



# Porous materials confining noble metals for catalytic nitroaromatics reduction: controllable synthesis and enhanced mechanism

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This review relates to the controllable synthesis and enhanced mechanism of porous materials confining noble metals in catalytic nitroaromatics reduction. The wide application of nitroaromatics in chemical industry and daily life has caused severe environmental contamination and health threats. To address the problems, catalytic nitroaromatics reduction with producing value-added anilines is considered to be an efficient strategy. Considering high catalytic activity and specific surface area of noble metals, noble-metal based catalysts are generally employed to catalyze nitroaromatics reduction. Among them, porous materials confining noble metals exhibit superior catalytic activity, selectivity and stability in catalytic nitroaromatic reduction, owing to confined active metallic sites, pore size restriction and well dispersion of noble metals. Therefore, we summarized the controllable synthetic strategies and enhanced mechanism of noble metals confined in four porous materials (porous carbon, zeolites, MOFs, and POPs).

> Porous materials confining noble metals for catalytic nitroaromatics reduction: controllable synthesis and enhanced mechanism

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# Abstract

In the field of nano catalysis, noble metals nanoparticles (NPs) have aroused tremendous attention owing to their superb catalytic efficiency, especially in catalytic nitroaromatics reduction. To overcome the disadvantages of noble-metal based catalysts, such as leach or aggregation of metal NPs, a wide variety of porous materials have been explored as confining units for improving the activity. By confining noble metal NPs in porous materials, unprecedentedly high catalytic activity and unique size selectivity, enhanced recyclability can be realized in catalytic reduction of hazardous nitroaromatic compounds. In this review, the advanced progress in controlled synthesis strategies of porous materials confining noble metals is elucidated. Then, the confinement effect mediated by cavities encapsulation of noble metals in porous carbon, zeolites, metal-organic frameworks (MOFs), and porous organic polymers (POPs) are emphatically outlined. Furthermore, the size effect from NPs to sub-nanoscale species (single atom, metal clusters) under confining environment is elaborated. We hope our work will provide a fundamental understanding about superiority of encapsulated catalysts over conventional supported catalysts, and pave an avenue for rationally designing multifunctional porous materials confining noble metals for more efficient reduction of nitroaromatic derivatives.

Keywords: Noble metals; Porous framework; Confinement effect; Nitroaromatics Reduction

#### 1. Introduction

Up to date, noble metals (e.g. Ru, Ag, Au, Pt, and Pd) have attracted tremendous attention as a kind of promising catalytic materials, ascribed to their excellent performances, such as unique surface plasmon resonance effect, large specific surface area, and fast charge transfer efficiency for general applications.<sup>1-4</sup> Nevertheless, there are also some disadvantages such as aggregation owing to their high surface energy, which destroy integrity and catalytic efficiency of noble metal-based catalysts and thus restrict the practical application.<sup>5-7</sup> To overcome the shortcoming, a series of strategies have been employed by anchoring noble metals onto the surfaces of the supports, encapsulating into the cavities of porous materials, and constructing multiple hybrid complexes. These protocols can acquire the highly diffused noble metal NPs and boost their stabilization, thus widening the applications.

Among them, encapsulating noble metal NPs into porous materials has been proved to be the most efficient strategy. Ascribed to corresponding spatial isolation of active metallic sites, encapsulated composites enhance the approachability of substrates and accelerate the electron transfer process. A variety of porous materials, including porous carbon, zeolites, MOFs, and POPs, have been developed as ideal supports.<sup>8-10</sup> Aroused from their well-defined framework, abundant cavities with hierarchical and tunable scales, and outstanding physiochemical stability, porous materials have been envisaged as perfect candidates to confine noble metal NPs for more efficient catalysis.<sup>11-13</sup> By pores confinement, higher catalytic activity, size-dependent selectivity, and enhanced stability can be obtained.<sup>14-16</sup>

Nitroaromatics, as crucial manufacturing products and raw materials in chemicals production, are widely used in chemistry industry and discharged into wastewater, which consequentially causes severe environmental risks and health hidden danger to human. For nitroaromatics contaminated water, catalytic reduction to produce corresponding anilines has been recognized as an effective treatment method. With extensive explorations, highly effective catalysts for nitroaromatics reduction have been tremendously advanced in several decades. As mentioned above, porous materials confining noble metals have been widely employed in catalytic nitroaromatics reduction, which exhibit enhanced catalytic efficiency. Assisted by the active metallic sites confined in porous materials, fast and highly selective conversion of nitroaromatics towards diverse anilines can be realized.<sup>17-19</sup>

At present, some relevant reviews have reported one certain type of porous framework confining noble metals, mainly including zeolites and MOFs. As for zeolites confining noble metals, some similar reviews gave broad overviews from confined synthesis to confined catalysis, which has been a relatively mature research area.<sup>20-22</sup> Other related reviews summarized the confined synthesis methods, characterization Au@MOFs.23 techniques and diverse catalytic applications of metal nanoparticles/MOFs,<sup>24</sup> nanoparticles/MOFs composites,<sup>25</sup> and nanoentities/MOFs.<sup>26</sup> As for noble metals confined in porous carbon and POPs, there are few comprehensive reviews involving their controllable synthesis and mechanistic analysis. In addition, as mentioned above, porous materials confining noble metals for catalytic nitroaromatics reduction has been widely investigated so far, whereas the related review is still lack.

Based on these considerations, a systematical summarization focusing on the synthesis methods of noble metals encapsulated inside four porous materials (porous carbon, zeolites, MOFs, and POPs), catalytic performance, and enhanced mechanism in nitroaromatics reduction are demanded. Therefore, we focus on the advancement of this field in recent years and investigate three typical synthesis strategies for porous materials confining noble metals, and then illustrate the confinement effect reflected in catalytic nitroaromatics reduction. Subsequently, unique representation of noble metals from nanoscale to sub-nano scale under confinement is outlined. Eventually, the review concludes the drawbacks encountered by porous materials confining noble metals, as well as their prospects and outlooks related to future development in catalytic nitroaromatics reduction.

#### 2. Controlled Synthesis Strategies of Porous Framework Confining Noble Metals

For porous materials confining noble metals, catalytic property is correlated with the synthetic process. Typically, more uniformly dispersed and ultrafine noble metals particles with high encapsulation efficiency will lead to more efficient catalytic performances in nitroaromatics reduction. Based on present methodologies, some researching groups have made different classification of synthetic strategies according to diverse standards (Fig. 1).<sup>27-29</sup>



**Fig. 1** (A) Strategies for fabricating NPs@MOFs composites: (a) ship-in-bottle, (b) bottle-around-ship, (c) sandwich assembly, and (d) in-situ confinement. Reprinted from Ref.<sup>27</sup> with permission from the Royal Society of Chemistry, copyright 2014. (B) Major synthetic strategies for fabricating NPs/MOFs composites. (a) Ship in bottle; (b) bottle around ship; and (c) in situ one-step synthesis. Reprinted from Ref.<sup>28</sup> with permission from Multidisciplinary Digital Publishing Institute, copyright 2017. (C) Different applied situations of atomic layer deposition. Reprinted from Ref.<sup>29</sup> with permission from American Chemical Society, copyright 2017.

In this section, the detailed illustration of controlled synthetic methods and catalytic performances of noble metals/porous materials were supplied. According to the sequence between reduction of metal precursors and self-assembly of porous framework, the synthetic methods could be classified into three main categories, which are (i) ordered assembly of porous frameworks before noble metals formation; (ii) controlled growth of porous framework around metal NPs; (iii) one pot synthesis. Three aspects in the synthesis process could be manipulated to enhance the catalytic performances including (i) downsizing the noble metal NPs to impede the detachment or aggregation of metal species and increase unit atom utilization efficiency and (ii) adjusting the steric location of noble metals via the ordered assembly inside the cavities including different exposed active facets as well as (iii) improving confining microenvironment such as the crystallinity of framework and adjusting the connectivity of cavities inside the framework during post-treatment procedures.

### 2.1 Ordered Assembly of Porous Frameworks before Noble Metals Formation

Ordered assembly of porous framework prior to reduction of noble metals precursors is the most previously reported method, which is represented by impregnation-reduction method, double solvent method (DSM), reverse double solvent method (RDSM), post-modification strategy, chemical vapor deposition (CVD), solid grinding and thermal decomposition. Basically, porous materials embody solid periodic structure and large pores openings which allow metal precursors to pass through, so they are desirable candidates for confining noble metals. By this means, the controlled interior growth of noble metals can be realized by the constraints of porous environment and strong binding force with porous frameworks.<sup>30</sup>

**2.1.1 Impregnation-reduction method.** A facile methodology for encapsulating metal NPs into porous framework is impregnation-reduction. Typically, metal ions are pre-introduced into porous materials by impregnating in a certain type of solvents and

then reduced by reactants to produce porous materials confining noble metals. (Fig. 2A).<sup>31</sup> The crucial issue is whether noble metals can be encapsulated smoothly into the cavities of porous materials with satisfying size dimension and dispersity. After all, impregnation becomes difficult when metal precursors are too large to completely embed into porous framework. As a topical example, Zhao' s group used polycondensation between piperazine and cyanuric chloride to synthesize PC-POP, then introducing H<sub>2</sub>PtCl<sub>6</sub> dissolved in methanol. The cationic platinum was thoroughly anchored inside PC-POP with the help of interaction between unpaired electrons of N atoms enriched in PC-POP framework and Pt<sup>4+</sup> (Fig. 2B).<sup>32</sup> Consecutively, hydrogen was employed as deoxidizers to reduce Pt<sup>4+</sup> and fabricate Pt@PC-POP catalysts. Asprepared Pt(5.82%)@PC-POP catalyst exhibited remarkable activity (>90%) and selectivity (>95%) in halogenated nitroaromatics conversion. Another group selected ammonia borane (NH<sub>3</sub>BH<sub>3</sub>) as reductants to form UiO-66-NH<sub>2</sub> encapsulating singleatom alloy catalysts (denoted as Pd<sub>10</sub>Pt<sub>x</sub>/UiO-66-NH<sub>2</sub>).<sup>33</sup>

For better encapsulation, adding stabilizers such as polyvinylpyrrolidone (PVP) in the impregnation process can function as a useful strategy to improve the dispersity of metal NPs. Chen et al. dissolved ZIF-8 in ethylene glycol and then incorporated PVP with H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O several times, followed by thermal reduction at 120 °C for 10 min.<sup>34</sup> As fabricated Pt/ZIF-8 composites exhibited a Pt size dimension of ~2.5 nm, much smaller than ~14 nm without PVP stabilization. However, these are also some flaws including partial leaching of noble metals or undesirable deposition on the outer surface of porous materials, awaiting further meliorative approaches.

2.1.2 Double solvent method. For better particle size control and more precise spatial confinement, a double solvent method (DSM) was employed to confine noble metal NPs in porous materials. Typically, less water-soluble porous materials are dissolved in hydrophobic organic solvents exemplified with n-hexane while metal salts are dispersed in water. Environmental distinction between hydrophobic surface of metal precursors and hydrophilic apertures inside porous framework brings about capillary force, thereby cationic metals can enter the internal pores of porous materials without any difficulty. For example, Fan's group fabricated Pd@COF-Ph and Pd@COF-BPh via DSM, in detail, as-prepared triazinyl-group-functionalized COF (COF-Ph, COF-BPh) was dispersed into the organic phase namely n-hexane before PdCl<sub>2</sub> aqueous solution was incorporated (Fig. 2C).<sup>35</sup> It is worth mentioning that modified COFs exhibited high content of N atoms with over 20%, which was favorable for sustainable encapsulation of Pd clusters owing to their capability for donating electrons, integrated with nanopores size restrictions. The analogous synthetic protocol was investigated by many groups to confine noble metal NPs inside porous organic or inorganic scaffolds.<sup>36-38</sup> As another proof, Aijaz et al. immobilized surfactant-free Pd into the pores of MIL-101 framework smoothly (Fig. 2D).<sup>39</sup> More concretely, H<sub>2</sub>PdCl<sub>4</sub> solution was introduced into MIL-101 dispersed n-hexane and then H<sub>2</sub>/He as reducing atmosphere coupled with high temperature were applied to the formation and growth of Pd NPs. Relevant characterization showed Pd NPs sized 1.8 nm was uniformly dispersed inside the mesoporous pores sized 2.9 nm and 3.4 nm of MIL-101 architecture.

2.1.3 Reverse double solvent method. This method mainly applies to confine

noble metal NPs within POPs, which feature tremendous hydrophobic inner pores. Therefore, introducing metal cationic salts wrapped in the organic phase into the inorganic phase will induce a relatively strong capillary force. This kind of driving force will induce noble metal precursors to enter hydrophobic pores of POPs more easily, which is imperative to achieve high encapsulation efficiency of noble metals inside POPs. One group then capsulized Pd NPs within POPs via a reverse double solvent method (RDSM) (Fig. 2E).<sup>40</sup> They dispersed as-prepared triazinyl-pentaerythritol porous organic polymers (TP-POP) into the inorganic phase (deionized water) and dissolved Pd(AcO)<sub>2</sub> into a kind of organic solvents (CH<sub>2</sub>Cl<sub>2</sub>). The mixture then underwent reduction treatment by NaBH<sub>4</sub> to produce TP-POP confining Pd (Pd@TP-POP). In this way, micro-droplets of CH<sub>2</sub>Cl<sub>2</sub> containing Pd(AcO)<sub>2</sub> would diffuse into the hydrophobic pores inside as-prepared TP-POP, which was convenient for uniformly dispersing Pd NPs within TP-POP after the reduction process. A convincing evidence was then provided by notably enhanced catalytic properties in 4-nitrophenol (4-NP) transformation and aldehyde hydrogenation. Note that the author made a comparison between the two samples, which were synthesized by impregnation-reduction method and RDSM, respectively. They finally drew a conclusion that confined composites synthesized via RDSM enabled to better control the steric position and size of metal NPs. And this modification helped increase catalytic activity in nitroaromatics reduction.

On the basis of integration between monometallic noble metal NPs and POPs, a more intriguing methodology was advanced which featured cooperation of

multicomponent hybrid system. Through constructing multiple schemes, improved catalytic efficiency in various practical applications will be recognized. It was found that the successful fabrication of multiple hybrids depended on the extent to which one counterpart could integrate tightly or be compatible with the adjacent other.<sup>41</sup> As an evidence, RDSM was employed to incorporate Pd NPs into the surface cavities of asconstructed ternary york-shell composite (Fe<sub>3</sub>O<sub>4</sub>@PDA@POP).<sup>42</sup> Among them, amino groups on dopamine (PDA) were the premise to coat POP shell and triazinyl groups enriched on the POP layer conduced to anchoring Pd NPs (Fig. 2F). Beyond that, almost a quarter of Pd<sup>2+</sup> were accountable for coordinatively binding with N and O atoms existed on the POP layer. All these factors contributed to the successful construction of Fe<sub>3</sub>O<sub>4</sub>@PDA@POP@Pd scheme.

**2.1.4 Post modification strategy.** It was proved that incorporating functionalized ligands to porous materials could anchor metal NPs better and achieve higher encapsulation efficiency.<sup>43</sup> In a latest report, thiol chains were rationally introduced into two-dimensional COF planes and served as nucleation sites via strong interaction with Au NPs.<sup>44</sup> Au@COF-S-SH was fabricated through in-situ reduction of HAuCl<sub>4</sub>·3H<sub>2</sub>O by L-glutathione (L-GSH) inside COF and subsequent nucleation of Au NPs (Fig. 2G). Synthesized COF-S-SH exhibited a pore diameter of ~50 nm and certain surface area of 290 m<sup>2</sup>g<sup>-1</sup>, which favored encapsulation of Au NPs. Thioether group also functioned as nucleation sites, where S atoms served as electron receptors and directed growth of metal NPs, finally forming Pt NPs@COF (Fig. 2H).<sup>45</sup> On the condition of high loading content of Pt NPs (34.36 wt %), unprecedentedly high stability was unveiled by

morphological characterization mingled with inductively coupled plasma (ICP) analysis, indicating the significance of anchoring effect of thioether group.

Combing the above statements, it is reasonable to conclude that incorporating surfactant, organic polymers, and stabilizers can effectively modify electronic environment of the metal centers and shield active centers from unnecessary loss owing to entry of different substrates. In order to avoid a negative impact on the catalytic performances such as overlaying exposed metallic sites, appropriate post-removal procedures towards stabilizers are usually indispensable, which may cause further issues of experimental complexity as well as operational costs.<sup>46</sup>



**Fig. 2** (A) Synthesis of the Au@POF aptasensor for oxytetracycline detection. Reprinted from Ref.<sup>31</sup> with permission from The Royal Society of Chemistry, copyright 2020. (B) Synthetic routes for fabricating PC-POP and Pt@PC-POP. Reprinted from Ref.<sup>32</sup> with permission from The Royal Society of Chemistry, copyright 2018. (C)

Preparation of Pd@COF-Ph and Pd@COF-BPh. Reprinted from Ref.<sup>35</sup> with permission from Elsevier, copyright 2019. (D) Schematic representation of Pd@MIL-101 for catalytically reducing vanillin. Reprinted from Ref.<sup>39</sup> with permission from The Royal Society of Chemistry, copyright 2015. (E) Preparation of Pd@TP-POP. Reprinted from Ref.<sup>40</sup> with permission from The Royal Society of Chemistry, copyright 2018. (F) Schematic information for Fe<sub>3</sub>O<sub>4</sub>@PDA@POP@Pd composites. Reprinted from Ref.<sup>42</sup> with permission from Elsevier, copyright 2019. (G) Synthesis of Au@COF. Reprinted from Ref.<sup>44</sup> with permission from Wiley Online Library, copyright 2020. (H) Schematic information of NPs@COF. Reprinted from Ref.<sup>45</sup> with permission from American Chemical Society, copyright 2017.

**2.1.4** Chemical vapor deposition (CVD). As a conventional method, Chemical vapor deposition (CVD) has been used and developed in the preparation of noble metals encapsulated in MOFs and zeolites for many years, spawning metal organic CVD (MOCVD), plasmon-enhanced CVD (PECVD) and so on. In the CVD method, the vapor of metal organic precursors generated under specific pressure diffuses into the pores of as-formed activated hosts in the flow of static vacuum at specific temperature. Subsequently, metal NPs are confined into porous materials by sequent reduction treatment including thermochemical treatment, plasmon-enhanced treatment and reduced atmosphere treatment. The earliest CVD for fabricating encapsulated composites was metal-organic chemical vapor deposition (MOCVD) method. For example, Zhang et al. reported the smooth incorporation of Pd NPs inside ZIF-8 via the MOCVD method.<sup>47</sup> Pre-activated ZIF-8 and metal organic precursors (Pd(C<sub>3</sub>H<sub>5</sub>)(C<sub>3</sub>H<sub>5</sub>))

were integrated separately and the diffusion process was accomplished under 1 Pa at 30 °C for 24 h. Then metal reduction occurred at the same temperature but higher pressure (10<sup>5</sup> Pa), with Pd@ZIF-8 generation after 1 h. Another CVD frequently used was PECVD, which applied plasmon reactors to generate high temperature for sufficient precursor vapors, which went through reduction to produce porous materials encapsulating metal NPs. According to the synthesized mechanism of PECVD, hydrogenated carbon encapsulating Au/Ag NPs<sup>48</sup>, graphene encapsulating Pd nanocrystals<sup>49</sup> and biomorphic carbon encapsulating Pd<sup>50</sup> were fabricated successfully.

**2.1.5** Solid grinding. In the early 2000s, solid grinding has been explored to confine metal NPs inside porous materials, mainly including MOFs and zeolites. The step-saving solid grinding method acts like this: (i) the volatile metal precursors and pre-activated porous materials are ground in a mortar for several hours to fully disperse metal precursors into pores. (ii) the mixture suffers thermal treatment and reactive gases to produce ultrafine metal NPs inside porous materials. Using the unified procedure, Au@ZIF-8<sup>51</sup> and Au@PCPs<sup>52</sup> have been successfully synthesized.

**2.1.6** Thermal decomposition. Basically, metal salts and porous materials are introduced into one homogeneous system to achieve encapsulation, followed by thermal decomposition at high temperature to reduce metal precursors inside the pores. The thermal decomposition method avoids the use of reductants, assisted agents and various solvents, which saves a lot of trouble. Luo' s group encapsulated Ag NPs into N-doped porous carbon (Ag-NPC) through a hydrothermal strategy.<sup>53</sup> They selected AgNO<sub>3</sub> and ZIF-8 as precursors, headed to mix them together under stirring. The metal

NPs was obtained after treating at 100 °C under the protection of Ar, with simultaneous encapsulation within NPC. Another group creatively applied platinum(II) acetylacetonate (Pt(acac)<sub>2</sub>) as both metal precursors and zeolite impregnation agents to synthesize Pt-in-NaX.<sup>54</sup> Followed by impregnation, the mixture of Pt(acac)<sub>2</sub> and NaX was heated to 350-400 °C under H<sub>2</sub> flow, with Pt(acac)<sub>2</sub> decomposition to generate Pt encapsulated NaX zeolite. Similar methods were employed for the fabrication of Pd@MOF<sup>55</sup> and Pd@NPC.<sup>56</sup>

#### 2.2 Controllable Growth of Porous Frameworks around Metal NPs

Though the above methods have been investigated widely, there are still some critical issues that need to be addressed. In detail, diffusion restrictions between the interior and exterior surface of porous framework will evoke the uneven dispersion of noble metal NPs. Besides, the collapse risks of pre-assembled porous framework during the post-reduction process limit its wide application.<sup>57, 58</sup> With these considerations in mind, another strategy which features reduction of metal precursors prior to porous framework assembly was put forward to conquer these limitations. Typically speaking, this methodology embodies two advantages, that is, homogeneity of encapsulated metal NPs and integrity guarantee of porous framework.<sup>59</sup> Comparable to the former synthesis route, preparing noble metal NPs in size, shape and topology.

The procedure about controlled growth of porous frameworks around metal NPs can be concluded as follows: Firstly, noble metals NPs with well-manipulated shape, size and property are synthesized. Then the porous framework will be constructed

around the metal seeds, with uniform confinement of nanometals into the pores of porous materials.<sup>60</sup> The morphological compositional changes and characteristics evolution at the evolving stages of encapsulation can be monitored using comprehensive characterization methods, such as scanning electron microscopy (SEM), transition electron microscopy (TEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) analysis.<sup>61, 62</sup> Combining the outcomes, it can be verified that noble metals are well encapsulated into porous materials with appropriate porosity and regularly-arrayed crystal architecture.

**2.2.1 Classifications.** The main synthetic methods can be classified into selfassembly, templated-assisted CVD, dry-gel conversion, thermal conversion and microemulsion. The self-assembly method is generally employed to synthesize MOF encapsulating metal NPs.<sup>63</sup> The detailed process can be ascribed as follows: i) Preformed noble metals and precursors of porous materials are dispersed in organic or inorganic solvents, such as N, N-dimethylformamide (DMF), methanol, benzyl alcohol and water. ii) The homogeneous solution suffers thermal treatment, and thus porous materials will self-assembly around metal NPs to form porous materials encapsulating noble metals. For instance, Xiao et al. dispersed Pt NPs, ZrCl<sub>4</sub>, 2-amino-1,4benzenedicarboxylic acid (NH<sub>2</sub>-BDC) and acetic acid in DMF solution. The homogeneous mixture was then healed at 120 °C to finish the crystallization and in-situ growth of UiO-NH<sub>2</sub>-66 around Pt NPs. With following centrifugation and washing, Pt@ UiO-NH<sub>2</sub>-66 was collected successfully.<sup>64</sup>

The templated-assisted CVD is developed based on the conventional MOCVD and their biggest difference lies in the generation of porous framework. In detail, incorporated porous frameworks are pre-synthesized in MOCVD while in templatedassisted CVD porous materials are produced by template etching after metal NPs formation. In 2020, Li's group applied silica-assisted CVD and coated graphene (G) on Au NPs to fabricate Au@G.65 Firstly, HAuCl<sub>4</sub> was adsorbed on the silica powder and reduced by H<sub>2</sub>/Ar to produce Au NPs. Then, the silica template underwent an etching process with hydrofluoric acid (HF) containing mixed agents (H<sub>2</sub>O: ethanol= 8: 1) under CH<sub>4</sub> flow to grow graphene shells on the surface of Au NPs. After washing and centrifugating, Au@G composites were collected and successfully prepared. In another report, Pd-coated zeolitic EMC-2 and acetonitrile functioned as both templates and carbon precursors, and suffered chemical vapor deposition process to generate porous carbon confining Pd.<sup>66</sup> Final Pd NPs evenly dispersed in porous carbon with a size range of 1-4 nm.

The dry-gel conversion method, characterized by higher productivity and bettercontrolled crystalline structure, is evolved from the conventional sol-gel method. In 2015, Gu et al. developed the dry-gel method to confine Pt NPs inside MFI zeolite (Fig. 3A).<sup>67</sup> Pt was initially deposited on ZSM zeolites in the existence of NaOH solution. Subsequently, a dry-gel layer containing silicalite-1 was coated outside of Pt/ZSM-5 as synthetic precursor of MFI zeolite, followed with its transformation into porous MFI shells around platinum centers after steam-assisted crystallization. Unchanged size scale and superb catalytic activity in high-temperature CO chemisorption test indicated

outstanding sintering-resistant properties of Pt@MFI catalysts, which outperformed Pt supported on the surface of ZSM-5.

Afterwards, an emerging protocol to confine Au or Pd NPs inside ordered mesoporous carbon spheres (Au@OMCs or Pd@OMCs) was presented. This thermal conversion based on the principle of self-transformation of three-dimensional multi-component spheric entities (Fig. 3B).<sup>68</sup> After self-assembly of mixed oleic acid capped Fe<sub>3</sub>O<sub>4</sub> NPs and Au NPs, high-temperature carbonization and targeted engraving to OMCs proceeded around pre-introduced Au NPs, with the fabrication of Au@OMCs. It was examined that Au NPs monodispersed on the OMCs endowed Au@OMCs with superb catalytic reactivity in phenylamine production over Au supported on activated carbon.

Another special report investigated the successful transformation from amorphous silica to crystalline birdcage-type zeolite in the media of water-in-oil microemulsion (Fig. 3C).<sup>57</sup> In details, PVP-stabilized Pt NPs were confined into amorphous silica, headed to the crystallization conversion to silicalite-1 under high-temperature treatment . Benefited from uniform dispersion within the prearranged zeolitic precursor, almost all the Pt NPs could enter the silica backbone. This can be envisaged as an effective strategy to lift up encapsulation efficiency and mitigate the amount of metal particulates situated on the outer surface of porous framework.

**2.2.2 Process modification.** Typically, subsequent growth of porous materials around noble metals relies on nucleation and growth of precursors of porous materials or/and adsorption of noble metal NPs onto the surface of porous materials. Thereby,

two factors will have an impact on the encapsulation efficiency of nanometals inside pores of porous materials, that is, nucleation rate of porous frameworks combined with binding force between two counterparts. Based on these considerations, two modification strategies are generally applied to improve the catalytic performances of encapsulated catalysts: (i) introduction of modulators to reduce the nucleation and growth rate of porous framework; (ii) optimization of reaction parameters during postassembly, such as concentration of precursors, incorporation timing node of metal NPs, pH and temperature.

As for the post-assembly process, two main nucleation mechanisms can be used to discuss respectively how to maximize the encapsulation efficiency of noble metals inside pores. Generally, too fast nucleation rate of porous framework will lead to excessive crystal sizes and unregular arrangement, which has a negative influence on the catalytic property of catalysts. Therefore, effective control measures over the crystallization procedure of porous materials are demanded to achieve high encapsulation efficiency. The first mechanism is homogeneous self-nucleation, featured uniform coating of porous materials around the metal seeds. In a recent publication by Wang et al., Pt or Pd NPs were smoothly confined into distinct nanoscale MOFs (Pt/Pd@UiO-66, Pt/Pd@UiO-66-NH<sub>2</sub>, Pt/Pd@MOF-801, Pt/Pd@ZnCo-ZIF-67, Pt/Pd@ZIF-8, Pt/Pd@ZIF-7).<sup>69</sup> They creatively employed acetic acid as modulators to restrict the nucleation rate of MOF shells around metal NPs. The growth control of MOFs during confining as-formed metal NPs induced thinner MOF shells. M@MOFs with a thinner shell possessed a shorter diffusion pathway from reaction medium to

Page 21 of 82

active metallic sites, which promoted mass transfer of various substrates and catalytic activity in cascade nitrobenzene reduction. Of particular interest of this report, asrecorded protocol can be extended to confine other noble metals into nanometer MOFs, which holds remarkable potential for generating efficient and multifunctional catalysts. As another example, mercaptoacetic acid (MAA) modified Au NPs was incorporated into liquid precursors of MIL-100(Fe) to construct Au@MIL-100(Fe) structure (Fig. 3D).<sup>70</sup> The results indicated changing the times of growth cycle can effectively regulate the thickness of MOF shells and the size dimension of metal NPs (Fig. 3E).

As for heterogeneous nucleation, experimental parameters optimization is paramount to enhance encapsulation percentage of noble metals within inferior cavities. It was suggested that alternating the timing node of adding metal NPs along with adjusting concentration of metal precursors could boost catalytic behavior of porous frameworks confining noble metals. As a proof, an effectively-controlled encapsulation strategy has been reported by Lu and co-workers.<sup>71</sup> They encapsulated preformed NPs with specific size, morphology and composition into zeolitic imidazolate frameworks. Distinctive from conventional reports where NPs were functioned as induced seeds to stimulate the nucleation of MOFs, this encapsulation strategy focused on the consecutive adsorption of metal NPs onto the emerging surface of ZIF-8 supports. Through alternation of NPs addition timing, at the initial time or after a certain reaction span, steric distribution of NPs can be consciously controlled, in or out of the pores. This kind of influence has been confirmed in other reports, such as Pt@MIL-125 synthesized by Jiang' s group.<sup>72</sup>

During the pre-synthesis process of metal NPs, assistants (capping agents, surfactants and coordinated ions) are usually prerequisite for the stabilization of noble metals. Better control over shapes, sizes and surface nature of nanometals will conduce to successful preparation of encapsulated composites, which leads to more efficient catalysis.<sup>73</sup> Outside of MAA, PVP is also envisioned as ideal candidates to assist the synthesis or dissolved procedure of metal particles, owing to its amphiphilic nature and non-ionic polymeric feature.<sup>74</sup> In another report, PVP was incorporated for the surface modification of Au NPs in order to obtain the uniformly disperse Au NPs in the polar solvent (methanol/water) and stabilize Au in the mixed aqueous solution (Fig. 3F).<sup>75</sup> TAPB-DMTP-COF was then fabricated via one-step condensation between 1,3,5tris(4-amino-phenyl)benzene (TAPB) with 2,5-dimethoxyterephthaldehyde (DMTP), triggered by acetic acid. In mechanistic details, planar COF monomer self-nucleated homogeneously and grew into hollow or dense polymeric spheres, served as COF precursors. After that, Au particles absorbed onto the surface of as-formed spheres through hydrophilic/hydrophobic interaction between PVP molecules and polymer spheres. In this way, noble metals particulates were confined into COF spheres, with few Au depositing on the outer surface and over 99% encapsulation efficiency. Note that lowering concentration of metal precursors would head to a decay of encapsulation efficiency. Surprisingly, two or more metal species can be introduced concurrently with this method, enabling flexibility, multi-functionality, and rational architecture design for porous materials confining noble metals.



**Fig. 3** (A) Synthetic approaches of Pt encapsulated in MFI Zeolite. Reprinted from Ref.<sup>67</sup> with permission from Elsevier, copyright 2015. (B) Synthetic strategies of Au NPs@OMCs-800°C composites. Reprinted from Ref.<sup>68</sup> with permission from The Royal Society of Chemistry, copyright 2017. (C) Preparation of Pt@Silicalite-1 for methane conversion. Reprinted from Ref.<sup>57</sup> with permission from Elsevier, copyright 2019. (D) Preparation of Au@MIL-100(Fe) catalysts for 4-NP reduction. And (E) SEM and TEM images of Au@MIL-100(Fe) after (a and e) 5, (b and f) 10, (c and g) 15, and (d and h) 20 assembly runs. Reprinted from Ref.<sup>70</sup> with permission from The Royal Society of Chemistry, copyright 2013. (F) Schematic information of PVP-functionalized Au NPs confined in TAPB-DMTP-COF. Reprinted from Ref.<sup>75</sup> with

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Based on present achievements, three issues await further improvement and more consideration: (1) Preservation of electrical performances coupled with geometric features despite surrounding growth of porous materials should be paid more attention during synthesis. (2) Maximized separation of metal particulates and no aggregation are prerequisite for isolation of active sites, which is favorable for the optimal atomic utility. (3) How to set up more advanced multi-component hybrids with an expectation of obtaining more sophisticated functions or employing in wider fields should evoke far-reaching researches.

# 2.3 One pot Synthesis

One pot synthesis (also denoted as in situ encapsulation), as the concept suggests, is introducing metal precursor solutions and porous framework precursors into one homogeneous scheme, thereby leading to simultaneous encapsulation of metal precursors and assembly of porous framework (Fig. 4A).<sup>76</sup> Subsequent reduction of metal precursors to metal NPs is generally assisted by confinement effect of porous materials, which helps control size, morphology and catalytic activity of metal NPs. <sup>77, 78</sup> Owing to these considerations, one pot synthesis has been recognized as a facile and step-saving strategy which is widespread employed to encapsulate noble metals NPs into porous framework.<sup>79</sup> In this way, the key point to prepare porous materials encapsulating noble metals is the balance control over nucleation and growth rates of porous materials and noble metals. Therefore, well manipulation of experimental conditions and proper assistants are significant in order to uniformly disperse and

smoothly encapsulate noble metals within porous materials.

Generally, four modified protocols are used in the synthetic process: (i) the functionalization or stabilization of metal precursors assisted by organic or inorganic ligands, such as -SH or -NH<sub>2</sub> ligands;<sup>43, 80</sup> (ii) introduction of structure-directing agents, cationic polymers included, to bridge between porous framework and metal ions through electrostatic interaction;<sup>81</sup> (iii) optimization of experimental parameters, including Si/Al radio, pH, hydrothermal temperature and metal loading amount;<sup>82</sup> (iv) synthetic routes reformation, such as the whole conversion of precursors.<sup>83</sup>

For instance, Chai et al. successfully encapsulated sub-nanometric Pd into MFI zeolites (denoted as Pd@ZSM-5).<sup>84</sup> They advanced modification from two aspects, that is, integrating Pd-SH functional precursors through a mixed-solvent strategy as well as a prehydrolysis approach to achieve a better crystallinity (Fig. 4B). In detail, Pd(NO<sub>3</sub>)<sub>2</sub> and (3-mercaptopropyl) trimethoxysilane (MPTS) were dissolved in the aqueous phase of equivalent mixed ethanol and water to construct Pd-SH complex. Eventually, homogeneously distributed Pd NPs sized 1.7-1.8 nm, clear-defined porous zeolite crystals, and considerable micropores as well as a small proportion of mesopores were acquired. The productivity reached over 90% and the regeneration rate was satisfactory.

Owing to stabilization of porous framework in one pot synthetic process, isolated noble metal sites can be constructed through interaction with high-electronegativity atoms on the backbone, which help improve catalytic performance. Otto et al. firstly constructed a homogeneous gel containing mercaptosilane ligand modified AuPd bimetallic species and LTA zeolite precursors.<sup>85</sup> Afterwards, AuPd@LTA was formed

via a whole crystallization of the homogeneous gel. Note that concurrent reduction of cationic metal precursors and transformation to LTA crystalline framework were achieved by bridging effect of 3-mercaptopropyl methoxy with the whole gel. In 2019, Liu et al. engineered single Pt atoms inside Y zeolites (Pt-ISAS@Y), assisted by backbone oxygen embedded on the six-membered rings (Fig. 4C).<sup>86</sup> As elucidated in Fig. 4D, mono-dispersion of Pt atoms and its stabilization by framework O species were confirmed by the existence of Pt-O peak as well as absence of Pt-Pt peak in Pt-ISAS@Y sample. Consequently, atomic platinum sites were embedded inside pores and could be accessed through  $\beta$ -cages in the zeolite framework with no obstacles, which promoted interaction between catalysts and substrates (Fig. 4E). Moreover, scalability of abovementioned in situ synthesis protocol was investigated with various metals (Pd, Ru, Rh, Co, Ni, Cu) replacing Pt species. All studied metal NPs were atomically solely dispersed in highly-crystallized M-ISAS@Y composites with a similar positive electronic state caused by O coordination. The extensive applicability of aforementioned one pot synthesis shed an innovative light on anchoring isolated single metallic active sites inside zeolite framework.

As another proof, Cui et al. reported an attractive synthetic strategy featured upgraded Kirkendall growth of silicalite-1 with well-defined mesopores.<sup>87</sup> The quantitative amount of water assisted with tetrapropylammonium hydroxide (TPAOH) could trigger the etching of zeolitic precursors and fabrication of zeolites at the interface, which was named as Kirkendall growth. In this method, chloropalladic acid and silica, functioning as the precursors of Pd NPs and silicalite-1 respectively, were initially Page 27 of 82

introduced into a homogeneous system and then passed through simultaneous Kirkendall growth procedure and palladium oxides reduction to construct Pd@mnc-S1 hybrid. TPAOH was used as linking agents and templates to direct the crystallization of silicalite and electrostatically integrate cationic metal precursors with negatively charged zeolite framework. The results manifested that as-formed metal-zeolite composites possessed obviously distinguished crystalline structures and uniformly distributed pores.

Although one pot synthesis brings about much convenience in preparing porous materials confining noble metals, some drawbacks such as decreased catalytic performance owing to aggregation still exist. In this respect, introducing other assisted species during adding precursors was verified to make sense. As investigated by this group, the existence of alkali cations (K<sup>+</sup>) was able to downsize Pt species within MFI zeolite, from nanometer region (3-5 nm) to sub-nanometer region (0.4-0.7 nm), and modulate catalytic reactivity by efficient confinement of Pt.<sup>88</sup> Mechanically speaking, the incorporation of  $K^+$  induced some basic sites to interact with Pt, thus leading to highly efficient catalysis. More interestingly, introducing Sn cluster with a reductive valence state (IV) was unveiled to enable to modify the dispersion and electronic properties of encapsulated Pt clusters by establishing interaction, which raised product selectivity in propane reduction. In another work, well-controlled synthesis of Ag or Au NPs inside ZIF-8 was obtained with the assist of confined-protein triggered biomineralization and porous frameworks generated steric restriction effect (Fig. 4F).89

Recently in 2020, a template-assisted strategy was advanced to confine ultrafine

Ru NPs inside 3D porous N-doping carbon nanosheets (Ru/3DNCN) (Fig. 4G).<sup>58</sup> Introducing N-doped carbonaceous and metallic precursors (citric acid, RuCl<sub>3</sub>·3H<sub>2</sub>O) coalesced with templates (NaCl) and modified agents (area) into the homogeneous system were accomplished at the initial stage. Confinement of Ru NPs and selfassembly of macroporous carbon framework occurred almost at the same time through pyrolyzation at 750 ° C, accompanied with removal of NaCl template. Negatively charged graphic N and interconnected hierarchical cavities on the carbon sheets could afford effective charge accumulation and rapid electron transfer, which favored the ultra-uniform dispersion of Ru, leading to an average size region of ~2.47 nm.

However, achieving perfect encapsulation of noble metal particles into porous framework is not to be easy all the time. It demands strict control over reaction parameters considering strong alkaline conditions during the formation of gel and high temperature employed in subsequent calcination. As another proof, Moliner and coworkers surveyed influence of distinct synthetic variables on catalytic properties of encapsulated catalysts.<sup>90</sup> Through experimenting under different conditions, they synthesized a series of chabazite zeolite encapsulating Pt (Pt-CHA-1/2/3/4). It was found that Pt-CHA-2, derived from higher pH, lower Pt loading amount and higher ratio of stabilizer to Pt, had the narrowest size distribution and neglectable aggregation, superior to other Pt-CHA composites. Following analysis disclosed that a rapid silica-aluminate nucleation, feasible mobility and no tendency to dissolute would occur in alkaline environment, which was favorable for perfect encapsulation of metals inside framework.

Page 29 of 82

In 2016, He et al. selected 2D hierarchical-pore MOF (H-MOF) nanosheets for the incorporation and growth of Pd NPs inside its apertures via in-situ Pd<sup>2+</sup> etching strategy without any surfactant.<sup>91</sup> Assisted by the reducibility of N,N-dimethylacetamide (DMAC), Pd diameter was restricted down to ~10 nm, bringing about no disruption to architecture, component and size of as-constructed H-MOF. Compared to surfactant-containing-prepared Pd-H-MOF and water post-treated Pd-H-MOF-5, Pd@H-MOF exhibited superior catalytic performance in nitroaromatics reduction, which provided enough proof for the advantages of surfactant-free routes.

Rasmussen and coworkers conducted a comparative experiment for two Pt@ MFI samples, prepared by incorporating metal precursors posterior or anterior to zeolites assembly, corresponding to impregnation-reduction method (Pt@ MFI (II)) and one pot synthesis (Pt@ MFI (I)) individually (showed in Fig. 4H).<sup>6</sup> It has been proved that the latter one realized better encapsulation of Pt within zeolites, thereby exhibiting better size selectivity in alkane hydrogenation and appearing more compelling in industrial applications.<sup>92</sup>



**Fig. 4** (A) Schematic representation of Pt@DUT-5 through one-step assembly method. Reprinted from Ref.<sup>76</sup> with permission from The Royal Society of Chemistry, copyright 2015. (B) A simple structural model of Pd@Na-ZSM-5. Reprinted from Ref.<sup>84</sup> with permission from American Chemical Society, copyright 2018. (C) Synthetic strategy of Pt-ISAS@Y zeolite. And (D) Fourier transforms of *k*3-weighted Pt L3-edge EXAFS experimental data and (E) Structural implication of Pt-ISAS@Y for Pt soil, Pt-ISAS@NaY, and PtO<sub>2</sub>. Reprinted from Ref.<sup>86</sup> with permission from American Chemical Society, copyright 2017. (G) Synthesis routes of Ru/3DNCN. Reprinted from Ref.<sup>58</sup> with permission from Elsevier, copyright 2021. (H) Recrystallization strategy for zeolites confining metal NPs. Reprinted from Ref.<sup>6</sup> with permission from American Chemical Society, copyright 2019.

# 3. Confinement Effect of Encapsulating Noble metals into Porous Systems: From Performance Improvement to Enhanced Mechanism for Nitroaromatics Reduction

Encapsulating noble metal NPs into porous framework, mainly involving zeolites, porous carbon, MOFs, and POPs, has been verified to be a more efficient strategy to fabricate heterogeneous catalysts in comparison with surface depositing strategies.<sup>80, 93,</sup> <sup>94</sup> Various porous materials confining noble metals have been reported to highly catalyze nitroaromatics reduction, exemplified with Pd-Ni-N@C,95 Ag@MOF,96 GaPt@S-1<sup>97</sup> and Pd-azo-POPs.<sup>98</sup> Indeed, confinement can be envisioned as a protocol, in which a determined volume is separated into several compartments. By segregating active metallic sites, improved catalytic activity, product selectivity and stability of confined catalysts in nitroaromatics reduction can be realized, which comprise the detailed implication of confinement effect. The superiority of encapsulated composites can be summarized into synergistic effect of pore confinement and charged metallic centers. By pore confinement, specific size-dependent selectivity can be realized because larger reactant molecules will be kept out, and only smaller substrates can pass through the pores. In addition, fabrication of cationic metallic centers because of interaction between porous materials and noble metals promote adsorption and reduction of nitroaromatics.

Herein, we enumerate four typical porous frameworks used to encapsulate noble metal NPs and provide straightforward paradigms and mechanism illustration over confinement effect, based on performance improvement in catalytic nitroaromatics reduction. Also, we briefly conclude the insights corresponding to different porous

materials confining noble metals.

#### **3.1 Porous Carbon**

Porous carbon materials, as compelling entities possessed with multidimensional architecture, interconnected pores, and outperforming specific surface areas have captured numerous attention in previous catalytic researches.<sup>99, 100</sup> These superior properties make porous carbon suitable for encapsulating noble metal particles. The catalytic performances of different porous carbon materials confining noble metals in nitroaromatics reduction are listed in Table 1.

Although several well-controllable synthesis approaches have been proposed to encapsulate noble metal NPs within nanocages of porous carbon framework, the concept of confinement effect in the field of porous carbon materials has not been well summarized. Strictly speaking, some cases of noble metals supported onto the surface of porous carbon materials can be classified into confined catalysis. The difference between surface depositing and pore encapsulation can be discriminated through relevant characterization methods to identify pore diameter or adsorption capacity of composite catalysts, including N<sub>2</sub> adsorption-desorption isotherms, BET analysis and hydrogen temperature-programmed desorption (H<sub>2</sub> TPD). TEM, SEM and HAADF-STEM characterization sometimes can also assist to determine the successful encapsulation of noble metals inside porous carbon. We can assure confinement of noble metals inside porous carbon when the pore volume of porous carbon decreasing after metal inserting, size of noble metals smaller than pore size, and catalytic activity exhibiting boosting improvement. For instance, Veerakumar and co-workers observed

Pd exhibited a matched size distribution (ca. 5 nm) with that of mesopores of carbon porous materials (CPM), indicating well encapsulation inside CPM.<sup>101</sup> The confinement effect of porous carbon framework can also get validated by comparing noble metal NPs supported commercial activated carbon (AC). Pd encapsulated CPM exhibited surpassing catalytic activity, selectivity and stability in nitroaromatics conversion. As conducted by Liang et al., Pt confined inside cubic-structured ordered mesoporous carbon held satisfying catalytic capacity (100% vs. 89%) and selectivity (99% vs. 90%) compared to commercial Pt/C catalysts in the hydrogenation of halogenated nitrobenzenes.<sup>102</sup>

According to the scale of pores, carbon materials can be classified into macroporous carbon, mesoporous carbon, and microporous carbon. Among them, the most frequent employed material for encapsulating noble metal NPs is mesoporous carbon. Mesoporous carbon is a group of carbon materials with nanopores sized 2-50 nm, simultaneously embodying the advantages of microporous carbon and microporous carbon. The modest pore dimension endows mesoporous carbon large surface area, high accessibility to substrates and well molecule shape selectivity.<sup>103</sup> By encapsulating noble metal NPs inside mesoporous carbon, remarkably improved catalytic efficiency can be achieved in nitroaromatics reduction.

Entry	Material	Reactants	Products	Yield (%)	TOF or k values	Selectivity (%)	Ref.
1	Pt/NOMC	p-chloronitrobenzene	p-chloroaniline	100	TOF=71.6 s <sup>-1</sup>	>99	102
2	Pt/CMK-3	2-methyl- nitrobenzene	2-methyl-aniline	98	TOF=43.8 s <sup>-1</sup>	>99	104
n		p-chloronitrobenzene	p-chloroaniline	100	r <sub>0</sub> =12.7 min <sup>-1</sup>		105
5	Au/MCN	4-NP	4-AP		r <sub>0</sub> =6.5 min <sup>-1</sup>		105
4		2/2/4 NID	2/3/4-AP 100	100	k'=0.020/0.022/0.200		106
4	Pl/NPC-900	2/3/4-INP		100	s <sup>-1</sup> g <sup>-1</sup> L		100
5	Pd/NHCs	nitrobenzene	aniline	100%	88		
6	Pd@PCF	nitroaromatics	anilines	>99	TOF>11400 h <sup>-1</sup>	>99	107
		2/4-NP,	2/4-AP	>98	TOF=0.27 s <sup>-1</sup>		108
7	Ag-1/C-370	2/4-NA			k=0.08 s <sup>-1</sup> (4-NP)		

			2/4-phenylenediamine				
			(2-PD)				
0	Au/CB	4-NP	4.4.D	-	k <sub>app</sub> =0.83012 min <sup>-1</sup>		
8			4-AP		TOF=492.50 h <sup>-1</sup>		10
9	Pd/Ni-N/C	4-NP	4-AP	100	k=7.93×10 <sup>-3</sup>	100	
10	D 1/HCNI	nitroaromatics with					
	Pd/HCN- 900	substituents (-X, -OH,	corresponding anilines	100	TOF=460.7 h <sup>-1</sup>	>80	
		-NO <sub>2</sub> , -CH <sub>3</sub> )					
11	Au/PCS	4-NP	4-AP	>99	k=28.46 s <sup>-1</sup> g <sup>-1</sup>		
In 2015, Li et al. encapsulated ultrasmall Pt NPs inside ordered mesoporous carbon materials (OMCs) and evaluated its catalytic behavior using hydrogenation of nitrobenzene and its derivatives.<sup>104</sup> In contrast experiments with commercial Pt/C composites, almost 10% higher conversion of nitrobenzene in a mixed agent (H<sub>2</sub>O: CH<sub>3</sub>OH=9:1) over Pt/OMCs was observed. No significant activity loss and wellretained morphology after fourteen turns indicated the outstanding catalytic sustainability of Pt/OMCs. The superiority of Pt/OMCs could be ascribed to more accessible pores for substrates in OMCs and smaller-scale Pd NPs. More importantly, they selected diverse substitutes (-Cl, -CH<sub>3</sub>) at different position of the aromatic ring and manifested that Pt/OMCs exhibited >99% selectivity and >77% activity in nitroaromatics reduction. The mechanism explained that electron-donating capacity and solubility of substitutes, attacking difficulty of nitro groups on different derivatives, and types of solvents worked together to influence catalytic efficiency. In addition, Fu et al. confined Au (sized 2.8 nm) into mesoporous carbon (MCN) and accessed its catalytic selectivity in catalytic reduction of p-chloronitrobenzene (p-CNB) and 4-NP. Almost complete inhibition of C-Cl bond cleavage in p-CNB and total reduction to 4aminonitrophenol (4-AP) without any unwanted byproducts proved that Au/MCN possessed wide potential in chemoselective reduction of nitroaromatics.<sup>105</sup> One research published in 2018 managed to disclose the impacting factors of chemoselective nitroaromatics reduction through alternating metal centers.<sup>106</sup> In detail, Pt NPs confined in nanoporous carbons (NPCs) together with Ni deposited on the outer surface of NPCs were prepared and applied in 2/3/4-NP hydrogenation. Final results showed that Pt/NPCs exhibited best catalytic activity in 4-NP reduction, because smaller 4-NP had more contacting opportunities with active metallic sites, while 2/3-NP could not access the pores feasibly (Fig. 5A). In drastic contrast, reduction rates of three molecules

exhibited no significant difference on Ni/NPCs, which could be assigned to almost equal exposure chances of nitroaromatics to Ni sites. We can notice that only partial encapsulation of noble metals in porous carbon was realized, which was unfavorable for highly efficient catalysis in nitroaromatics reduction. It deserves more investigation on how to obtain complete encapsulation of noble metal NPs and maximize the utilization of composites to catalyze nitroaromatics reduction.

One crucial reflection of confinement effect lies in size restriction and uniform distribution of noble metal NPs by porous carbon, which enables to reinforce catalytic activity and recyclability in nitroaromatics reduction. An evidence was provided by Ji et al. that ultrafine Ag sized below 5 nm was confined inside carbon framework via a chemical-free strategy. Correspondingly, evenly distributed and well-manipulated nano-sized region of Ag in carbon volumes led to outperforming stability in four kinds of different nitroaromatics.<sup>108</sup> Qin's group applied 4-NP catalytic reduction as a probe reaction and selected four carbon materials as Au confining tools for comparison (multiwalled carbon nanotubes (MWCNTs), active cokes (Ack), AC, carbon black (CB)).<sup>109</sup> The results demonstrated that Au/CB possessed the highest apparent kinetic constant (k<sub>app</sub>=0.8302 min<sup>-1</sup>), originated from highest BET surface area of CB and smallest size diameter of inner Au (ca. 2.5 nm) owing to pore restriction. In detail, as for Au/CB, steric confinement by the hierarchical porous structure and anchoring effect of oxygencontaining groups in CB contributed jointly to the smaller-scale dimension of Au particles, thus promoting conversion rate of 4-NP. Also, the catalytic applicability of Au/CB to other substituted nitroaromatics (2/3-nitrophenol, 2,4-dinitrophenol) was clarified by the high apparent kinetic constants ( $k_{app}$ >0.4287 min<sup>-1</sup>) in the reduction process.

Besides, it is significant to thoroughly understand the mechanism of catalytic

enhancement by confinement effect. Basically, abundant pores accelerate mass transfer of nitroaromatics from the reaction media to active metallic sites, and confined noble metals function as reaction centers to catalyze nitroaromatics conversion through anchoring active H\* species and bridging electron transfer. This kind of synergistic effect has been clarified by Chen's group and they employed a COF-based synthetic route to develop N-doped hollow carbon spheres (NHCs) confining Pd (Fig. 5B).<sup>113</sup> The results showed that ultrasmall Pd was successfully encapsulated because defects generated after N doping could disperse and stabilize Pd efficiently. Nitrobenzene reduction under H<sub>2</sub> atmosphere with alcohol as reaction media was conducted to examine catalytic behavior of Pd/NHCs. Accordingly, Pd/NHCs showed almost no Nalkylation reaction and 88% product selectivity. In contrast, lower activity on Pd-N/C(500) and extremely poor aniline selectivity (12%) on Pd/C(500) verified the synergistic effect between NHCs and Pd. In detail, NHCs could promote migration of substrates and positively charged Pd could preclude the adsorption of ethanol and consecutive N-alkylation of nitrobenzene. Later in 2018, various ultrafine noble metal NPs (Ru, Rh, Pd, Pt) were confined inside porous carbon framework (UNMPs@PCF) (Fig. 5C).<sup>107</sup> Among them, Pd@PCF showed the best catalytic property, that was, Pd@PCF catalyzed complete chemoselective conversion of nitroaromatics to anilines within 4 min with a turnover frequency (TOF) value of 11400 h<sup>-1</sup> and its catalytic performances suffered from rare destruction after 10 runs. Inspiringly, they proposed a plausible reaction mechanism in which Pd mediated the nitroaromatics reduction by active H\* generated from BH<sub>4</sub>, declined the work function of carbon framework through donating electron and made H\* capturing (hydrogenation) easier to transform aniline (Fig. 5D). These principles are general while understanding nitroaromatics reduction catalyzed by porous carbon confining noble metals.

Page 39 of 82

#### **Environmental Science: Nano**

Further reports argued doping of negatively charged heteroatoms such as N, O, and S could reinforce the confinement effect. In 2017, Liang's group elucidated the corresponding mechanism using N-doped ordered mesoporous carbon (NOMC) confining Pd NPs (Fig. 5E).<sup>102</sup> They presented that nitrogen dopants worked from two aspects: (i) allowed Pd NPs precisely anchored into the pores with high stability and no uncontrolled growth outsides; (ii) downsized Pd NPs to ~1.0 nm and held back undesirable aggregation or leach. Therefore, entire transformation within 30 min and exceptionally high selectivity (>99%) of p-chloroaniline over Pt/NOMC with rare dechlorination were accomplished. Wu and co-workers encapsulated Ni modified Pd with Pd loading amount of 3.0 wt % into hollow nitrogen doped carbon spheres (3.0Pd/Ni-N/C) and tested its catalytic behavior using 4-NP reduction.<sup>110</sup> Accordingly, 4-NP converted to 4-aminophenol completely within 9 min and achieved a high kinetic value of 7.93×10-3. They also pointed out that N doping conduced to size restriction and spatial confinement of Pd particles inside nanopores, thus endowing Pt/NOMC with superb catalytic behavior in p-chloroaniline production. For good measure, combining a second element with noble metals should be envisioned as a potential strategy to meliorate catalytic activity towards nitroaromatics reduction.

In the light of multi-functional desires, hierarchical porous architecture was constructed to implant noble metals particles, aiming to gain further improvement for nitroaromatic catalytic reaction. In 2019, Zhu's group synthesized hierarchically structured micro-mesoporous hollow carbon nanospheres (HCN) with a 1.54% loading amount of Pd NPs and N as electron donors to anchor Pd as well as hinder metal aggregation.<sup>111</sup> They manifested hydrogenation of nitroaromatics with different substituents (-X, -OH, -NO<sub>2</sub>, -CH<sub>3</sub>) could finish over Pd/HCN, with average 100% conversion and >80% selectivity. As proved by Cheng et al., mono-dispersion of Au

NPs was achieved because of confinement in hierarchically porous carbon spheres (PCS), showed in Fig. 5F, bringing about extraordinarily high kinetic constants  $(k=28.46 \text{ s}^{-1}\text{g}^{-1})$  over nitroaromatics catalytic reaction.<sup>112</sup>



**Fig. 5** (A) Diffusion and adsorption diagrams of 2/3/4-NP over Pt@NPCs and Ni/NPCs. Reprinted from Ref.<sup>106</sup> with permission from American Chemical Society, copyright 2018. (B) Synthesis of Pd@NHCS. Color coding: grey, C; blue, N; orange, Pd precursors or NPs. Reprinted from Ref.<sup>113</sup> with permission from The Royal Society of Chemistry, copyright 2016. (C) The general strategy for constructing M@PCF (M = Fe, Co, Ni, Mo, Ru, Rh, Pd and Pt). (D) Mechanistic diagrams for nitroaromatics reduction over Pd@PCF catalysts. Reprinted from Ref.<sup>107</sup> with permission from The Royal Society of Chemistry, copyright 2018. (E) Preparation of Pt/NOMC. Reprinted from Ref.<sup>102</sup> with permission from Elsevier, copyright 2017. (F) Synthesis strategy of Au/C. Reprinted from Ref.<sup>112</sup> with permission from Elsevier, copyright 2014.

# **3.2 Zeolites**

Zeolites are extensively used ideal supports for noble metals, which possess flexibly tailored acid-base sites, interconnected pores combined with unique electrostatic interaction.<sup>114</sup> Capsulizing noble metal NPs inside zeolites can protect metal particles against destruction or aggregation and hold back unfavorable contacts with harmful impurities, thereby exhibiting persistent catalytic activity during the overall reduction process and superhigh selectivity towards target aniline compounds.<sup>115</sup> The catalytic performances of different zeolites confining noble metals in nitroaromatics reduction are outlined in Table 2.

Entry	Material	Reactants	Products	Yield (%)	Selectivity (%)	Ref.	
1	Pd@mnc-S1	4-nitrobenzene	aniline	94 -		116	
1		1-nitronaphthalene	1-aminonaphthalene	3.5	-	110	
2	Pd@MFI	4-nitrostyrenes	4-aminostyrene	100	83%	67	
3	PtZn@MFI	p-chloronitrobenzene	p-chloroaniline	83	67	117	
	Pt-CeO <sub>2</sub> @SG-ZSM-5	nitrobenzene	aniline	100	100		
4		1,3-dimethyl-2-nitrobenzene	2,6-dimethylaniline	100	100	88	
		4-bromo-nitrobenzene	4-bromo-aniline		<6		
-	Pd@MFI.	4-nitrotuluene	4-aminotoluene	>99	>99	118	
5		1, 3-dimethyl-5-nitrobenzene	1,3-dimethyl-5-aniline	5.8	>99		
6	Pd@Beta	4-chloronitrobenzene	4-chloroaniline			119	
		4-nitrobenzaldehyde	4-aminobenzaldehyde	>99.0			

Table 2 Catalytic performance of different zeolites confining noble metals in nitroaromatics reduction

Among all the zeolites, MFI zeolites are the most generally reported ones in nitroaromatics reduction, which possess characteristic 10-membered rings and special porous structure to encapsulate noble metals inside the cavities. Through confinement of noble metals inside MFI zeolites, shape-selective and size-dependent catalysis in the hydrogenation of diverse nitroaromatic molecules can be obtained. In particular, enhancement of chemical selectivity in nitroaromatic compounds by zeolite encapsulating noble metals was widespread reported. Cui et al. synthesized silicalite confining Pd NPs via one pot method and chose nitrobenzene hydrogenation as a prototype reaction.<sup>116</sup> As-prepared Pd@mnc-S1 exhibited superior shape-dependent selectivity compared with supported composites. In detail, superb conversion rate (94%) of small-molecular 4-nitrobenzene and suppressed conversion (3.5%) of large 1nitronaphthalene over Pd@mnc-S1 were reported (Fig. 6A). In contrast, Pd/C composites showed ignorable difference in the catalytic transformation of 4nitrobenzene and 1-nitroaphthalene. The outcomes indicated that micropores (ca.5.3×6.6 Å) of mnc-S1 limited larger-scale 1-nitroaphthalene (7.6×6.6 Å) to pass through, while 4-nitrobenzene was small enough to react within the cavities. Analogous size-selective catalysis on Pt@MFI zeolite was observed in hydrogenation of 4nitrostyrenes by contrast with Pt/ZSM-5.67 When using Pt/ZSM-5 to catalyze reduction, undesirable product (4-ethylaniline) was the only resultant, whereas over Pt@MFI industrially valuable 4-aminostyrene became major product with a productivity of 83%, which suggested superiority of encapsulated catalysts in chemoselective hydrogenation of nitroaromatics. Other than 4-nitrostyrene, reduction of nitrobenzene and 2,3dimethylnitrobenzene could proceed smoothly over Pt/ZSM-5 but the access of the molecule was suppressed to a certain degree when using Pt@MFI catalysts. This was ascribed to the pore restriction of pore dimension of ZSM-5 (0.51×0.55 nm and

0.56×0.53 nm), which was accessible for nitrobenzene molecules with the smallest cross-sectional diameter of 0.60 nm and hard for 2,3-dimethylnitrobenze (0.73 nm) to pass through. Another investigator supplemented the mechanistic explanation for size-selective catalysis and employed Pd@MFI to promote the reduction process of 1, 3-dimethyl-5-nitrobenzene and 4-nitrtoluene.<sup>118</sup> As depicted in Fig. 6B, a negative correlation between molecular size and conversion rate was concluded, evoked by molecule-sieving effect and mass transfer restrictions of limited-sized pores of MFI zeolite. Wang's group encapsulated Pd NPs into the mesopores of ZSM-5 framework and explored its stability and poison resistance in 4-NP conversion.<sup>120</sup> Pt@ZSM-5 showed only a slight activity decline after 5 runs and almost unchanged conversion rate inder the poison of thiophene and 4,6-dimethyldibenzothiophene, which indicated its high sulfur tolerance in 4-NP reduction.

Except for size-dependent selectivity towards above-mentioned nitroaromatic with no substitutes, different substituted groups in nitroaromatics will influence the substrate selectivity. Take halogenated nitroaromatics as examples, dichlorination and cleavage of C-Cl bonds often accompany with reduction process, thus leading to undesirable side products. However, with the assist of encapsulated catalysts, oriented reduction of nitro groups will act as a major reaction with a high product selectivity. Zhang et al. introduced PtZn bimetallic clusters inside the micropores of MFI zeolites (ca. 6.7 Å) and probed the substrate selectivity towards nitroaromatics.<sup>117</sup> P-chloronitrobenzene gave 68% conversion and 56% yield to p-chloroaniline whereas 1,3-dimethyl-5-nitrobenzene held a slight selective conversion of 3.7% towards 1,3-dimethyl-5-aniline. The mechanism of chemoselective catalytic reduction could be assigned to the bimetallic synergistic effect of PtZn alloys and limited substrate transfer by confinement of MFI zeolites (Fig. 6C). Wang and co-workers incorporated Pt and

Page 45 of 82

cerium oxide into the bulky ZSM zeolites (Pt-CeO<sub>2</sub>@ZSM-5) and applied the catalysts in nitroaromatics conversion.<sup>88</sup> As illustrated in Fig. 6D, product yield of nitrobenzene exhibited no distinct difference between encapsulated catalysts (Pt-CeO<sub>2</sub>@SG-ZSM-5, Pt-CeO<sub>2</sub>@SG-Silicalite-1) and supported catalysts (Pt-CeO<sub>2</sub>/MS-ZSM-5, Pt-CeO<sub>2</sub>/MS-Silicalite-1). For larger-scale 1,3-dimethyl-2-nitrobenzene, rather low conversion rate and poor selectivity (7%) towards ideal product (2,6-dimethylaniline) were gained over Pt-CeO<sub>2</sub>@ZSM-5. By comparison, Pt-CeO<sub>2</sub> supported on the hierarchical zeolite showed higher product selectivity (92%). This kind of difference could be ascribed to a so-called "size-exclusion effect", which was that mesoporous pores were open to small-molecular nitrobenzene but hindered the diffusion of 1,3-dimethyl-2nitrobenzene. In addition, 4-bromo-nitrobenzene was applied to investigate specific selectivity of Pt-CeO<sub>2</sub>@SG-ZSM-5 towards different substituted groups (-Br, -NO<sub>2</sub>). The outcomes manifested that MFI confining Pt NPs benefited the hydrogenation of nitro groups prior to bromo groups. Explanation for this phenomenon has been given that the location of Pt NPs affected the type of reducible groups adsorbing preferentially onto Pt sites. Therefore, catalytic selectivity towards diverse substitutes of nitroaromatics can be recognized by pores confinement, including molecule sieving effect and favorable adsorption of certain groups onto the active metallic sites.

Apart from MFI-type zeolite, X zeolite can also be applied as encapsulating hosts for noble metals to realize highly efficient catalytic hydrogenation of nitroaromatics. For instance, Zhang et al. enclosed Pt clusters within interconnected pores of X zeolite with different centric cations (Na<sup>+</sup>, Ca<sup>2+</sup>, Cs<sup>+</sup>, La<sup>3+</sup>) (Pt@MX) and evaluated their performances in catalytic nitrobenzene derivatives reduction.<sup>121</sup> As-fabricated Pt@MX composites exhibited notable catalytic activity for the transformation of nitrobenzene, o-chloronitrobenzene and o-nitroanisole. An intriguing phenomenon was that the TOF values of three nitroaromatic substitutes followed the rule of "Pt@LaX > Pt@CaX > Pt@NaX > Pt@CsX". Discrete Fourier Transform (DFT) calculations revealed the electronic state of platinum center significantly impacted catalytic behavior of confined catalysts in nitroaromatics reduction. It was proposed that  $Pt_n$  clusters in Pt@CsX possessed the lowest electronic density and Fermi levels, which favored for the rapid adsorption, activation and consecutive hydrogenation of nitroaromatic molecules (Fig. 6E). Thus, constructing electron deficient metallic center by selecting proper cations of X-zeolite could be treated as a promising strategy to alternate the catalytic performance in nitrobenzene substitutes.

Additionally, Beta zeolites and mordenite (MOR) have also been utilized to confine noble metal NPs inside inferior cavities to improve the catalytic selectivity, activity and recyclability in nitroaromatics reduction. Exemplified with Zhang's study, Pd@Beta zeolite core-shell architecture was constructed to selectively catalyze transformation of p-chloronitrobenzene and 4-nitrobenzaldedehyde.<sup>119</sup> In contrast experiments with conventional supported catalysts, Pd@Beta exhibited an extremely 99% towards products high conversion rate over (p-chloroaniline, 4aminobenzaldehyde) and generated no side products (Fig. 6F). It was then confirmed that the combination form between Pd NPs and Beta zeolites caused a final impact on higher selectivity over Pd@Beta. Originating from confined space inside Beta zeolites, nitro groups would exhibit preferential adsorption via  $\pi$ - $\pi$  interplay and stronger binding force with active palladium sites than chloro substitutes, which simultaneously promoted production of amino groups and held back dechlorination. Subsequently, recyclability tests were carried out and the results indicated encapsulated MNPs (Pd@Beta, Pd@MOR, Ru@Beta and Pt@Beta) outperformed supported MNPs (Pd/Beta, Pd/MOR, Ru/Beta and Pt/Beta) in the catalytic conversion of different



nitroaromatics with diverse substitutes at three positions (meta, para and ortho).

**Fig. 6** (A) Nitroaromatics reduction over Pd@mnc-S1 or Pd/C. Reprinted from Ref. <sup>116</sup> with permission from Wiley Online Library, copyright 2016. (B) Nitroaromatics reduction over Pt@MFI\_ImILs and Pt@MFI\_Imp. Reprinted from Ref.<sup>118</sup> with permission from Elsevier, copyright 2021. (C) Mechanistic illustration for *p*-chloronitrobenzene selective reduction in the existence of 1,3-dimethyl-5-nitrobenzene. Reprinted from Ref.<sup>117</sup> with permission from Wiley Online Library, copyright 2018. (D) Product yield of nitrobenzene reduction over several catalysts. Reprinted from Ref.<sup>88</sup> with permission from American Chemical Society, copyright 2018. (E) The correlation of Fermi levels of Pt clusters in Pt<sub>n</sub>@MX (M = Cs<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> or La<sup>3+</sup>) and catalytic behaviors of Pt<sub>n</sub>@MX in nitroaromatics reduction. (F) Product yield and selectivity for the catalytic reduction of 4-nitrochlorobenzene and 4-nitrobenzaldehyde over several noble metal-based catalysts. Ref.<sup>121</sup> with permission from The Royal Society of

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## 3.3 Metal-Organic Frameworks (MOFs)

In the last decades, MOFs have been investigated tremendously as noble-metal encapsulating materials due to its feasible tuning morphology, diverse molecular shapes, robust porous framework as well as multiplicate functionalities.<sup>122-126</sup> From the structural perspective, numerous pores with hierarchical scales and orderly arranged molecular scaffolds make active metallic sites stable and accessible, thus improving catalytic activity and recyclability in nitroaromatics reduction. In addition, MOFs comprise metal nodes and organic linker, which make it possible to interact with encapsulated noble metals via complexation or  $\pi$ - $\pi$  bonding force.<sup>127-130</sup> The catalytic performances of different MOFs confining noble metals in nitroaromatics reduction are outlined in Table 3.

	Table 3 Catalytic performa	nnces of different MOFs	confining noble metal	s in nitroaror	natics reduction	
Entry	Material	Reactants	Products	Yield (%)	Selectivity (%)	Ref.
		4-NP	4-AP			
		2/3-NP	2,3-AP	> 00	_	
1	Au <sub>NC</sub> @ZIF-8(Cu) NRAs	m-dinitrobenzene	m-dianiline	>98		131
		3/4-nitrotoluene	3,4-aminotoluene	>//		
		p-nitrobromobenzene	p-bromoaniline			
2	Pd-in-UiO-67	nitrobenzene	aniline	>99	100	27
3	Pd@MIL-101-F <sub>3</sub>	p-nitrochlorobenzene	p-chloroaniline	>99	98	132
4	Pd/UiO-66@PDMS	nitrobenzene	aniline	100	_	133
		4-NP	4-AP	<5		
5	Au-1@NMOF-Ni	4-NP	4-AP	100	_	134
	PdAu@MIL-100 (Fe)	2-(4-nitrophenyl)-	2-(4-aminophenyl)-		99	135
6		1H-benzimidazole	1H-benzimidazole	100		

As a typical proof, Gao et al. confined Au nanoclusters inside Cu-centered ZIF nanorod arrays (Au<sub>NC</sub>@ZIF-8(Cu) NRAs) and applied to catalytic conversion of nitroaromatic derivatives.<sup>131</sup> Taking 4-NP as probe molecules, up to 98% conversion after a period of 6 min and a high k value (0.489 min<sup>-1</sup>) over Au<sub>NC</sub>@ZIF-8(Cu) NRAs were gained, equal to 8 and 4.7 folds of sole ZIF-8(Cu) NRAs and Au NCs. The corresponding mechanism could be explained as follows (Fig. 7A): (i) Well-structured crystalline morphology, high surface areas, and affluent cavities of ZIF-8(Cu) framework made substrates accessible to active Au sites; (ii) The organic counterparts of ZIF-8 enhanced adsorption of 4-NP via  $\pi$ - $\pi$  stacking interplay; (iii) The coordinatively unsaturated organic linker (CuN<sub>x</sub>) accepted electrons to Au centers with the generation of positively charged Au, which facilitated electron transfer process from BH<sub>4</sub> to N atoms of 4-NP and produced amine group. We can see the binding force between metal and MOFs will induce charged metal centers with varied valence state and boost interplay among MOFs and substrates. As manifested in Chen's study, aromatic rings as well as carboxylate group in MOF architecture were accountable for donating electrons to Pd atoms.<sup>27</sup> Consequently, over 99% yield of aniline within 3 h was gained using Pd-in-UiO-67, exceeding many Pd-based catalyst ever reported. As another proof, Koo et al. confined ultrafine Pt and Pd NPs into conductive MOFs (C-MOFs) and observed the presence of Pt (II) and Pd (II) species, which interacted with MOFs more strongly.<sup>136</sup>

Furthermore, more positively charged metallic centers can be obtained by incorporating heteroatoms into MOFs. By covalently bonding to adjacent atoms with lower electronegativity, such as N and O atoms, electron-insufficient metallic centers will generate. Thus, interaction between metal sites and MOFs enhances at the interface, which accelerates the reduction rate of nitroaromatics.<sup>131</sup> One typical study conducted

by Jiang's group modified MIL-101-NH<sub>2</sub> with hydrophobic perfluoroalkyls and confined Pd NPs to form Pd@MIL-101-Fx.<sup>132</sup> As-fabricated Pd@MIL-101-Fx exhibited >90% conversion and >94% selectivity in p-nitrochlorobenzene hydrogenation. Corresponding DFT calculations revealed -NO<sub>2</sub> substitutes preferentially adsorbed on the surface of positively charged Pd species rather than Pd<sup>0</sup>, ascribed to lower adsorption energy (-0.26 eV vs. -0.25 eV). From the reaction pathways over Pd<sup> $\delta$ +</sup> and Pd<sup>0</sup> surfaces, it could be seen that both generation and hydroxyl dissociation of ClPhNHOH occurred favorably on the surface of positively charged Pd compared to neutral Pd. Therefore, strengthened binding force between metals and MOFs contributes to catalytic performance improvement of encapsulated catalysts.

Besides of electronic state adjustment, surface wettability modification of active metals enables to enhance catalytic activity, selectivity and sustainability in nitroaromatics reduction. A report published in 2016 investigated the roles of surface hydrophobic coating (polydimethylsiloxane, PDMS) over Pd/UiO-66 in catalytic performance towards nitroaromatics reduction. The catalytic tests denoted that the reduction rate after hydrophobic modification reached almost 8 times of the original Pd/UiO-66 and the conversion of hydrophobic nitrobenzene was much rapider and more thorough than hydrophilic 4-NP conversion over Pd/UiO-66@PDMS. Corresponding mechanistic insight was given that surface hydrophobic modification favored the accumulation of hydrophobic nitroaromatics via strengthened affinity and hampered the aggregation of metal NPs, thus improving the catalytic behavior of encapsulated catalysts.<sup>133</sup>

Benefitted from confinement effect, superb stability and leaching-and-aggregation resistance of  $Au_{NC}$ @ZIF-8(Cu) NRAs were verified through well-maintained catalytic activity and unchanged morphology of the composites within 10 runs. The applicability

of  $Au_{NC}@ZIF-8(Cu)$  NRAs towards other nitroaromatics with diverse functional group was verified, whether electron-donating or electron-accepting group. The results manifested that nearly all the substituted nitroaromatics (2/3-NP, nitrobenzene, mdinitrobenzene, 3/4-nitrotoluene and p-nitrobromobenzene) could transform to corresponding anilines with an average yield over 77%.

As for selectivity, pore dimension impact accessibility of reactants (denoted as "molecule-sieving effect"), that is, molecules smaller than pore size will suffer from slightest diffusional resistance relative to superlarge ones, thus passing through interior pores more readily. Shorter transporting access and more efficient exposure of metallic active sites to reactants under confinement will help boost catalytic activity, selectivity and stability in nitroaromatics reduction. Likewise, Yan and coworkers took the initiative in confining Au NPs sized lower than 1 nm into two-dimensional MOF sheet and accomplished highly effective and size-selective catalytic reduction of nitrophenol (Fig. 7B).<sup>134</sup> Theoretical explanation was given that confined pores limited the mobility and aggregation of noble metals and protected reactivity of active Au sites, with MOF pores hindering entry of larger-scale substrates like a molecular sieve.

Except for the monometallic species encapsulated with MOFs, simultaneously introducing two or more noble metals or other functional moieties inside MOF pores can be envisaged as a promising modified strategy for better catalytic performance. By this means, we can make flexible integration of multifunctionalities based on several counterparts. Thus, it will be possible to satisfy more complex treating demands, in particular, extending the applied system to all types of actual contaminated water body, which often contain two or more categories of nitroaromatic pollutants.<sup>137</sup> There has been tremendous publications about MOFs confining noble metals in multistep reactions, exemplified with PdAu@MIL-100 (Fe) as tandem reaction catalysts.<sup>135</sup>

Page 53 of 82

Likewise, Chen et al. combined the advantages of Pd, Ag and MIL-101 to obtain extraordinarily good activity and outperforming selectivity in cascade nitroaromatics conversion (Fig. 7C).<sup>138</sup> As a consequence, PdAg@MIL-101 exhibited full conversion and product selectivity of ~99% in cascade catalysis of 2-(4-aminophenyl)-1Hbenzimidazole, exceeding monometallic Pd@ MIL-101 or Ag@MIL-101 in comprehensive behavior. It is noteworthy that host-guest cooperation and bifunctionalities synergistic enhancement were responsible for the outstanding catalytic performances, which was, Lewis acidic sites of MIL-101, reduction reactivity of Pd as well as product selectivity of Ag. Except for bimetallic alloys within MOFs, MOFs encapsulating bimetallic core-shell structures can also catalyze nitroaromatics reduction. Jiang's group confined Au@Ag within ZIF-8 via a deposition-reduction method and tested its catalytic performance using 4-NP reduction. Compared to MOF encapsulating AuAg alloy catalysts, Au@Ag /MOF exhibited higher kinetic constants  $(4.97 \times 10^{-3})$  and better recyclable behavior. The outstanding catalytic activity and stability over 4-NP reduction indicated the superiority of MOFs encapsulating coreshell structure in electronic structure modification.<sup>139</sup>

# 3.4 Porous Organic Polymers (POPs)

Porous organic polymers (POPs), emerging as a promising porous material with organic crystalline architecture, have stimulated dramatic interest in the field of catalysis.<sup>140-143</sup> Its feasibility to functionalize, intrinsic bonding environment, periodical topology structure and well-isolated pores create ideal environment for confinement of nanometer pieces of matter.<sup>144, 145</sup> Among them, POPs confining noble metals were more extensively investigated to catalyze the reduction of nitroaromatics with outstanding catalytic behavior. The catalytic performances of different POPs confining noble metals in nitroaromatics reduction are listed in Table 4.

ntry	Material	Reactants	Products	Yield (%)	TOF (h <sup>-1</sup> )	Selectivity (%)	Ref.
Au/		1-chloro-4-nitrobenzene	4-chloroaniline	97	6115	98	146
	Au/IM-POP-2BrB	Nitrobenzene	Aniline				
		4/3/2-nitrotoluene	4/3/2-aminotoluene,	≥92	5460	≥94	146
		4-nitrobenzaldehyde	4-aminobenzyl alconol				
	Pt@PC-POP	halogenated nitrobenzenes	halogenated anilines	>90	-	>87	32
		4-NP	4-AP	67.7	5155.4	100	35
	Pd@COF-BPh	substituted nitrobenzenes	substituted anilines	>99	3807.5		
Pd@CN		4-nitroacetophenone	4-aminoacetophenone	95		95	147
	Pd@CNT-P	1-nitronaphthalene	1-aminonaphthalene	100	-	100	
	Pd@PC-POP	nitroaromatics	anilines	100	>7738.2	>99	148
	Fe <sub>3</sub> O <sub>4</sub> @COF-Au NPs	4-NP	4-AP	100	354.6	>99	149

The first example of POPs encapsulating noble metal NPs for nitroaromatics reduction was reported in 2018 by Fang's group. They grew Au NPs along the internal walls of imidazolium-functionalized POPs and constructed a microfluidic reactor to accelerate catalytic reduction of nitroaromatics.<sup>146</sup> Notably improved catalytic performance in 1-chloro-4-nitrobenzene over Au/IM-POP was reported, with 97% conversion, 98% selectivity and a TOF value of 6115 h<sup>-1</sup>, which surpassed previously reported supported catalysts. Simultaneously, rare loss of activity and well-retained Au content after four runs indicated the superb stability of Au/IM-POP in nitroaromatics reduction. Furthermore, catalytic behavior towards other typical nitroaromatic molecules (nitrobenzene, 2/3/4-nitrotoluene) over Au/IM-POP was investigated, with sufficient conversion ( $\geq$ 92%), product selectivity ( $\geq$ 94%) as well as high TOF values ( $\geq$ 5460 h<sup>-1</sup>) within 1.5 h.

For POPs confining noble metals, the most crucial reflection in nanoconfinement effect is the improvement of catalytic activity and chemical selectivity in nitroaromatics reduction. In 2018, Zhao et al. encapsulated ultrasmall Pt NPs into triazinyl-containing POPs (PC-POP) to catalyze nitroaromatics reduction.<sup>32</sup> Unprecedently high catalytic activity (100%) surpassing previously reported composites and intriguing stability during eight cycles indicated that PC-POP confining Pt NPs held great potential for nitroaromatics conversion. Abundant mesopores and large surface area based on three-dimensional spatial folded morphology of PC-POPs endowed nitroaromatics high accessibility to active Pt sites, which resulted in high catalytic efficiency (100%). Outside of this, they found types of solvents (H<sub>2</sub>O, ethyl acetate, tetrahydrofuran, methanol and ethanol) and noble metals centers (Pd, Pt) would affect the catalytic behavior. For the choice of solvents, high solubility and uniform dispersion of Pt@POP inside were demanded to achieve efficient conversion of p-chloronitrobenzene. Also,

Pt/C with a complete conversion rate and selectivity of 95.48% in one hour exceeded Pd-based catalysts remarkably with a poor selectivity. More importantly, comparison experiments were conducted among nitrobenzene with a bromo group at the para, meta and ortho position. The results revealed that a stronger steric hinderance of halogenated groups from para- to ortho- led to longer reaction time and lower selectivity.

Besides, encapsulating noble metals inside pores of POPs can prolong catalysts lifetime and retard leaching or aggregation of metal NPs.<sup>35</sup> Examinations towards morphology and activity after several consecutive cycles of 4-NP catalytic reduction capture no signals of active sites leaching or agglomerating into bulk particles, suggestive of outstanding sustainability over previously reported noble metals supported materials. In 2019, Sadjadi et al. constructed a polymeric framework consolidating cyclodextrin (CD), imidazolium group (IL) and carbon nanotube (CNT) to confine Pd (Pd@CNT-P) and applied 4-nitroacetophenone and 1-nitronaphthalene as targeting reactants to explore catalytic selectivity towards nitro groups of composites, with an observation of extremely good catalytic activity and size-dependent selectivity.<sup>147</sup> Comparable tests with various supported hybrids highlighted unprecedentedly superiority of Pd@CNT-P in catalytic efficiency under mild reacting conditions (Fig. 7D). Also, well-retained catalytic capacity after six successive recyclable runs, slight Pd leaching on the fourth cycle, undamaged morphological architecture as well as almost consistent Pd size range signified exceptionally outstanding reusability.

Similarly, with a propose to promote nitroaromatics reduction, incorporating rich elements like N, S, and O into the POPs backbone has been explored as an attractive strategy, by bridging stronger interaction (coordination or  $\pi$ - $\pi$  interplay) with metal species. Generally speaking, those atoms with more electronic negativity can further

Page 57 of 82

anchor noble metals particles and accelerate the mutual transformation between metal sites with different valency, thus acting as redox centers to mediate nitroaromatics reduction.<sup>150</sup> As an instance, Yuan et al. functionalized POPs with N-containing triazinyl groups and uniformly distributed Pd NPs inside PC-POPs to accelerate the catalytic reduction process of nitroaromatic derivatives.<sup>148</sup> Unprecedently good catalytic performance was realized with complete conversion, superhigh selectivity (>99%) and TOF values up to 7738.2 h<sup>-1</sup> after 15 min towards most nitroaromatics with diverse substitutes (-NO<sub>2</sub>, -OH, -Cl, -F, -NH<sub>2</sub>, -CHO, -CH<sub>3</sub> and -COCH<sub>3</sub>). Taking 4-NP reduction as an example, relevant mechanistic explanation was given as shown in Fig. 7E, which can be described as follows: (i) BH<sub>4</sub> and 4-NP were firstly absorbed onto the active palladium sites within pores via  $\pi$ - $\pi$  stacking interplay; (ii) Nitroso groups were produced after electron transfer between H\* species of Pd-H bonds and nitro groups of 4-NP; (iii) Active H\* attacked positively charged N atoms to form hydroxylamine, followed by catalytic reduction and desorption to generate free amine. Therefore, synergistic effect existed between stabilization by heteroatoms anchoring on the POPs framework and nanopore confinement, which helped disperse metal particles uniformly, hinder the leaching or aggregating tendency of noble metals and improve the activity of metallic centers. By this means, enhanced catalytic efficiency, meliorative product selectivity and prolonged lifetime in nitroaromatic catalysis can be obtained.

Furthermore, imparting multifunctional species and affluent active sites into POP framework can be envisioned as intriguing strategies to reinforce the catalytic performance in nitroaromatics reduction.<sup>151</sup> For instance, Xu et al. coated Au NPs on the spheric shell of Fe<sub>3</sub>O<sub>4</sub>@COF and applied this hybrid in 4-NP reduction, resulting in considerable catalytic activity together with superb magnetic separable reproducible properties (Fig. 7F).<sup>149</sup> In these cases, theoretical and experimental understanding are

still in urgent demand over POPs encapsulating noble metals, about reaction thermodynamics and rate kinetics illustrations.



**Fig. 7** (A) The mechanistic reflection of 4-NP catalytic reduction. Reprinted from Ref.<sup>131</sup> with permission from The Royal Society of Chemistry, copyright 2019. (B) a) Mechanism of molecular sieving effect of Au-1@NMOF-Ni applied to reduce 4-NP and MG 17. Reprinted from Ref.<sup>134</sup> with permission from Wiley-VCH, copyright 2018. (C) Mechanistic insights into catalytic nitrobenzene reduction over PdAg@MIL-101. Reprinted from Ref.<sup>138</sup> with permission from American Chemical Society, copyright 2015. (D) Stability tests of Pd@CNT-P. Reprinted from Ref.<sup>147</sup> with permission from Elsevier, copyright 2020. (E) Mechanism of 4-NP catalytic reduction over Pd@PC-

#### **Environmental Science: Nano**

POP. Reprinted from Ref.<sup>148</sup> with permission from Elsevier, copyright 2019. (F) Systematic information of Fe<sub>3</sub>O<sub>4</sub>@COF-Au in 4-NP conversion. Reprinted from Ref. <sup>149</sup> with permission from Elsevier, copyright 2020.

## 4. Size Effect of Noble metal NPs

It is well acknowledged that catalytic performance of noble metal-based catalysts always exhibits size-dependent effect, indicating that decreasing the size dimension of noble metals often leads to enhanced catalytic performance. Evoked by this "quantum size effect", reduction of metal scales represents higher surface area, more exposed active sites lied on per molecular.<sup>152, 153</sup> Previous researches have emphasized the influence of noble metals size on catalytic property of noble metal/porous materials hybrids towards other reactions.<sup>154</sup> However, the size-dependent catalytic performance in nitroaromatics reduction catalyzed by noble metals confining in porous materials has not been systematically concluded.

In this section, we illustrated the influence of different dimension ranges of noble metals confined in porous materials on the catalytic performance in nitroaromatics reduction, emphasizing on improving electronic and geographic property caused by confinement.

## 4.1 Nanoscale Noble metals

For porous framework confining noble metal NPs, reducing the size dimension of metal particles typically brings about improved catalytic performance in nitroaromatics reduction. The mechanism of this size-dependent catalytic activity can be concluded from three main aspects: (i) Small-sized noble metal NPs possess higher specific surface area available for nitroaromatic substrates; (ii) Small-sized noble metal NPs display lower adsorption energy and more positive metallic state, which helps adsorb and successively reduce nitroaromatic molecules; (iii) Small-sized noble metal NPs can interact more strongly with porous materials because of enhanced unsaturated surface

atoms and surface energy, which favors the electron transfer at the interface and accelerates reduction rate of nitroaromatics. Typically in DFT calculations, the higher surface energy of smaller-size noble metals is correlated with lower work function. In that case, noble metals are prone to donate electrons to porous supports or electroninsufficient nitroaromatic substrates and exhibit more positive electronic states.<sup>155</sup> This kind of enhanced interaction between two counterparts is advantageous to catalytic performance improvement in nitroaromatics reduction.<sup>156</sup> Chen's group demonstrated that noble metals at a smaller scale within mesoporous hollow carbon spheres (NHCS) could exert a positive influence on the catalytic activity in nitroaromatics reduction.<sup>113</sup> Pd@NHCS(500) and Pd@NHCS(600) were prepared using the same carbonization method but under different pyrolysis temperature (500 °C, 600 °C), and displayed a size dimension of ~7 nm and ~19 nm respectively. Pd@NHCS(500) achieved a complete reduction of nitrobenzene within 50 min whereas Pd@NHCS(600) demanded a longer time (100 min). The superiority of Pd@NHCS(500) over Pd@NHCS(600) in the catalytic efficiency of nitrobenzene transformation could be ascribed to a smaller Pd size in Pd@NHCS(500). As another proof, noble metal NPs with distinct sizes, including Au NPs sized 15 nm, Au NPs sized 50 nm as well as Au nanorods sized 25  $\times 100$  nm, were synthesized inside the pores of COF using the identical strategy.<sup>75</sup> By comparison, highest kinetic constant (0.46 min<sup>-1</sup>) towards nitrophenol reduction on 15 nm Au NPs was observed. This size-dependent activity was originated from highest surface-volume ratio led by smaller size scale of Au species. Lately, Aslam et al. employed an ultrasound assisted impregnation-reduction method to successfully incorporate 1.0 wt % Au NPs inside hierarchically porous zeolites (i.e. MMZ and ZSM-5).<sup>157</sup> The as-synthesized 1.0Au/MMZ displayed a much smaller Au diameter of 2.7 nm compared to 1.0Au/ZSM-5 sized 10 nm. Thus, 1.0Au/MMZ obtained a complete

conversion to 4-AP in 5 min while 1.0Au/ZSM-5 composite used 60 min to accomplish 80% 4-NP conversion. Relevant mechanistic explanation was given that Au NPs at a smaller scale on 1.0Au/MMZ held more accessible surface area to substrates, rapider electron transfer and Au sites with higher activity. Those factors worked together to achieve the size-dependent catalytic activity of MNZ confining Au NPs in 4-NP conversion. Another publication in 2021 confined Pd NPs inside MOFs via three different strategies, including impregnation, one-pot and coating approaches.<sup>158</sup> It was found that the smallest NPs synthesized by impregnation method constructed more chemical bonds with porous materials. Changed charge density at the interface led to improved catalytic performances of Pd/MOFs.

Similarly, porous materials confining bimetal NPs show the size-dependent activity, related to the mole ratios of the two metals. Sareen et al. introduced bifunctional species of AuAg into SBA-15 zeolite and selected nitrobenzene reduction and p-aminoacetophenone evolution as prototype reactions.<sup>159</sup> By alternating concentration of cationic metal solution, AuAg alloys with different loading amount ratios were confined in cavities of mesoporous SBA-15. The average alloy size of partial samples followed the order Au-Ag(5:1)/m-SBA-15 (5.7 nm) < Au-Ag(10:1)/m-SBA-15 (17.9 nm) < Au-Ag(1:10)/m-SBA-15 (37 nm). Accordingly, reverse order in the catalytic activity over nitroaromatic was followed by these products (Fig. 8A). This negative correlation reflected that the catalytic performance of AuAg confining SBA-15 composites relied on the particle size to a certain extent. However, some opposite phenomenon was also captured in this paper. For instance, the particle diameter of Au-Ag(1:1)/m-SBA-15 (18 nm) was larger than Au-Ag(1:5)/m-SBA-15 (8-10 nm) while the former held higher rate constant in p-nitroacetopheneone (P-NAP) and nitrobenzene conversion. Therefore, particle size cannot be the only determining factor for catalytic activity of nitroaromatics reduction.

As for porous framework confining noble metal NPs, more mechanistic insight into size-dependent catalytic performance in nitroaromatics reduction should be further gained. Furthermore, it should be ascertained to what extent catalytic properties over nitroaromatics reduction for encapsulated catalysts depend upon the metal diameter. Therefore, more state-of-the art techniques await developing in the future and wider attention to this issue should be poured.

# 4.2 Subnanometric Noble metals inside Encapsulated Pores : From Isolated Atomic Sites to Noble metals clusters

The shrinking of dimensions of noble metals to sub-nano single atoms or clusters often has a positive contribution to the catalytic activity and durability in nitroaromatics reduction. By downsizing noble metal NPs to sub-nanometer regions, more unsaturated coordination junctions, higher surface area, and surface free energy will occur. This will lead to promoted unit mass activity, enhanced interaction between noble metals and porous materials, and more favorable reaction pathways with minimum outer energy inputs. Fang et al. made contrast experiments towards Pt NPs and single Pt atom confined in MOFs, and the results indicated single Pt atom confined in MOFs, and the results indicated single Pt atom confined in MOFs benefited interaction enhancement induced by electron transfer access incorporation from aluminum based porphyrinic MOF (denoted as AI-TCPP) to Pt.<sup>160</sup> Hence, it can be concluded that porous materials confining sub-nano metals always induce higher catalytic activity and stability in nitroaromatics reduction compared to confining nano metal NPs.

#### 4.2.1 Single Atoms Catalysts

When downsizing noble metals NPs below single-atom scale, tremendous alternation will take place in electronic and geometric structures, thus bringing about

#### **Environmental Science: Nano**

highly efficient catalysis.<sup>161, 162</sup> The superiority of single-atom catalysts can be attributed to two major aspects: (i) maximized atomic efficiency and optimal catalytic activity by oligo-dispersed active metallic sites more accessible to substrates; (ii) more coordinatively unsaturated sites favorable for interaction with chemical groups of porous materials and electron transfer with reactants, intermediates and products.

Owing to these special features, single-atom noble metals catalysts confined in porous materials will display exceeding catalytic properties to most noble metal NPs when applying in nitroaromatics reduction. As a proof, Tian and co-workers implanted Ru single atoms into isolated pores of 3D dendritic mesoporous silica nanospheres (MSNSs) via a typical ligand exchange strategy to catalyze 4-NP reduction.<sup>163</sup> Benefitted from the restriction of interior cavities, ultrafine Ru atoms with a size dimension below 1 nm were formed. Ru@MSNS-NH<sub>2</sub> exhibited extremely high catalytic activity, selectivity and durability in 4-NP conversion. Wang et al. confined pseudo single-atom Au into MOFs to generate pseudo-single-atom catalysts (PSAC) Au/MOF through a facile one pot method.<sup>164</sup> In 4-NP reduction, PSAC Au/MOF showed higher catalytic activity among conventional noble-metal based catalysts under the identical ambient environment. Derived from ultralow activation energy barrier (15.9 kJ mol<sup>-1</sup>), over 90% conversion to 4-AP within only two minutes was accomplished by PSAC Au/MOF hybrids.

From the perspective of reaction mechanism, single-atom catalysts at the ultrasmall size range feature higher surface-to-volume ratio, more coordinatively unsaturated sites on the metal surface, higher adsorption energy of substrates and reduced d band density of metallic states. These contributors are jointly responsible for enhanced catalytic performance in nitroaromatics reduction. Gao et al. encapsulated sub-nanosized PtRu alloys inside mesoporous carbon (MCN) with different Pt/Ru mole

ratios of 2.0 and 4.0 (denoted as Pt<sub>2</sub>Ru/MCN and Pt<sub>4</sub>Ru/MCN) and as-prepared products were reduced under H<sub>2</sub> atmosphere to generate Pt<sub>2</sub>Ru/MCN-R and Pt<sub>4</sub>Ru/MCN-R respectively.<sup>165</sup> In catalytic 4-NP reduction, a negative correlation between PtRu particulate size and rate constant k was observed between Pt<sub>2</sub>Ru/MCN(-R) and Pt<sub>4</sub>Ru/MCN(-R). It is known that relatively strong adsorption of nitroaromatics on the surface of noble metals is prerequisite for their subsequent reduction to yield anilines. In this case, PtRu bimetallic atoms smaller than 2 nm possessed considerable coordinatively unsaturated sites on their surface and essentially favored the rapid adsorption of nitroaromatics and hydrogen, which determined the reaction rate. Following DFT calculation suggested smaller-sized Pt<sub>2</sub>Ru/MCN(-R) held higher adsorption energy and shortened Pt-O bond, which enhanced its adsorption and reduction capability towards nitroaromatics (Fig. 8B).

In the research field of single-atom encapsulated catalysts applied in nitroaromatics reduction, further work about size-dependent properties should be done, such as the coordination environment, electronic natures as well as energy changes, which matters a lot to catalytic activity, sustainability and selectivity.<sup>166</sup> More detailed insights into single-atom confined catalysis are in need, such as how mixed valance state of metallic cores cooperatively work in nitroaromatics reduction.<sup>167, 168</sup>

#### 4.2.2 Noble metals Atom Clusters

Apart from NPs and single atoms, sub-nano noble metals clusters with ultrafine size dimension and atomic-scale dispersity in porous frameworks enable to catalyze nitroaromatics reduction with improved activity and chemoselectivity (see Fig. 8C).<sup>169</sup> Metal-metal bonds existed on metal clusters may induce specific reaction activity and stability, which will not present on single-atom catalysts over whether homogeneous or heterogeneous catalysis field.<sup>170, 171</sup>

Page 65 of 82

The meliorative catalytic efficiency of noble metals clusters confined in porous materials for nitroaromatics reduction can be assigned to the unique surface features of smaller-size clusters. Compared to noble metal NPs, smaller-sized metal clusters often possess higher atomic utility led by specific area increase and higher electron donating ability owing to higher unsaturated degree. Downsizing metals from nanometer regions to sub-nanometric region will cause shortened metal-metal bond distance, which enhances the catalytic capacity of encapsulated catalyst.<sup>172</sup> Additionally, reducing size from NPs to sub-nanometer clusters will induce notable alternation of coordination numbers of central atoms. Noble metal clusters with lower coordination numbers have more unoccupied density of states of d orbitals, leading to enhanced electron transfer and stronger interaction with encapsulating porous hosts.<sup>83, 173</sup> As an example, Gao's group encapsulated Au clusters into Cu-centered ZIF-8 nanorod arrays (denoted as Au<sub>NC</sub>@ZIF-8(Cu)NRAs), with Au<sub>NC</sub> sized 2 nm.<sup>131</sup> Combing the results of XPS and XANES characterization, it was found that the tiny size of Au clusters contributed to the presence of unsaturated Au sites, which was advantageous for strengthening interaction with ZIF-8. Subsequent catalytic tests of 4-NP reduction denoted that Au<sub>NC</sub>@ZIF-8(Cu)NRAs could convert 98% 4-NP during 6 min with k values of 0.489 min<sup>-1</sup>, which was 4.7 folds higher than bulk Au NPs. From the comparison experiments, it is not hard to see the enhanced catalytic efficiency in nitroaromatics reduction led by positive surface properties of noble metals clusters.



**Fig. 8** (A) Comparing results of reaction rate for p-nitroacetopheneone and nitrobenzene reduction by SBA-15, Au/SBA-15, Ag/SBA-15, diverse wt % Au-Ag (x: y)/m-SBA-15. Reprinted from Ref.<sup>159</sup> with permission from Elsevier, copyright 2018. (B) Side and top views of 4-NP adsorbed on the surfaces of (a) Pt(111), (b) Pt<sub>2</sub>Ru(111), and (c) Ru(001), comprising related adsorption energies. Density of atomic states of Pt, Ru and the O in nitro group of 4-NP adsorption on (d) Pt(111), (e, f) Pt<sub>2</sub>Ru(111) and (g) Ru(001). Reprinted from Ref.<sup>165</sup> with permission from Elsevier, copyright 2019. (C) Superiority of atomically precise metal nanoclusters for catalysis. Reprinted from Ref.<sup>169</sup> with permission from American Chemical Society, copyright 2020.

## 5. Conclusions and Outlooks

Encapsulating noble metal NPs into porous materials has been envisaged as an appealing strategy to obtain more efficient and permanent catalytic performance in nitroaromatics reduction. Nevertheless, achieving complete encapsulation becomes tough, which is because noble metals with high surface energy and low Tammann temperatures are prone to aggregate into bulk particles or sinter. Thus, in the aspect of controlled synthesis strategies, how to manipulate the properties of noble metal NPs, nucleation and growth rate of porous materials and achieve higher encapsulation efficiency demands to be deeply explored.

Considering the synergistic effect between noble metal NPs and various porous materials, efficient removal of diverse nitroaromatic derivatives from the

#### **Environmental Science: Nano**

environmental media can be accomplished. Confining noble metals into porous materials can boost the catalytic behavior in nitroaromatic reduction from the aspect of catalytic activity, size selectivity, and sustainability. Thereinto, it is necessary to further recognize how confinement effect functions in nitroaromatics reduction and understand the factors that may pose influence on the catalytic performances of noble metals encapsulated in four porous materials (porous carbon, zeolite, MOFs, and POPs).

Besides of confinement effect, size dimension of noble metal NPs can become a dominant factor, which impacts catalytic performance for substituted nitroaromatics reduction. With downsizing noble metals from NPs to sub-nanoscale clusters or atoms, catalytic properties of the confined systems in nitroaromatics reduction can be modified in the respects of catalytic activity, selectivity, and recyclability. With these in mind, it is imperative to investigate the positive correlation between smaller-scale noble metals and enhanced catalytic performance under pores confinement.

In summary, basic recognition and preliminary researches tend to perfect for porous materials confining noble metals in nitroaromatics reduction. Nevertheless, there is still deficiency for mechanistic and experimental evidence about strategic design, precise orientation coupled with activity manipulation, in the light of confining two or more nanoscale functional species including (but not limited to noble metals) simultaneously into porous materials. In addition, micro-scale perception in a confining system relies on advanced characterization techniques and calculation methods, which remains a sticky challenge. As a conclusion, several following prospects await further stretching:

(1) Experimental parameters and functionalization strategies in the synthetic process should be optimized to improve encapsulation efficiency and to utilize catalytic capability of each counterpart to the fullest degree. Then feasible structural design

according to practical requirements and precise modulation over distribution of active metallic sites can be achieved. As for sub-nanometric metals, synthetic methodologies need to be further explored to confine well-isolated active sites within pores at a remarkable encapsulation efficiency.

(2) More intensive investigation on mechanisms over how confinement effect works and what unique reflections size effect of noble metals will exhibit under confinement for catalytic nitroaromatics reduction should be conducted in the future. In this aspect, effective and progressive monitoring techniques, especially real-time insitu characterization, more delicate theoretical calculation methods, and unique analysis perspectives over on-hand data are demanded urgently to gain comprehensive insights of structural relations between every component in the atomic level. It appeared to be more significant especially for sub-nanometer species with large detection difficulties and instability under high-speed electron flow.

(3) Probabilities to encapsulate multifunctional nanometer pieces of matter simultaneously into porous materials should be explored, so that endowing confining system with more complicated treatment functions based on the selective removal of nitroaromatics. It will be promising to consolidate fluorescence properties, optimal response of noble metals with abundant features of porous materials, hence achieving extension to photoinduced nitroaromatics reduction. At the same time, in-depth understanding on structure-performance correlation of multifunctional catalysts will be rewarding for rational design of multifunctional confined composites to realize highly efficient nitroaromatics reduction.

#### **Author Contribution**

All the authors contributed to the paper. Yixia Li wrote the initial manuscript and made subsequent modifications; Yukui Fu proposed the conceptualization, modified the structures of this article, and reviewed. Cui Lai acquired the funding and directed the writing. Lei Qin and Shiyu Liu were responsible for the reviewing; Bisheng Li, and Huan Yi supplemented the references. Fuhang Xu, Ling Li and Mingming Zhang made further modification; Mengyi Xu, Chunyan Du and Wenjing Chen polished the manuscript.

## **Conflicts of interest**

There are no conflicts to declare.

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