8$ and 47.5°) corresponding to (111) and (200) reflections, respectively. The above mentioned PXRD results indicated that the Au and Pd NPs were successfully immobilized in the pores of the mesoporous MPC support.

![XPS wide-scan spectra of (a) Au/MPC and (b) Pd/MPC nanocatalysts. EDS spectra of (c) Au/MPC and (d) Pd/MPC nanocatalysts.](image)

XPS was performed to investigate the chemical state of the surface of obtained Au/MPC and Pd/MPC nanocatalysts (Fig. 3). Both the Fig. 3a and b show the broad peaks assigned to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively. Moreover, characteristic peak for $\gamma$-Fe$_2$O$_3$ at 719.9 eV is also observed. Fig. 3a shows the XPS spectrum of Au/MPC nanocatalyst displaying two obvious Au 4f peaks, indicative of metallic Au at binding
energies of 83.9 and 87.4 eV, in Au 4f\textsubscript{7/2} and Au 4f\textsubscript{5/2} levels, respectively. Moreover, for the Pd/MPC nanocatalyst (Fig. 3b), the characteristic peaks of metallic Pd NPs are also clearly observed, the peaks at 335.3 and 340.5 eV are assigned to Pd 3d\textsubscript{5/2} and Pd 3d\textsubscript{3/2}, respectively. The energy dispersive spectroscopic (EDS) analysis was utilized to determine the chemical composition of Au/MPC and Pd/MPC (Fig. 3c and d). Fig. 3c exhibits the peaks corresponding to Fe, Au, C, and O revealing the compositions of Au/MPC. The peaks corresponding to Fe, Pd, C, and O are presented in Fig. 3d, indicating the compositions of Pd/MPC.

Table 1. The physical property parameters of MPC, Au/MPC and Pd/MPC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Samples</th>
<th>Surface area (m\textsuperscript{2}/g)</th>
<th>Pore size (nm)</th>
<th>Au loading (wt%)</th>
<th>Pd loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MPC</td>
<td>138.74</td>
<td>10.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Au/MPC</td>
<td>118.06</td>
<td>8.5</td>
<td>3.93%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd/MPC</td>
<td>101.9</td>
<td>8.9</td>
<td>5.11%</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. N\textsubscript{2} sorption isotherms of MPC, Au/MPC and Pd/MPC (Inset is the pore size distributions of MPC, Au/MPC and Pd/MPC).

The mesoporosity of the as-synthesized materials was determined by nitrogen physisorption measurements. The nitrogen adsorption–desorption isotherms of MPC, Au/MPC and Pd/MPC are type-IV with a distinct hysteresis loop (Fig. 4). The main pore size distribution of MPC, Au/MPC, and Pd/MPC is in the range from 5–20 nm (Fig. 4 inset). Both the results indicated that the MPC support, the Au/MPC and Pd/MPC nanocatalysts had the mesoporous architecture. The physical property parameters of MPC, Au/MPC, and Pd/MPC are listed in Table 1. The surface area and pore size for MPC are 138.74 m\textsuperscript{2} g\textsuperscript{-1} and 10.9 nm, respectively. When loaded with Au or Pd NPs, the surface area and pore size of the samples reduced to 118.06 m\textsuperscript{2} g\textsuperscript{-1} and
8.5 nm, respectively for Au/MPC, and 101.9 m$^2$ g$^{-1}$ and 8.9 nm, respectively for Pd/MPC. The values of weight percentage of Au or Pd loading obtained from ICP–AES measurement are also listed in Table 1. There are about 3.93 wt% of Au NPs and 5.11 wt% of Pd NPs in Au/MPC and Pd/MPC nanocatalysts, respectively.

The superparamagnetic behaviour of the magnetic NPs is demonstrated by VSM curves (Fig. 5). The magnetic saturation value for MPC composite was 76.5 emu g$^{-1}$. When loaded with Au or Pd NPs, the magnetic saturation values reduced to 48.5 and 51.3 emu g$^{-1}$, respectively for Au/MPC and Pd/MPC nanocatalysts. Therefore, the Au/MPC and Pd/MPC nanocatalysts could be efficiently separated from the reaction solution by an external magnetic force, and could be reused and recycled (Fig. 5 inset).

![Fig. 5. Room temperature magnetization curves of MPC, Au/MPC and Pd/MPC.](image)

**Reduction of 4-NP**

![Scheme 1. MPC utilized as catalysts support to fabricate Au and Pd NPs based nanocatalysts.](image)

Notably, metallic Au and Pd NPs are excellent catalysts with high activity and
Thus, Au and Pd NPs immobilized on MPC support could serve as a practical recyclable heterogeneous catalyst (Scheme 1).

The catalytic performance of the as-prepared Au/MPC and Pd/MPC nanocatalysts was initially evaluated by the reduction of 4-NP to 4-AP using excess of NaBH₄ under ambient conditions. Aqueous solution of 4-NP is pale yellow and exhibits a characteristic absorption peak centered around 317 nm (Fig. 6a). However, on addition of NaBH₄, the color of the solution changes to yellow (Fig. S1a) indicating the formation of 4-nitrophenolate ions due to the alkalinity of the solution. A new absorption band appears at 400 nm (Fig. 6a) and the initial absorption band at 317 nm vanishes completely. Interestingly, the reduction of the nitro-group does not proceed in the absence of catalysts because the kinetic barrier between the mutually repelling negative ions, 4-NP and BH₄⁻, is extremely high. Moreover, the reaction does not proceed even for 5 h when catalyzed by MPC alone (Fig. S1b). In contrast, addition of an appropriate amount of catalyst (0.3 mg Au/MPC or 0.03 mg Pd/MPC) into the solution resulted in decolorization of the 4-nitrophenolate solution, and simultaneously the peak intensity at 400 nm successively decreased with the appearance of the new adsorption peak at 300 nm (Fig. 6b and 6c). The above phenomena indicated that the catalyst support MPC had no catalytic activity in the reduction of 4-NP. When MPC was functionalized with Au or Pd NPs, high catalytic activity was then endowed to reduce 4-NP to 4-AP. The catalytic mechanism of the reduction reaction was described as follows: adsorption of both the donor BH₄⁻ ions and the acceptor 4-NP molecules onto the catalytic centers led to the electron transfer from BH₄⁻ to 4-NP which resulted in the reduction of 4-NP. The UV–Vis spectra showed an isosbestic point (313 nm), illustrating that the catalytic reduction of 4-NP resulted in the formation of only 4-AP; thus excluding the formation of any byproduct.
Fig. 6. UV-Vis spectra of 4-NP before and after adding NaBH₄ solution (a), the successive reduction of 4-NP to 4-AP over Au/MPC nanocatalyst (b) and Pd/MPC nanocatalyst (c).

In the catalyzed reduction reaction, the concentration of NaBH₄ was very high and could be considered as a constant during the reaction period; therefore, the rate constant for the reduction of 4-NP followed first-order kinetics. Plot of ln(C_t/C₀) versus time is obtained based on the absorbance as the function of time, and good linear correlations are observed, as shown in the reduction reaction catalyzed by Au/MPC (Fig. 7a) and Pd/MPC (Fig. 7b), indicating that the reactions follow first-order kinetics. The reaction rate constant k was calculated to be 1 × 10⁻² s⁻¹ and 1.2 × 10⁻² s⁻¹ for the reaction catalyzed using Au/MPC and Pd/MPC nanocatalyst, respectively. For a quantitative comparison, the activity parameter k' = k/C_M was introduced, which is defined as the ratio of the rate constant k to the concentration of the active sites (Au or Pd) added. Thus, the k' was calculated to be k_Au' = 2.54 L s⁻¹ g⁻¹ and k_Pd' = 23.48 L s⁻¹ g⁻¹ for Au/MPC and Pd/MPC nanocatalyst, respectively. Obviously, Pd/MPC exhibited higher catalytic activity than Au/MPC. The values of activity parameter k' reported for Au NPs based catalysts, namely, Au/graphene...
catalyst was 0.396 L s\(^{-1}\) g\(^{-1}\). However, the Pd NPs based catalyst Pd/PPy has the activity parameter k’ of about 2.94 L s\(^{-1}\) g\(^{-1}\). Thus, it could be concluded that the synthesized nanocatalysts, Au/MPC and Pd/MPC, exhibited comparable or much better catalytic activity than the reported catalysts for 4-NP reduction owing to their higher catalytic performance, better selectivity, and longer stability.

**Fig. 7.** Plots of C\(_t\)/C\(_0\) and ln(C\(_t\)/C\(_0\)) versus reaction time for the reduction of 4-NP over Au/MPC nanocatalyst (a) and Pd/MPC nanocatalyst (b).

**HDC of 4-CP**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>C(_2)H(_5)OH</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>CH(_3)COOC(_2)H(_5)</td>
<td>22.7%</td>
</tr>
<tr>
<td>3</td>
<td>NaOH</td>
<td>DMF</td>
<td>14.7%</td>
</tr>
<tr>
<td>4</td>
<td>NaOH</td>
<td>H(_2)O</td>
<td>99.9%</td>
</tr>
<tr>
<td>5</td>
<td>Na(_2)CO(_3)</td>
<td>H(_2)O</td>
<td>78.7%</td>
</tr>
<tr>
<td>6</td>
<td>CH(_3)COONa</td>
<td>H(_2)O</td>
<td>93.4%</td>
</tr>
<tr>
<td>7</td>
<td>NH(_3)·H(_2)O</td>
<td>H(_2)O</td>
<td>58.9%</td>
</tr>
<tr>
<td>8</td>
<td>(C(_2)H(_5))(_3)N</td>
<td>H(_2)O</td>
<td>68%</td>
</tr>
</tbody>
</table>

Table 2. Effect of different solvents and different bases.

Conditions: 4-CP (0.5 mmol, 64.3 mg), base (0.5 mmol), solvent (30 mL), Pd/MPC (10 mg), H\(_2\) balloon (30 mL/min), 25 °C, 2 h.

The abovementioned results clearly indicated that the Au/MPC and Pd/MPC nanocatalysts exhibited the favorable catalytic performance toward reduction of 4-NP. Their catalytic property and recyclability were also evaluated by performing HDC of
4-CP. Pd/MPC was used as a probe catalyst to optimize the reaction conditions and to screen the best reaction conditions; therefore, a series of reactions was performed using several bases and solvents to obtain the best possible combination (Table 2). In order to prevent the poisoning of the catalysts, hydrochloric acid (HCl) produced during the HDC process was neutralized by the bases added to the reaction system. Therefore, NaOH was first used as neutralizer to test different solvents (Table 2, Entries 1–4). The yields of phenol in C₂H₅OH, CH₃COOC₂H₅, DMF, and H₂O were 5, 22.7, 14.7, and 99.9%, respectively. These low yields of phenol obtained in the abovementioned organic solvents were mainly attributed to the low solubility property of NaOH that leads to the poisoning of the nanocatalyst. Therefore, based on the above mentioned results, H₂O was considered to be the best solvent for the HDC of 4-CP. To further optimize the reaction conditions; different bases were tested in the aqueous solution (Table 2, Entries 4–8). The results indicated that the yield of the phenol in the HDC reaction was significantly affected by the basicity of neutralizer for HCl as reported by Zahara M. de Pedro. The highest reaction rate and phenol yield were achieved when the process was carried out in strong base (NaOH) solution. In contrast, when a weak base was employed (Na₂CO₃, CH₃COONa, NH₃·H₂O, or (C₂H₅)₃N), low yield of phenol was obtained under the same reaction conditions. Therefore, NaOH was considered as the optimized base for HDC reaction.

![Fig. 8. Time evolution of the yield of phenol with Au/MPC and Pd/MPC nanocatalysts.](image-url)
Thus, the catalytic property of Au/MPC and Pd/MPC in the HDC of 4-CP was investigated using NaOH and H₂O as the optimized base and solvent, respectively. Fig. 8 shows that the time-dependent yield of phenol increases gradually, and reaches almost 100% in 2 h when catalyzed by Pd/MPC composite under the optimized reaction conditions, indicating that the Pd/MPC was highly active in HDC of 4-CP. However, negligible amount of phenol was generated when the reaction was catalyzed by Au/MPC, indicating that Au/MPC was almost inert toward the HDC of 4-CP. The reason was that the catalyst support mesoporous carbon was non-reducible, thus, like other non-reducible material (Al₂O₃ or SiO₂) supported Au catalysts, Au/MPC was almost inert toward the hydrogen-mediated reactions. However, Au supported on the reducible support TiO₂ and Fe₃O₄ has been achieved superior catalytic response in nitroaromatic and acetylene hydrogenation, respectively.

The reaction pathway of HDC of 4-CP over Pd/MPC was described as follows: First, hydrogen was allowed to adsorb on the surface of the Pd NPs which dissociated into two active hydrogen atoms; subsequently, the C–Cl bond of the adsorbed 4-CP was attacked by the active hydrogen atoms to afford HCl and phenol. Simultaneously, HCl was neutralized rapidly by NaOH; thus, avoiding the accumulation of HCl on the surface of the catalyst.

Fig. 9. (a) Time evolution of the yield of phenol and conversion of 4-CP with Pd/MPC nanocatalyst, (b) plots of Cᵣ/C₀ and ln(Cᵣ/C₀) versus reaction time for the HDC of 4-CP over Pd/MPC nanocatalyst.

The time evolution curves corresponding to the yield of phenol and conversion of 4-CP using Pd/MPC nanocatalyst are shown in Fig. 9a. H₂ was in the excessive amount compared to 4-CP because it was bubbled into the reaction mixture; therefore,
it was considered as constant during the reaction period, thus the HDC reaction was assumed to be pseudo first-order.\(^{56}\) Therefore, by using the reaction kinetic \(\ln(C_t/C_0) = -kt\), the reaction rate constant \(k\) was calculated to be 0.084 min\(^{-1}\) for the reactions catalyzed at room temperature with Pd/MPC nanocatalyst (Fig. 9b). The activity parameter \(k'\), which is defined as the ratio of the rate constant \(k\) to the concentration of the active sites, was calculated to be 4.93 L g\(^{-1}\) min\(^{-1}\). Compared to the reported Pd NPs based catalytic systems PdAl-IMP-1.5 (2.33 L g\(^{-1}\) min\(^{-1}\)),\(^{57}\) and Ni@Pd/KCC-1 (1.88 L g\(^{-1}\) min\(^{-1}\)),\(^{58}\) obviously, the Pd/MPC nanocatalyst exhibited higher catalytic activity, which was mainly attributed to the highly dispersed Pd NPs in the pores of the MPC that enhanced the accessibility between the Pd active sites and 4-CP. Thus, easy accessibility of the active sites favored the high catalytic activity.

![Fig. 10. Time evolution of the conversion of 4-CP and yield of phenol and cyclohexanone with 50 mg (a) and 100 mg (b) Pd/MPC nanocatalyst.](image)

**Table 3.** Catalytic HDC of different substrates over Pd/MPC nanocatalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants</th>
<th>Main products</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Reactant" /></td>
<td><img src="image" alt="Product" /></td>
<td>99.8%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Reactant" /></td>
<td><img src="image" alt="Product" /></td>
<td>99.9%</td>
</tr>
<tr>
<td>3(^a)</td>
<td><img src="image" alt="Reactant" /></td>
<td><img src="image" alt="Product" /></td>
<td>96.8%</td>
</tr>
<tr>
<td>4(^b)</td>
<td><img src="image" alt="Reactant" /></td>
<td><img src="image" alt="Product" /></td>
<td>99.9%</td>
</tr>
</tbody>
</table>

Conditions: Chlorophenol (0.5 mmol), base (1 equiv.), solvent (30 mL), Pd/MPC (10 mg), \(H_2\) (30 mL/min), 25 °C, 2 h.

\(^a\) 1 equiv. of NaOH, \(^b\) 2 equiv. of NaOH.
Under the optimized reaction conditions using Pd/MPC nanocatalyst (10 mg), the HDC of 4-CP was completed in 2 h, and phenol was the only product detected by the GC–MS. When the catalyst dosage is increased to 50 and 100 mg, the HDC of 4-CP is completed in 30 (Fig. 10a) and 20 min (Fig. 10b), respectively. When the reaction is continued for 2 h, 1.47% and 2.8% of cyclohexanone are generated along with phenol (Fig. 10). This was attributed to the high concentration of catalyst that showed activity for hydrogenation of phenol to form cyclohexanone as the byproduct. This phenomenon has also been reported in the literatures.\textsuperscript{56, 59, 60} Effect of dosage of 4-CP on the HDC of 4-CP catalyzed by 10 mg of Pd/MPC was also studied, and the results are illustrated in Fig. S2a. A decrease in yield of phenol was observed with increasing dosage of 4-CP. The HDC reaction could be completed in 2 h under the optimized reaction conditions with 10 mg Pd/MPC nanocatalyst and 0.5 mmol of 4-CP. However, when 2 and 8 mmol of 4-CP were introduced, the yields of phenol were only 81 and 64.4% in 2 h, respectively (Fig. S2a). Effect of Pd loading of the Pd/MPC for the HDC of 4-CP was further investigated. As shown in Fig. S2b, with higher Pd loading (7.83%), the Pd/MPC catalyzed HDC of 4-CP could be completed in 1 h. While with lower Pd loading (2.56%), in the same reaction conditions, the HDC reaction could not be completed in 2 h, the yield of phenol was about 97%.

In order to investigate the application of the Pd/MPC nanocatalyst for HDC of chlorophenols, we also studied the HDC of 2-CP, 3-CP and 2,4-dichlorophenol (2, 4-DCP) catalyzed by Pd/MPC nanocatalyst and the corresponding results are listed in Table 3. The values listed in Table 3 reveal that, 3-CP and 2-CP are also almost completely transformed into phenol within 2 h. However, for 2, 4-DCP, when just 1 equivalent of NaOH was introduced, the main product was 2-CP; further, it was completely transformed into phenol when 2 equivalents of NaOH were added into the reaction mixture. Thus, 2-CP was the only intermediate product identified in the HDC of 2, 4-DCP reaction system as described in the previous work.\textsuperscript{61} The completely HDC of 2, 4-DCP was accomplished by two steps.\textsuperscript{50} The reason was ascribed probably to the electronic and steric hindrance of 2, 4-DCP.
Fig. 11. The reusability of Au/MPC for the reduction of 4-NP with NaBH$_4$ and Pd/MPC for the HDC of 4-CP.

Moreover, the advantage of the Au/MPC and Pd/MPC nanocatalysts prepared in this study was that the catalysts were conveniently recovered by magnetic separation. It is well known that magnetic separation is an appealing alternative for filtration or centrifugation as it prevents the loss of catalyst and improves its reusability for the liquid-phase reactions.$^{62}$ The recovery and reusability of Au/MPC and Pd/MPC were investigated by the reduction of 4-NP and HDC of 4-CP, respectively. Fig. 11 shows that the Au/MPC nanocatalyst could be successfully recycled and reused for at least six times with a stable conversion above 96% within 10 min in the reduction of 4-NP. However, in the HDC of 4-CP, there was a slight decrease in the conversion of 4-CP with the increase in the number of runs, probably due to the gradual leaching of Pd NPs with repeated magnetic separation and poisoning of Pd NPs active centers via oxidation or catalyst inactivation. The ICP–AES analysis also showed that after six catalytic runs there were about 3.76 wt% of Au and 4.92 wt% of Pd in Au/MPC and Pd/MPC nanocatalysts, respectively, indicating slight leaching of the noble metals. However, the TEM revealed that the morphologies of the Au/MPC and Pd/MPC nanocatalysts were still maintained even after six catalytic cycles (Fig. S3a and b). The EDX mapping indicated that the Au and Pd NPs were still dispersed on the MPC support (Fig. S3c and d). Additionally, the EDS spectra of Au/MPC and Pd/MPC nanocatalysts also confirmed that the chemical composition did not change after six cycles (Fig. S3e and f).
Conclusions

This study demonstrated that the immobilization of Au and Pd NPs within the pores of the mesoporous MPC efficiently enhanced the catalytic activities, separation, and reusability of the Au/MPC and Pd/MPC nanocatalysts. Both the Au/MPC and Pd/MPC nanocatalysts exhibited comparable or better catalytic activity than most of the reported catalysts used for the reduction of 4-NP. Moreover, the Pd/MPC nanocatalyst displayed high efficiency in the HDC of chlorophenols. Further, the MPC based nanocatalysts could be easily recovered from the reaction mixture by using a magnet and reused for the next catalytic run. These methods represent an eco-friendly strategy to dispose nitro- and chloro-compounds. This study provides a general methodology for the preparation of other NMNPs/MPC nanocomposites with high catalytic activity and good magnetic recycling properties for various industrial catalytic applications.

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References

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C. B. Molina, L. Calvo, M. A. Gilarranz, J. A. Casas and J. J. Rodriguez, J.


Graphical Abstract

The magnetic porous carbon composite which has been synthesized from metal organic framework is used as catalysts support to fabricate Au and Pd NPs based nanocatalysts.