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Internally Supported Metal-oxide Nanocatalyst for Hydrogenation of Nitroaromatics

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Keywords: metal, catalyst, internally dispersed, mesoporous, hydrogenation

Abstract: The uncalcined but highly dispersive oxide supported metal catalyst for liquid phase reactions may suffer from the agglomeration of metal nanoparticles and the drop of metal catalyst in solution, which will decrease the activity and shorten their life in catalysis. Here, a one-pot successive polyol reaction was developed to prepare $M-E_xO_y$ colloidal particles as heterogeneous nanocatalysts, which merge the controlled synthesis of metal catalysts and oxide supports, the in-situ loading of catalyst and even the mesopore amplification into a highly integrated process. Unlike the traditional surface deposited catalysts, the noble metal nanoparticles even with a large amount of loading are internally dispersed in the mesoporous oxide particles, which shows higher activity and stability in the hydrogenation of nitroaromatics compared to the isolated nanocatalysts or surface deposited catalysts. The improved activity and stability comes from the physical confinement of metal nanoparticles and good mass

transportation of substrate/product within the support particles. This work proposed a novel method to prepare highly dispersed metal catalysts, which could be potentially useful to heterogeneous catalytic reactions with high throughput and long life demands.

Introduction

 Noble metal is one kind of most important nanocatalysts in heterogeneous catalysis, and its size effect¹⁻⁷, separability⁸⁻¹⁰, stability^{8, 11}, crystal facet effect¹²⁻¹⁵ and localized surface plasmon resonance¹⁶⁻¹⁸ have been widely investigated in the past decades. With the breakthrough of synthetic method, great success has also been achieved in the utilization of these metal nanoparticles in catalysis. For instance, Tatsuya Tsukuda' group had synthesized a series of Au nanoclusters with well-defined sizes, in which a sample with an optimal size exhibited highest activity and selectivity in the oxidation of cyclohexane to cyclohexanol and cyclohexanone.⁴ Li et al. had reported an oleylamine-assisted synthesis of Pd nanocrystals with various shapes, which exhibited good separability and reusability in Miyaura-Suzuki reaction compared to traditional homogeneous catalysts because of their different solubility in polar and nonpolar organic solvent.⁸, ⁹ Based on similar amine-assisted synthesis, Zheng et al. have prepared concave polyhedral Pt nanocrystals, which showed excellent electrocatalytic activity comparing with the commercial Pt black due to the explosion of high-index crystal facets.¹³

In practical heterogeneous catalysis, the metal catalysts are generally supported by various metal oxides due to their contributions in the enhancement of activity and improvement of catalyst life.¹⁹⁻²² For example, Xiao et al. have reported Au nanocatalysts supported by MgO-Al₂O₃ layer double oxide (LDO) for CO oxidation to CO₂, where the strong metal–support interaction renders the catalyst sinter resistance at high temperature and long life in reaction.²¹

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For another instance, Guo et al. have prepared flower-like Pd/MgO-ZnO composites, which exhibit excellent catalytic activity for CO oxidative coupling to dimethyl oxalate compare to Pd/ZnO catalyst, because the doping of MgO can increase the number of Lewis basic sites and facilitate the donation of electron from Pd active sites.²³ Furthermore, metal oxides with large surface area usually provide adequate positions for loading of metal nanoparticles, which is favorable to the high dispersion of active sites. For example, Pt catalyst loaded on mesoporous CeO_2 show outstanding activity and high selectivity for CO oxidation in the presence of hydrogen due to large surface area of catalyst support.²⁴ Traditionally, the metal-oxide heterogeneous catalysts are prepared by deposition or in-situ generation of metal catalysts on the surface of metal oxides, which directly expose the active sites to the substrate molecules and lead to a high activity in catalysis. However, when these catalysts are used in liquid phase reactions, they usually are not calcined to insure the good dispersion in solution and sufficient interaction with the substrate molecules. Without calcination, the interaction between metal catalyst and oxide support is relatively weak so that the metal catalysts may drop from the oxide support and agglomerate in the solution, which decrease the activity and shorten the life of nanocatalysts. Therefore, a heterogeneous nanocatalyst for liquid phase reaction which possesses the high activity and good stability at the same time will be highly desired.

In this work, we shall report a one-pot successive polyol reaction to synthesize metal nanocatalysts supported within the mesoporous oxide, which integrated the controlled synthesis of metal catalysts and oxide supports, the in-situ loading of catalyst and even the mesopore amplification into a compatible process. Unlike the traditional surface deposited catalysts, the noble metal nanoparticles are internally dispersed inside the mesoporous oxide particles, which shows higher activity and stability in the hydrogenation of nitroaromatics. The improved activity

and stability comes from the physical confinement of metal nanoparticles and good mass transportation of substrate/product within the mesoporous oxide particles. Moreover, we shall also investigate the promotion of catalyst activities by amplification of mesopores in oxide particles through protective etching.

Experimental

Materials: Palladium(II) acetylacetonate (Pd(acac)₂, 99%), platinum(II) acetylacetonate (Pt(acac)₂, 98%), gold (III) chloride trihydrate (AuCl₃·H₂O, 99%) and ethylene glycol (EG, 99%) were purchased from J&K Co. Ltd. Zinc acetate (ZnAc₂, 99%) and cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.5%) were obtained from Aladdin CO. Ltd. Polyvinyl pyrrolidone (PVP, Mw = 29,000) and diethylene glycol (DEG, 99%) were purchased from Sigma Aldrich. Copper(II) acetate monohydrate (CuAc₂·H₂O, 98%), hydrochloric acid (HCl, 36-38 vol%), sulfuric acid (H₂SO₄, 95-98%) and ethanol (EtOH, 99.7%) were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals were directly used without further treatments.

Synthesis of Pd, Au and Pt nanoparticles: Monodisperse Pd nanoparticles (NPs) were synthesized through pyrolysis of $Pd(acac)_2$ in DEG at high temperature with PVP as surfactants. Typically, $Pd(acac)_2$ (80 mg) was first dispersed in DEG (5 mL) by sonication to generate a yellow suspension. At the same time, PVP (400 mg) was added to DEG (15 mL), which was heated to 160 °C to form a transparent and pale yellow solution. Once the Pd precursor was injected to the PVP solution, it turned to black mixture rapidly in 1 min, which was maintained at 160 °C for 1 hour to produce Pd nanoparticles. The reaction solution was cooled down to room temperature and directly kept as a stock solution of Pd NPs (1.39 mg/mL) for the following

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synthesis. The Pt nanoparticles were prepared by similar polyol process except that $Pt(acac)_2$ (80 mg) was used as precursor. The Au nanoparticles could be synthesized by this method, where HAuCl₄ (80 mg) and oleyamine (0.5 mL) were used as precursor and surfactant, respectively. Their reaction solutions were also kept as Au NPs (1.96 mg/mL) and Pt NPs (1.98 mg/mL) stock solutions for the following synthesis.

Synthesis of Pd-ExOy (E = Zn, Cu, Ce) composite nanostructures: For the synthesis of Pd-ZnO nanocomposites, the aforementioned stock solution of Pd NPs (6.17 mL) was mixed with ZnAc₂ (2 mmol) and DEG (13.83 mL) to form a black homogeneous solution. Then, it was heated to 160 °C and kept at that temperature for 2 hours to produce Pd-ZnO composite nanoparticles. After the reaction solution was cooled down to room temperature, the Pd-ZnO particles were separated by centrifugation and washed by ethanol for several times. The theoretical loading amount of Pd was calculated to be 5% according to the dosage of Pd and Zn, and it could be adjusted from 1% to 15% by changing the volume of Pd NPs stock solutions in the synthesis.

For the synthesis of Pd-Cu₂O nanocomposites, the Pd NPs stock solution (5.43 mL) was mixed with CuAc₂·H₂O (2 mmol), PVP (4 mmol) and DEG (14.57 mL) to form a greenish black solution. Then, it was heated to 155 °C under N₂ protection and kept at that temperature for 1 hour to produce Pd-Cu₂O composite nanoparticles. After the reaction solution was cooled down to room temperature, the Pd-Cu₂O particles with 5% of Pd were separated by centrifugation and washed by ethanol for several times.

For the synthesis of Pd-CeO₂ nanocomposites, the Pd NPs stock solution (39.16 mL) was mixed with $Ce(NO_3)_3 \cdot 6H_2O$ (6 mmol), PVP (10 mmol) and DEG (0.84 mL) to form a black

solution. Then, it was heated to 155 °C under N_2 protection and kept at that temperature for 1 hour to produce Pd-CeO₂ composite nanoparticles with 5% of Pd. After the reaction solution was cooled down to room temperature, the Pd-CeO₂ particles were separated by centrifugation and washed by ethanol for several times.

Synthesis of M-ZnO (M = Pd, Au, Pt) composite nanostructures: The Pt-ZnO and Au-ZnO nanocomposites were prepared by similar reaction and post-treatments as described in the synthesis of Pd-ZnO. The Pt NPs stock solution (4.32 mL) and the Au NPs stock solution (4.37 mL) were used as precursors respectively, which generate composite particles with theoretical loading amount of noble metals to be 5%.

Synthesis of porous Pd-ZnO nanocomposites by protective etching: The porous Pd-ZnO could be directly prepared by etching the freshly generated Pd-ZnO particles in their original reaction solution. After the growth of Pd-ZnO particles was performed at 160 °C for 2 hours, the original reaction solution was cooled down to 120 °C and maintained at that temperature for 10 min. Then, the aqueous solution of HCl (0.1 mL, 12 mol/L) was quickly injected to the above dispersion to initiate the etching. After 20 min etching, the reaction solution was cooled down to room temperature and the porous Pd-ZnO nanocomposites could be obtained by centrifugation, ethanol washing and drying in oven.

Characterization: Transmission electron microscope images (TEM) and high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) images were captured by a FEI Tecnai G^2 F30 microscope operated at 300 kV. Powder X-ray diffraction (XRD) patterns were measured on Rigaku Ultima IV X-ray diffractometer operated at 35 kV and 40 mA with Ni-filtered Cu-K α radiation as X-ray beam source. Nitrogen adsorption-desorption

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isotherms and BET (Brunauer-Emmett-Teller) surface areas were measured by a Belsorp-Max analyzer at 77 K. The precise mass percentages of Pd content were measured by Thermo IRIS Intrepid II XSP inductively coupled plasma atomic emission spectrometer (ICP-AES). The conversion of substrate in catalysis were analyzed by Agilent 7890A gas chromatography (GC). X-ray photoelectron spectroscopy (XPS) analyses on the surface of the samples were performed in AXIS Ultra DLD. Metal dispersion were measured by chemical absorption of CO on Micromeritics AutoChem II chemisorption Analyzer.

Catalytic hydrogenation of Nitroaromatics: Typically, nitrobenzene (51 μ L, 0.5 mmol) and the Pd-E_xO_y nanocatalyst (Pd, 0.5 mg) were dispersed in methanol (5 mL) in a reaction tube. The reaction tube was vacuumed and filled with H2 for 3 times, and then it was connected to H₂ source (1 atm) during the reaction. With the presence of nanocatalyst, the hydrogenation of Nitroaromatics were performed at room temperature. The reaction solution was sampled at specific times and the conversion of Nitroaromatics can be analyzed by gas chromatography.

Results and Discussions

The Pd-ZnO composite nanostructures were prepared by a polyol synthesis of ZnO in the presence of freshly made Pd nanoparticles (NPs). (**Figure 1**) In a typical process, monodisperse Pd NPs were first synthesized through pyrolysis of $Pd(acac)_2$ in DEG at high temperature with PVP as surfactants. Without any post treatment, the reaction solution containing the Pd NPs were directly mixed with the polyol solution of $ZnAc_2$ to form a new homogenous suspension. After the temperature being raised to 160 °C, zinc oxide nanocrystals began to nucleate and then agglomerate with Pd NPs to form a small and heterogeneous nanocrystal cluster. TEM images of

Pd-ZnO particles produced by 30 min of reaction clearly confirmed that the Pd NPs had been attached to the ZnO particles since the beginning of reaction. As the polyol reaction proceeded, the heterogeneous agglomeration of Pd NPs and ZnO nanocrystals continued, so that the small clusters eventually grew into uniform composite nanostructures with Pd NPs embedded inside them.

The as-prepared Pd-ZnO composite nanostructures were composed of a large number of internally dispersed Pd NPs and the porous ZnO framework, which formed useful structural characteristics for heterogeneous nanocatalysts. In order to locate the distribution of Pd, a typical Pd-ZnO sample with theoretically 5% of Pd were embedded in resin and cut by quartz knife for TEM observation. (Figure 2) The cross-section TEM images of almost every composite particle indicated that Pd NPs were distributed inside the ZnO particle but not on its surface. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image as well as the energy dispersive X-ray spectroscopy (EDS) mapping of a single Pd-ZnO particle also confirmed the above TEM observations, and the measured Zn/Pd ratio (97.6/2.4) was consisted with the ICP-AES results as well. The STEM images of the partially etched Pd-ZnO particle showed the encapsulated Pd NPs more clearly. The high dispersity of Pd NPs not only ensured the synergistic interaction between catalyst active sites and supporting materials, but also inhibited the loss or merging of Pd NPs during the catalytic reaction. On the other hand, the cross-section TEM images suggested that the ZnO particles should have porous characteristics since they were composed of small ZnO nanocrystals. The cluster-like structure of ZnO actually agreed with many colloidal nanoparticles synthesized in polyol process, and the induced porous structure would effectively contribute to the transportation of substrate molecules and their access to the Pd nanocatalyst deeply embedded inside the ZnO particles. In a word, an interesting

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combination of internally dispersed and confined Pd and a slightly porous ZnO as catalyst supports might form an ideal nanocatalyst for effective and long-life catalysis.

The one-pot successive polyol reactions reported in this work provided a convenient and much simplified method for the synthesis of supported nanocatalysts, which integrated the controllable synthesis of metal catalysts and support materials, the in-situ loading of catalyst and even the mesopore construction in a compatible reaction system. Thanks to the fast development of nano synthesis in polyol solution, metal nanostructures with various chemical compositions, shapes and exposed facets could be obtained by polyol reaction. Without any post treatment, the reaction solution of metal nanostructures could be directly introduced to the preparation of oxide supporting materials, which produced highly dispersed nanocatalyst within oxide particles. The addition of appropriate acid or base could controllably etch the oxide particles to create more mesopores and thereby increase the reactivity. Although the total synthesis was composed of several steps, these reactions actually could be performed in a same flask and no separation or purification were required between each steps, which effectively simplified the procedures for preparation of composite nanostructures.

In addition to the simplification of procedures in synthesis, the current one-pot reactions also provided good tunabilities and flexibilities to the choice of metal catalyst and oxide supports. For example, Pd-ZnO, Pd-Cu₂O and Pd-CeO₂ composite particles could be prepared in the presence of Pd NPs, when ZnAc₂, CuAc₂ and Ce(NO₃)₃ were used as reactants respectively in polyol reactions. (**Figure 3**) TEM images of these particles showed that they all had similar structures, where Pd NPs were internally dispersed inside the oxide particles. The only difference lies in the small particle size of Pd-Cu₂O (40 nm) compared to the other two samples (150 nm), which might be caused by the relatively fast nucleation and growing speed of Cu₂O in poly reaction.

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The XRD patterns suggested that the composite nanostructures were majorly composed of crystalline oxides, while the diffraction peak around 40° corresponding to the (111) plane of Pd indicated that each of them contained a small amount of Pd, both of which were well consistent with the formation of Pd-E_xO_y composite particles. For another instance, M-ZnO with different metallic active sites could be obtained when different metal NPs were introduced to the polyol synthesis of ZnO. (**Figure 4**) For demonstration, premade monodisperse Pd NPs (10 nm), Au NPs (10 nm) and Pt (5 nm) were coupled to the pyrolysis of ZnAc₂ at high temperature, which produced Pd-ZnO, Au-ZnO and Pt-ZnO composite particles, respectively. Similarly, TEM images showed that the metal nanoparticles were dispersed inside ZnO, and the XRD patterns confirms the formation of composite nanostructures. The great flexibility in tuning the metals catalysts and oxide supports not only provided ideal materials for the systematic study of catalytic mechanism but also lay a solid foundation for the screening of highly active nanocatalysts.

In the following discussion, we shall demonstrate the structural advantages of the as-prepared nanocatalysts through hydrogenation of nitroaromatics, which was widely used as a probe reaction to evaluate the activity and stability of metal catalysts. (**Table S1**) In a typical reaction, the substrate (0.5 mmol) and Pd-ZnO catalyst (10 mg) were dispersed in methanol to form a homogeneous suspension under stirring. The reaction tube was vacuumed and filled with H_2 , and the reaction was then performed under atmospheric H_2 at room temperature. After the removal of nanocatalyst by centrifugation, the products were analyzed by gas chromatography. For the catalytic hydrogenation of nitrobenzene, the yield of aniline was 64.8% in 1 hour and the substrate were completely converted in 2 hour. For hydrogenation of 4-nitroaniline and 1,3-dinitrobenzene, the yields of p-phenylenediamine and m-phenylenediamine are only 5.3% and

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8.5% in 1 hour, and they increased to 30.0% and 48.2% in 6 hours as the hydrogenation continued. For the hydrogenation of 4-nitroacetophenone, the substrate completely reduced to 4-aminoacetophenone in 1 hour. The Pd-ZnO showed different catalytic activities for different nitroaromatics (**Table 1**), which proved that it was a universal catalyst for a broad range of substrate in hydrogenation. Although the confinement of Pd within mesoporous ZnO does suppress the activity to some extent, the TOF value (1.15 min^{-1}) for the hydrogenation of nitrobenzene using 1-atm H₂ and 10-nm Pd at room temperature was comparable to most literature results under similar conditions (**Table S2**), which confirms the good accessibility to internally dispersed metal catalysts.

We have prepared Pd nanoparticles (NPs), ZnO particle, internally dispersed Pd(i)-ZnO particles and surface deposited Pd(s)-ZnO particles and studied the function of Pd and ZnO in reaction by absorption experiments and comparison of catalytic activities. Generally, H_2 molecules are adsorbed on the surface of Pd nanoparticles and disassociated to active H to reduce the nitrobenzene. The mesoporous ZnO particles serve as supporting materials to stabilize the Pd catalysts. In the previous research works, transition metal oxide with oxygen vacancies, such as WO_x^{25} , can behave as active sites for catalysis due to the adsorption of nitrobenzene. However, the substrate molecules are not adsorbed to ZnO particles in this work, which is concluded from the similar UV-Vis absorption of nitrobenzene with and without the presence of ZnO particles. (See supporting information Figure S1) When the Pd nanoparticles (NPs), ZnO particle, Pd(i)-ZnO particles and Pd(s)-ZnO particles were used as catalyst for hydrogenation, the corresponding conversion of nitrobenzene at 1 hour were determined to be 99.9%, 0%, 56.8% and 99.4%, which proved that ZnO has no catalytic activity for hydrogenation. Therefore, the high activity of Pd(i)-ZnO catalyst comes from the metal active site (Pd), and the mesoporous

ZnO particle serve as a good supporting material to stabilize the Pd catalysts.

The current M- E_xO_y nanocatalysts provided a good opportunity to understand the influence of supporting materials upon the electron structure and thereby the activity of catalytic centers, as these composite particles were prepared under similar conditions and were similar in structure either. Here, Pd-ZnO, Pd-Cu₂O, Pd-CeO₂ nanocomposites (10 mg) containing the same amount of Pd (0.5 mg) were used as catalysts for the hydrogenation of nitrobenzene (0.5 mmol) in methanol (5 mL) at room temperature with 1-atm H₂. (**Figure 5**) The kinetic curves for the production of aniline showed that the conversion of nitrobenzene catalyzed by Pd-ZnO was completed in 2 hours and the conversions catalyzed by Pd-Cu₂O, Pd-CeO₂ only reached 56.4% and 35.9% at the same time. The corresponding TOF values for these hydrogenation reactions are 0.89, 0.49 and 0.33 min⁻¹, respectively.

In order to explain the different activities, XPS analysis for the doublet state $(3d^{5/2} \text{ and } 3d^{3/2})$ of Pd were performed to characterize the electronic structures of Pd.^{23, 26, 27} The XPS spectrum for Pd-E_xO_y catalysts before hydrogenation can be explained by the chemical environment in synthesis, because they were not calcined or treated by H₂ at high temperature. According to the Figure 5, the Pd²⁺/Pd⁰ ratio for Pd-ZnO, Pd-Cu₂O and Pd-CeO₂ before catalysis were determined to be 0.14, 0 and 11.8. (**Table S3**) For Pd-ZnO particles, most of the Pd content are kept as Pd⁰ species, and only a small amount of Pd was oxidized to Pd²⁺ due to the oxygen in reaction system. For Pd-Cu₂O particles, only Pd⁰ species exist in the product because the oxidation is suppressed by the reductant species (Cu⁺). It is just the opposite situation for Pd-CeO₂ particles, where most of the Pd content are Pd²⁺ species since the oxidation of Pd⁰ is greatly promoted by the oxidant species (Ce⁴⁺, NO₃⁻) in synthesis. After catalytic hydrogenation, the Pd-ZnO, Pd-Cu₂O and Pd-CeO₂ catalysts were analyzed by XPS again (**Figure S2**), and their Pd²⁺/Pd⁰ ratio

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were determined to be 0.246, 0.165 and 0.596, respectively. It can be concluded that a small amount of Pd⁰ in Pd-ZnO and Pd-Cu₂O were oxidized to Pd²⁺ in hydrogenation, while a net 60% of Pd²⁺ in Pd-CeO₂ were reduced to Pd⁰ in hydrogenation. Combined with the reaction mechanism of hydrogenation of nitroaromatics, it is not difficult to understand that Pd-Cu₂O and Pd-ZnO have better activity than Pd-CeO₂, since Pd⁰ was the active center for hydrogenation. However, we cannot clarify the function of Pd²⁺ due to the lack of in-situ characterizations in catalysis. The catalytic activity of Pd-ZnO is higher than that of Pd-Cu₂O, probably because the electron density of Pd on Cu₂O was decreased during hydrogenation due to the reduction of surface Cu₂O to Cu. The decreased electron density was unfavorable to the dissociation of H₂ into active H species on Pd, so that the catalytic activity decreased accordingly.

One advantage for the current nanocatalysts with internally dispersed noble metals was the high stability and good reusability compared to isolated nanocrystals and surface deposited catalyst. Here, three kinds of nanocatalysts (10 mg) with same amount of Pd (0.5 mg), including Pd nanoparticles, Pd(s)-ZnO with surface-deposited Pd (prepared by impregnation) and Pd(i)-ZnO with internally dispersed Pd, were used for successive hydrogenation of nitrobenzene, and its conversion was measured at 1 hour in each cycle. (**Figure 6**) The experimental results showed that the initial conversions of nitrobenzene catalyzed by Pd and Pd(s)-ZnO were much higher than that of Pd(i)-ZnO, because the isolated Pd nanoparticles dispersed in solution and the surface deposited Pd nanoparticles had better accessibility to the substrate. The as-prepared Pd(i)-ZnO particles only had about half of the activity in the first round probably because the Pd nanoparticles were embedded inside the porous ZnO, which slow down the transportation of substrate and product. However, when these catalysts were recycled for 5 successive reactions, the conversion of nitrobenzene decreased from 99.9% to 1.6% for isolated Pd nanoparticles and

from 99.4% to 33.2% for Pd(s)-ZnO, respectively. For Pd(i)-ZnO with internally dispersed Pd, the conversion steadily decreased from 56.8% to 44.2%, which suggest it had higher stability than both of the other two catalysts.

We have also examined the structure and composition of Pd(i)-ZnO catalyst after hydrogenation to further confirm its high stability in reaction. TEM images show that the Pd nanoparticles were dispersed inside mesoporous ZnO particle, which was almost the same as those before the reaction. (Figure S3) ICP-AES analysis indicated that the practical Pd content was 4.83%, which was also close to 4.85% before the reaction. After 5 continuous reactions, we noticed a loss of catalyst from 10.2 mg to 7.75 mg, which corresponded to a loss of 24% in mass. This loss was inevitable in separation since the catalysts used here was only several milligrams in weight. Meanwhile, the conversion of nitrobenzene catalyzed by Pd(i)-ZnO decreased from 56.8% to 44.2% after 5 cycles, which corresponded to a decline of 22% in conversion. Therefore, it can be concluded that the decline of catalytic activity was majorly caused by the loss of catalyst during separation. If the loss is counted in evaluation, one can find that the activity of Pd(i)-ZnO are almost unchanged after 5 cycles. These results indicated that the porous ZnO framework effectively prevents the agglomeration and drop of metal nanocatalysts during the violent reactions. Although the initial activity of the internally dispersed nanocatalysts is lower than that of the isolated or exposed catalyst, it still will be a preferred model for supported catalyst when long life is required in practically reactions.

Another advantage for the $M-E_xO_y$ nanocatalysts was the high loading of metallic active sites and thereby a good conversion efficiency in practical catalytic reactions with high throughput demands. Similar to the impregnation process, the loading of noble metals can be precisely controlled by adjusting the dosage of metal nanoparticle stock solution in synthesis. For the case

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of Pd-ZnO, we can prepare a series of nanocatalysts with practical Pd weight percentage of 0.7%, 4.8%, 9.7% and 13.1% through the one-pot successive polyol reactions, where the Pd contents were originally set to be 1%, 5%, 10% and 15% according to the dosage of Pd nanoparticles. The deviation of ICP-MS results from the theoretical values was caused by the incomplete encapsulation of Pd nanoparticles by ZnO, especially when the loading of Pd content is high. It should be noted that the highest loading of Pd that can be reached by current synthesis is about 13%, because excessive Pd nanoparticles can be found outside the composite particles when the dosage of Pd is further increased to 20%. (Figure S4) With the increase of Pd content, the aqueous solution of Pd-ZnO nanocatalysts turned from greyish white to black, and their XRD patterns showed an increased peak around 40° which was attributed to the diffraction of (111) crystal plane of elemental Pd. (Figure 7) When these Pd-ZnO nanocatalysts (10 mg) were used for hydrogenation of nitrobenzene in methanol, they presented an accelerated conversion along with the increasing of Pd loading, but the TOF values were measured to be 1.19 min⁻¹, 0.86 min⁻¹ ¹, 0.48 min⁻¹ and 0.57 min⁻¹ accordingly. The low TOF value for high loading Pd(i)-ZnO might be attributed to the aggregation of Pd nanoparticles inside ZnO framework, which can be confirmed by the decreased metal dispersion for Pd catalyst. Through chemical absorption of CO, the metal dispersions were measured to be 3.04%, 3.14%, 1.26% and 1.29% with the increasing of Pd content. As a reference, we had also measured the metal dispersion and TOF value of hydrogenation for Pd(s)-ZnO catalyst (5% Pd), which turned out to be 5.6% and 1.9 min⁻¹, respectively. The comparison of Pd(i)-ZnO and Pd(s)-ZnO catalyst suggested that the encapsulation of Pd within mesoporous ZnO did suppress the metal dispersion and decrease the TOF value to some extent. However, Pd(i)-ZnO catalysts with Pd loading of 4.8% might be the optimal one with both good stability and catalytic activity. (Table S4) From the viewpoint of

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economy of Pd species, the internally dispersed Pd-ZnO catalysts with extremely high loading of Pd was less valuable compared to the general catalysts. However, they could be very useful in high throughput conversions with limited space for catalysts only if their activity were maintained. Our experiments proved that the Pd-ZnO nanocatalyst with 13% of Pd helped to complete almost every conversion of nitrobenzene for 10 continuous reactions, in which the steady conversion rates around 96% showed the valuable stability of this catalyst even with dense distribution of metals active sites.

The activities of these M-E_xO_y nanocatalysts can be further improved by amplification of mesopores through a one-pot protective etching reaction which is conveniently integrated into the synthesis of $M-E_xO_y$ particles. (Figure 8) For the original Pd-ZnO, its BET surface area and BJH average pore size were measured to be 22.49 m^2/g and 4.77 nm by N₂ adsorption-desorption test. It indicated that the original Pd-ZnO colloidal nanocrystal clusters composed of small and aggregated nanoparticles already had mesoporous characteristics. Once these particles were etched by HCl solution at 120 °C in the presence of PVP as protective agent, their mesopore diameters were found to increase to 4.92 nm, 5.13 nm and 6.82 nm with the increasing of HCl concentration, and their surface areas increased to 37.4 m²/g, 46.1 m²/g and 47.0 m²/g accordingly. (Table S5) The positive correlation between pore size and surface area suggested that the acidic etching amplified the mesopores and increase the surface area. Once the etched particles are washed and dried, their weight loss from the original Pd-ZnO are measured to be 5.3%, 11.3% and 18.4%, which was consistent with the etching reaction. TEM image of the etched Pd-ZnO showed that many small and individual Pd nanoparticles were uniformly dispersed inside the ZnO particle (Figure 2d), which might be favorable to the mass transportation of reactants and products.

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The etched Pd-ZnO were proved to have higher catalytic activity due to the easy access of substrate molecules to the Pd catalysts. Here, 4 catalysts including Pd-ZnO (10 mg), Pd-ZnO E1 (9.5 mg), Pd-ZnO E2 (8.9 mg) and Pd-ZnO E3 (8.3 mg) were used for hydrogenation of nitrobenzene. All the catalysts contained the same amount of Pd (0.5 mg) according to the ICP-AES analysis of Pd percentage. In the parallel experiments, the conversion of nitrobenzene at any specific time increased when the Pd-ZnO catalyst is further etched. (Figure 9a) In the recycle experiments, the initial conversion for Pd-ZnO, Pd-ZnO E1, Pd-ZnO E2 and Pd-ZnO E3 were determined to be 50.9%, 54.6%, 59.4% and 62.3%, which proved again that the activity increased with the etching of catalyst support. (Figure 9b) According to the N₂ adsorptiondesorption test, the mesopores within the Pd-ZnO particles were amplified along with the etching of ZnO by HCl. These amplified mesopores were certainly favorable to both the transportation of nitrobenzene molecules towards the Pd catalyst and the leaving of aniline molecules from the catalyst. In other words, the Pd catalysts became more accessible when the supporting ZnO particles were gradually etched. The etching process address the concerns of relatively low initial activity for internally dispersed Pd-ZnO catalyst due to the embedding of Pd nanoparticles inside ZnO. After five repeated catalytic reactions, the activities of these 4 catalysts decreased 24.8%, 22.2%, 27.1% and 23.3% respectively due to the loss of catalyst in separation, which suggested that the catalysts' stability was not affected by the etching treatment.

Conclusions

In summary, $M-E_xO_y$ composite nanostructures were prepared by polyol synthesis of E_xO_y in the presence of freshly made noble metal nanoparticle. Unlike the traditional surface deposited

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catalysts, the noble metal nanoparticles are internally dispersed inside the porous E_xO_y particles. The one-pot successive polyol reactions provided a simplified method to synthesize supported nanocatalysts, which integrated the flexible and controlled synthesis of metal catalysts and oxide supports, the in-situ loading of catalyst and even the mesopore amplification into a compatible process. Using the hydrogenation of nitroaromatics as probe reaction, the internally dispersed noble catalysts have been proved to possess higher activity and stability compared to the isolated nanocatalysts or surface deposited catalysts. At the same time, they are also capable of loading large amount of metallic active sites without aggregation, which is useful to practical reactions with high throughput demands. Moreover, the catalytic activities can be further improved by amplification of mesopores through protective etching reaction and easier access of substrate molecules to the active sites. This work proposed a novel way to prepare highly dispersed metal catalysts supported by oxide nanoparticles, which could be potentially useful to other heterogeneous catalytic reactions after changing the chemical composition of active center and supporting material.

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Supporting Information.

Conditions for all catalytic reactions, comparison of activity with literature results, metal dispersion and TOF values for Pd(i)-ZnO catalysts with different Pd loading, BET results for etched Pd(i)-ZnO catalyst, TEM and XPS analysis of Pd(i)-ZnO catalysts before and after catalysis were supplied as Supporting Information.

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Figure 1. a) Schematic illustration to the formation of Pd-ZnO composite nanostructures. TEM images of b, e) Pd nanoparticles, c, f) small clusters of Pd-ZnO nanocrystals and d, g) Pd-ZnO composite particles.



Figure 2. a, b) Cross-section TEM images of Pd-ZnO composite particles. STEM image and EDS mapping of c) a typical Pd-ZnO particle and d) an etched particle.





Figure 3. TEM images of a, d) Pd-ZnO, b, e) Pd-Cu₂O and c, f) Pd-CeO₂ composite particles and g) their XRD patterns. The JCPDF card numbers for ZnO (*), Cu₂O (#) and CeO₂ (&) are 36-1451, 05-0667 and 43-1002 respectively.



Figure 4. TEM images of a) Pd, b) Au and c) Pt nanoparticles. TEM images of d) Pd-ZnO, e) Au-ZnO and f) Pt-ZnO composite particles and g) their XRD patterns. The JCPDF card numbers for Pd (*), Au (#) and Pt (&) are 46-1043, 04-0784 and 04-0802 respectively.



Figure 5. a) Kinetic curves for the hydrogenation of nitrobenzene catalyzed by Pd-ZnO, Pd-Cu₂O and Pd-CeO₂. b-d) The XPS spectra of Pd 3d for the above three catalysts.

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Figure 6. Conversion of nitrobenzene in 5 successive hydrogenation reaction catalyzed by isolated Pd nanoparticles, surface-deposited Pd catalyst (Pd(s)-ZnO) and internally dispersed Pd catalyst (Pd(i)-ZnO).



Figure 7. a) Solution of Pd-ZnO particles with different loading of Pd NPs, b) their XRD patterns and c) corresponding kinetic curves in hydrogenation when using these particles as catalysts. d) Conversion of nitrobenzene in 10 continuous reaction catalyzed by Pd(13%)-ZnO particles.

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Figure 8. N₂ adsorption-desorption of a) porous Pd-ZnO particles and b-d) the corresponding products etched by HCl with increased concentration.



Figure 9. a) Catalytic activity of Pd-ZnO particles with different etching extent and b) their gradual decrease of conversion in 5 continuous reactions.

Tables

Table 1. Conversions of substrate in 1h and 6h for catalytic hydrogenation of 4 nitroaromatics.

Entry	Substrate	Product	Conv. / % (1h)	Conv. / % (6h)	TOF / min ⁻¹ (60 min)
1			64.8	99.9 *	1.15
2	NH2	NH2 NH2	5.35	30.0	0.095
3	O_N NO2	H ₂ N NH ₂	8.45	48.2	0.15
4			99.9	/	1.77

* The conversion of aniline has reached 99.9% at 2 hour.

Internally Supported Metal-oxide Nanocatalyst for Hydrogenation of Nitroaromatics

Bo Wei, Kefa Sheng and Jianping Ge*



A one-pot successive polyol reaction was developed to prepare $M-E_xO_y$ colloidal particles as heterogeneous nanocatalysts, which combined the controlled synthesis of metal catalysts and oxide supports, the in-situ loading of catalyst and even the mesopore amplification into a highly integrated process. Unlike the traditional surface deposited catalysts, the noble metal nanoparticles are internally dispersed in the mesoporous oxide particles, which shows higher activity and stability in the hydrogenation of nitroaromatics due to the physical confinement of metal nanoparticles and good mass transportation of substrate/product.