Monodispersed Pd Nanoparticles Supported on Mg–Al Mixed Metal Oxides: A Green and Controllable Synthesis

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Supporting Information

ABSTRACT: Aimed at the green synthesis of supported noble metal nanoparticles without any additional reducing agents or stabilizers at room temperature, a new strategy in which monodispersed Pd nanoparticles were successfully immobilized on Mg–Al mixed metal oxides derived from layered double hydroxides was developed, and the reduction mechanism was also proposed. It allowed the in situ immobilization of monodispersed Pd nanoparticles with a face-centered cubic structure, using only alcohols with α-hydrogen atom as the solvent and reducing agent. Control over the mean particle size and content of Pd nanoparticles was realized by adjusting the temperature, initial concentration, and type of alcohol. With the content of Pd varied from 6.4 to 42.3 mg/g, the mean particle size of Pd increased from 1.1 to 4.9 nm. The as-prepared catalyst showed high catalytic activity for oxidation of benzyl alcohol: when the Pd content was 6.4 mg/g, conversion of 60.3% and selectivity of 99.2% were obtained with a turnover frequency of 4807 h⁻¹. Similarly, on the basis of the high stand electrode potentials, immobilized Ag (5.6 nm) and Au (4.7 nm) nanoparticles were also prepared through this methodology. Moreover, the choice of supports was extended to other powder supports that would react with the byproduced acid. Overall, this facile method opens up new opportunities for controllable synthesis of supported nanoparticle catalysts in a green way.

1. INTRODUCTION

Metal nanoparticles exhibiting high activity and selectivity have attracted intense attention. Although some homogeneous catalysts (e.g., organometallic complexes) show remarkable catalytic activity, they still face serious challenges in separation and recycling. As a result, immobilization of metal nanoparticles has become a field of continuing interest. In particular, supported Pd has the reputation of being one of the most efficient transition metals in catalysis. It is widely used in many industrial processes, such as hydrogenation, oxidation, hydrocracking, and Suzuki coupling reaction processes.

In our previous work, it was found that Pd²⁺ ions adsorbed on the surface of porous glass would be reduced to Pd nanoparticles successfully by alcohol. However, there are still two problems with this method. First, the reduction mechanism is not clear: it was just hypothesized that the reduction was catalyzed by a solid base, such as porous glass beads; second, the choice of support is very limited. The weak mechanical strength of porous glass beads (the porous shell part would be easily destroyed by stirring) limits their further application.

Taking into account the above problems, other supports with a broader range of applications and better mechanical strength should be considered. Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTLcs), are a type of anionic clay of inorganic layered materials and their general formula is

\[ [M^{2+} \ldots M^{3+}(OH)_2]^{x+}(A^{y-})_n \cdot mH_2O \]

where M²⁺ and M³⁺ represent a divalent cation (e.g., Mg²⁺, Ni²⁺) and a trivalent cation (e.g., Al³⁺, Cr³⁺), respectively. A⁻ is the interlayer anion (e.g., CO₃⁻, SO₄²⁻). The value of x is typically in the range of 0.20–0.33, representing the molar ratio of M⁺⁺/(M²⁺ + M³⁺), and m indicates the amount of water. Thermal decomposition of LDHs gives well-mixed metal oxides (MMOs). Both of them have been utilized as promising supports for metal nanoparticles. As the support, MMOs offer a number of advantages: variable composition and ratio of cations, tunable acidity—basicity of the surface, high metal-adsorption abilities, and a confinement effect, which would help in obtaining highly dispersed supported nanoparticles.

Considerable effort has been devoted to the preparation of Pd nanoparticles supported on LDHs and MMOs. Generally, the immobilization would be separated into two steps. First, the Pd species is immobilized in the form of ions; second, the supported Pd²⁺ ions are reduced to the metal nanoparticles in the presence of an alcohol.
of a reducing agent and a surfactant, when necessary. Thermal treatment with H₂ at high temperature is the most common strategy, especially when surfactants are used.¹⁻¹¹ For example, in the work of Onyestyak and co-workers,¹² Pd nanoparticles supported on hydrotalcite were prepared through the impregnation method and reduced with H₂ at 623 K. However, this approach often suffers from aggregation and an inhomogeneity in the distribution of metallic nanoparticles, and difficulties in removing of surfactants as well, leading to loss of monodispersity and catalytic activity. Alternatively, chemical reduction agents, for instance, borohydride¹⁵⁻¹⁷ hydrazine hydrate¹⁸,¹⁹ hexamethyleneetetramine,²⁰,²¹ soluble starch,²² and cyclohexene, were also involved in the synthesis process.²³ Accordingly, other chemical reagents, such as NaOH, was necessary or the temperature was higher than 353 K. For example, as reported by He,²⁴ Pd²⁺ ions supported on Mg₂Al−LDH were reduced by NaBH₄ as follows: first, NaOH was added into the aqueous solution containing LDH until the pH value reached 10; second, Na₂PdCl₄ was added, and the pH value of the solution was kept at 10 by adding more alkaline solution; third, NaBH₄ was added starting the reduction. Therefore, it is of great significance to develop a facile and effective method for controllable preparation of highly dispersed Pd nanoparticles in the immobilization mode.

In this work, we explored feasibilities of both preparing monodispersed Pd nanoparticles supported on MgAl−MMO through an in situ method at room temperature and obtaining a deeper insight into the reduction scheme. As there is no need for subsequent thermal treatment, the structure of the metal particle could also be retained, preserving the active sites associated with high catalytic activity. It is worth noting that the in situ preparation was conducted without any additional reducing agents or stabilizers. Additionally, the choice of metal nanoparticles could be extended to other noble metal nanoparticles (Ag and Au), and the choice of support could be other powder supports that would react with the byproduced acid. As far as we know, a green and facile strategy for the preparation of noble metal nanoparticles immobilized on MgAl−MMO at room temperature has never been reported before. The effects of temperature, initial concentration, and type of alcohol on the morphology and loading amount of Pd nanoparticles have been studied systematically, and the catalytic performance of the as-prepared catalyst has also been investigated.

2. EXPERIMENTAL

2.1. Materials and Chemicals. Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, PdCl₂, NaOH, and Na₂CO₃ were all analytical reagents and purchased from Beijing Chemical Plant. Methanol, ethanol, 1-propanol, and tert-butyl alcohol were all analytical grade and purchased from Fuchen Chemical Plant in Tianjin, China. AgNO₃ and H₂AuCl₄·3H₂O and MgO nanoparticles (the mean particle size was 50 nm) were purchased from Aladdin Industrial Co.

2.2. Preparation and Characterization of MgAl−MMO Supported with Pd Nanoparticles. Preparation of MgAl−MMO support (by the modified coprecipitation method at a pH value of 10.0): typically, alkaline solution containing Na₂CO₃ and NaOH was added dropwise into deionized water until the pH value reached 10 (detected by Mettler Toledo FE20). Then, 9.0 mmol Mg(NO₃)₂·6H₂O and 3.0 mmol Al(NO₃)₃·9H₂O were dissolved in 100 mL of deionized water. The mixture was added dropwise into the as-prepared alkaline solution, maintaining the pH value around 10 by adding more alkaline solution. The resulting suspension was stirred at room temperature for 8 h; then the precipitates were separated from the solution by centrifugation and washed with deionized water until the pH value reached 7. After being dried at 353 K for 12 h, the precipitates were calcinated at 823 K for 4 h.

Immobilization of Pd species: 0.1 g of MgAl−MMO was suspended in 30 g of PdCl₂−alcohol solution (the initial concentration varied from 30 to 400 ppm) at a speed of 750 rpm. The mixtures were stirred for 1 h at different temperatures. After the immobilization process, the solid was separated from the solution by centrifugation and dried for 12 h at 373 K. The yield of supported nanoparticles (Y) through the immobilization process can be described as eq 1.

\[
Y = \frac{C_a - C_i}{C_o} \times 100\%
\]

where C₀ and Cᵢ mean the concentration of the target metal element before and after the immobilization process, respectively.

SEM images were obtained via SEM (S-4500; Hitachi Ltd., Japan). The morphology of the prepared composite was studied by TEM (JEOL JEM-2011). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced powder X-ray diffractometer using Cu Kα radiation. Contents of metal elements in the prepared composite were measured via inductively coupled plasma (ICP; IRIS Intrepid II XSP from ThermoFisher Corp.). Nitrogen adsorption−desorption isotherms were analyzed on a Quantachrome Autosorb-1-C chemisorption−physisorption analyzer. The pore size distribution was obtained using the Barrett−Joyner−Halenda (BJH) method. Surface compositions and binding energies were detected using an X-ray photoelectron spectrometer (XPS) (PHI-1600 spectrometer, Perkin-Elmer).

2.3. Catalytic Activity for Benzyl Alcohol Oxidation. The catalytic oxidation of benzyl alcohol was performed in a two-necked round bottomed flask (25 mL) equipped with a reflux condenser. Benzyl alcohol (substrate, 5 mL) and the Pd-based catalyst (0.1 g) were loaded into the reactor. Then, KOH was added to the reactor, followed by anhydrous DMSO as solvent. Dodecane was used as an internal standard for quantitative GC analysis. The conversion, selectivity, and turnover frequency (TOF) are defined by eqs 2, 3, and 4, respectively.

\[
\text{conversion (\%)} = \frac{\text{moles of reactant converted}}{\text{moles of reactant in feed}} \times 100\% \quad (2)
\]

\[
\text{selectivity (\%)} = \frac{\text{moles of product formed}}{\text{moles of reactant converted}} \times 100\% \quad (3)
\]

\[
\text{TOF (h}^{-1}) = \frac{\text{moles of reactant converted}}{\text{(moles of Pd × reaction time (h))}} \quad (4)
\]
3. RESULTS AND DISCUSSION

3.1. Proposal of the New Strategy and Reduction Scheme. During the catalyst synthesis process, color changes in MgAl−MMO powder and the Pd²⁺-containing solution were clearly observed (Figure 1). The Pd²⁺-containing solution turned much lighter, and white powders turned to black after the mixing.

SEM images of the MgAl−MMO powder before and after the immobilization of Pd are provided in the Supporting Information (Figures S1 and S2, respectively), and BET results of the MgAl−MMO powder before and after the immobilization of Pd are given in Table S1 and Figure S3, respectively. After the immobilization of Pd, the surface area increased from 144.7 to 300.7 m²/g due to the formation of micropores of around 1 nm (the reason is discussed later). As expected, the successful immobilization of Pd nanoparticles on MgAl−MMO could be supported by XRD, XPS, and TEM analyses. The wide-angle XRD patterns of the sample are shown in Figure 2a; the characteristic peak at around 40° could be readily indexed to the (111) reflection of Pd (JCPDS 87-0641). Figure 2b reveals the XPS result. Sharp peaks with binding energy values of 335 and 340 eV for Pd 3d5 and Pd 3d3 could be observed, respectively, indicating the formation of Pd nanoparticles. As shown in Figure 2c, Pd nanoparticles are homogeneously dispersed on the surface of MgAl−MMO. The EDS analysis confirmed the introduction of Pd (as shown in Figure S4 and Table S2). As shown in the HRTEM image (Figure 2d), lattice fringes of 0.227 nm are clearly observed, attributing to the (111) lattice spacing of the Pd crystal with the face-centered cubic (fcc) structure.

To investigate the reduction mechanism, we designed three groups of experiments.

First, 0.1 g of the prepared MgAl−MMO was suspended in the Pd²⁺-containing solution and stirred for 1 h at room temperature. Then, the solution was analyzed by GC. Results showed that acetaldehyde was produced during the process, proving that Pd²⁺ ions were reduced by alcohol. In addition, the molar amounts of the formed acetaldehyde and Pd nanoparticles were equal in value. Detailed GC analysis results are given in Figure S5 and Table S3, respectively. Similar results have also been reported by Mori and co-workers; monomeric PdCl₂ species, which was chemisorbed on the hydroxyapatite (HAP) surface, transformed into Pd nanoclusters in the presence of alcohols at 363 K, and the corresponding aldehydes were detected as the byproduct.

Second, the influence of the type of alcohol was studied. Depending on whether there is an α-hydrogen atom, these alcohols were separated into two groups: the first group with an α-hydrogen atom, for example, methanol and 1-propanol; the second group without an α-hydrogen atom, for example, tert-
butyl alcohol. Dark powders and the corresponding carbonyl compounds were obtained in cases of methanol and 1-propanol, whereas no dark powder was observed when tert-butyl alcohol was used. Samples treated with different alcohols were characterized by XPS, and the results are summarized in Table 1. Obviously, Pd nanoparticles could just be obtained using Al2O3 as the support after 24 h. After the mixing.

Obviously, elemental Pd was enriched on the surface of the MMO is composed of MgO and Al2O3, these two kinds of oxides were used as the support separately to investigate their individual contributions. Moreover, SiO2 powders, which are usually used as a catalyst support, were also tested in this work. After 3 h of mixing with the Pd2+–containing solution at room temperature, only MgO powders became dark, indicating immobilization of Pd nanoparticles. We detected the concentrations of Mg2+ and Pd2+ through ICP. As shown in Table 2, the concentration of Mg element increased from 0.08 mg/L (0.00 mmol/L) to 0.03 mg/L (0.00 mmol/L), whereas the concentration of Pd element decreased from 233.40 mg/L (2.20 mmol/L) to 2.20 mg/L (0.09 mmol/L), respectively.

Herein, a series of MgAl−MMO supported with Pd nanoparticles were prepared at different temperatures, and their TEM images are shown in Figure 3. With the reaction temperature increased from 303 to 343 K, the mean diameter of Pd nanoparticles grew gradually from 1.6 to 3.5 nm. Moreover, the loading amount of Pd, which were determined by ICP, and it is well known that the size of nanoparticles plays a key role in determining the catalytic performance, and we still face serious challenges in precise control over their size distribution. On the basis of the mechanism mentioned above, several key parameters, such as the reaction temperature, the initial concentration of Pd2+, and the type of alcohol, are dominant in the formation of Pd nanoparticles.

Table 1. Pd Nanoparticles Prepared with Different Alcohols

| alcohol          | formation | binding energy of Pd 3d5 (eV) | binding energy of Pd 3d3 (eV) |
|------------------|-----------|-----------------------------|-----------------------------|
| ethanol          | yes       | 335.1                       | 340.2                       |
| 1-propanol       | yes       | 355.0                       | 339.9                       |
| tert-butyl alcohol | no       | 336.7                       | 342.9                       |

Table 2. Concentrations of Metal Elements before and after Mixing

| element | concentration before mixing (mg/L) | concentration before mixing (mmol/L) | concentration after mixing (mg/L) | concentration after mixing (mmol/L) |
|---------|-----------------------------------|-------------------------------------|----------------------------------|-----------------------------------|
| Pd      | 233.40                            | 2.20                                | 0.03                             | 0.00                              |
| Mg      | 0.08                              | 0.00                                | 27.80                            | 1.16                              |

As reported by Fievet et al. and Xia et al.,29–31 in a solution of ethylene glycol, metal ions could be reduced to nanoparticles after stirring at 413 K for 1 h, byproducing HCl. It provided referable thoughts for our work.

Thus, upon consideration of the above results and reaction features between HCl and MgO (MgO was taken as an example here), a possible scheme for the reduction is proposed as eq 5. Ethanol serves as the solvent and reducing agent at the same time. According to this hypothesis, the reduction would occur in a similar manner as that in the case of MgO when solids that would react with HCl (the anion Cl− came from the precursor PdCl2, and if the precursor is changed to nitrate, HNO3, would be obtained here) are used as the support. For example, immobilization of Pd nanoparticles on Al2O3 was realized but in a much slower way. It also explains why the reduction takes place just at room temperature (under mild conditions). On the basis of Le Chatelier’s principle, the elimination of HCl would enhance the reduction process of metal ions, yielding Pd nanoparticles simultaneously. Furthermore, the increase in surface area and the formation of micropores of around 1 nm would be explained as a result of the reaction between the support and HCl. In other words, because of the reaction between the support and the byproduced acid, the reduction took place at room temperature and the surface area of the catalysts increased after immobilization of metal nanoparticles.

\[
\text{MgO + PdCl}_2 + \text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{Pd} + \text{CH}_2\text{CHO} + \text{MgCl}_2 + \text{H}_2\text{O}
\]  

3.2. Highly Controllable Synthesis of Pd Nanoparticles Supported on MgAl−MMO. It is well known that the size of nanoparticles plays a key role in determining the catalytic performance, and we still face serious challenges in precise control over their size distribution. On the basis of the mechanism mentioned above, several key parameters, such as the reaction temperature, the initial concentration of Pd2+, and the type of alcohol, are dominant in the formation of Pd nanoparticles.

Herein, a series of MgAl−MMO supported with Pd nanoparticles were prepared at different temperatures, and their TEM images are shown in Figure 3. With the reaction temperature increased from 303 to 343 K, the mean diameter of Pd nanoparticles grew gradually from 1.6 to 3.5 nm. Moreover, the loading amount of Pd showed the same trend, increasing from 11.9 to 26.8 mg/g. Concentrations of Pd element before and after the immobilization process were detected, and they are listed in Table 3. An increase in the reaction temperature greatly promoted the yield of Pd nanoparticles from 44 to 99%, and the utilization efficiency of the noble metal was also enhanced. Obviously, the reaction temperature showed significant influence on the particle size, loading amount, and even the yield of Pd nanoparticles. It may have resulted from the faster rate of the formation of Pd nanoparticles and their frequent collisions in the course of stirring for a given period at higher temperatures.

The initial concentration of Pd2+ ions is another crucial factor influencing the mean particle size and loading amount of Pd nanoparticles. As shown in Figure 4, with the increase in initial concentration from 30 to 400 ppm, the mean diameter of Pd nanoparticles increased steadily from 1.1 to 4.9 nm, and the loading amount increased from 6.4 to 42.3 mg/g. However, the yield of Pd nanoparticles decreased from 71 to 35%. The loading amount of Pd nanoparticles would be promoted efficiently by increasing the initial concentration; however, it also results in lower utilization efficiency.

The catalysts prepared with different alcohols showed different loading amounts of Pd, which were determined by ICP, and it decreased from 22.2 to 7.5 mg/g when methanol and propanol were used as the solvent, respectively. Accordingly, the yields of Pd nanoparticles were 58 and 32%, respectively. TEM images and the corresponding distribution histograms of supported Pd nanoparticles are shown in Figure 5. The immobilized Pd
nanoparticles exhibited the largest size of 2.8 nm using methanol as the solvent, whereas the mean particle size of Pd nanoparticles was the smallest (1.4 nm) using propanol as the solvent. It may have resulted from two reasons: first, the difference in the dielectric constant. It is assumed that palladium chloride is partially dissociated in alcohol, and a higher dielectric constant of the solvent means higher extent of dissociation and higher concentration of Pd\(^{2+}\) ions; second, the different reducing reactivities caused by the +I effect of the methyl group (The Hammett constant of methyl is \(-0.170\))\(^,\)\(^32\).

### 3.3. Extension to Other Immobilized Metal Nanoparticles

This facile and green method could be extended to other supported metal nanoparticles. Ag\(^+,\) Au\(^{3+},\) Cu\(^{2+},\) Ni\(^{2+},\) Co\(^{3+},\) and Fe\(^{3+}\) ions were examined using the method stated above, and it turned out that Ag and Au nanoparticles in the immobilization mode would be obtained (Figure S7). The mean particle sizes of Ag and Au nanoparticles are 5.6 and 4.7 nm, respectively, and the corresponding yields are 68 and 75\%, respectively. XRD patterns of the immobilized Ag and Au nanoparticles are given in Figure S7. The corresponding XPS results of the immobilized Ag and Au are given in Figure S8. No reduction process was observed for other metal ions. This may be explained by their stand electrode potentials (Pd\(^{2+}\): +0.83 V; Ag\(^+\): +0.799 V; Au\(^{3+}\): +1.42 V; Cu\(^{2+}\): +0.344 V; Ni\(^{2+}\): −0.250 V; Co\(^{3+}\): −0.277 V; and Fe\(^{3+}\): −0.036 V).\(^33,\)\(^34\) Metal ions with higher stand electrode potentials exhibit higher potential for oxidation–reduction and are thus easier to be reduced. In addition, the higher yield of Au nanoparticles compared with that of Ag may have also resulted from the higher stand electrode potential.

### 3.4. Catalytic Activity for Benzyl Alcohol Oxidation

Pd-based catalysts have been proved to be highly efficient in the oxidation of alcohols, which is the most important reaction in
organic synthesis. To examine the catalytic performance of the as-prepared catalyst (MgAl-MMO supported with Pd nanoparticles), catalytic oxidation of benzyl alcohol under solvent-free conditions was chosen as the model reaction. Then comparisons were made with other works, and the results are summarized in Table 4. Under the same reaction condition, our catalyst showed a conversion of 60.3% and a selectivity of 99.2%, much higher than the conversion of 28.4% and the selectivity of 94.4% given.
by Pd−MCM-41. Moreover, the TOF (4807 h$^{-1}$) is also obviously higher than that of Pd−MCM-41 (2434 h$^{-1}$). The excellent catalytic performance would be ascribed to the much smaller mean particle size of Pd nanoparticles (1.1 nm) compared with that of Pd−MCM-41 (7.4 nm).

The 1H NMR spectra of the oxidized product are shown in Figure S9. In the work of Polshettiwar and co-workers, they have developed a simple and sustainable method to prepare monodispersed Pd nanoparticles (the mean particle size varied from 1.5 to 4 nm) supported on fibrous nanosilica, and the catalyst showed high catalytic activity for the hydrogenation and Suzuki coupling reactions. The TOF values for the hydrogenation of phenyl acetylene and styrene are 122 and 732 h$^{-1}$, respectively.

The TEM image of the catalyst after the reaction is shown in Figure S10, and the XRD patterns before and after the reaction are provided in Figure S11a,b, respectively. After the reaction, Pd nanoparticles are still highly dispersed on the surface of MgAl−MMO with the mean particle size of 1.2 nm, confirming the good stability of the as-prepared catalyst.

In addition, catalytic activities of the as-prepared catalyst toward other alcohols have also been investigated, and the detailed results are listed in Table S5. As expected, the Pd−MgAl−MMO catalyst also exhibited good catalytic performance for oxidation of 4-methoxybenzyl alcohol (with a TOF value of 4656 h$^{-1}$) and 2-naphthalenemethanol (with a TOF value of 1826 h$^{-1}$). Furthermore, in view of green process, this in situ method proposed in this work exhibited obvious advantages of easy operation and environmental friendliness without any use of ligands or stabilizers. In summary, it can be seen that Pd−MgAl−MMO catalysts not only could be synthesized through a facile in situ method but also showed high catalytic performances, providing high promises for selective oxidation of alcohols.

4. CONCLUSIONS

A facile and green strategy without stabilizers for the synthesis of supported Pd nanoparticles and the corresponding mechanism have been proposed. Monodispersed Pd nanoparticles with fcc structure were homogeneously immobilized on the surface of MgAl−MMO, providing good catalytic activity for the selective oxidation of benzyl alcohol.

Table 4. Comparisons in Catalytic Performances for Oxidation of Benzyl Alcohol

| catalyst          | solvent | reaction temperature (K) | reaction duration (h) | molar ratio of reactant to Pd | conv. (%) | sel. (%) | TOF (h$^{-1}$) | ref |
|-------------------|---------|--------------------------|----------------------|-----------------------------|-----------|---------|----------------|-----|
| Pd−MCM-41        | no      | 373                      | 1                    | 8571                        | 28.4      | 94.4    | 2434           | 35  |
| Pd−MgAl−MMO      | no      | 373                      | 1                    | 7973                        | 60.3      | 99.2    | 4807           | this work |
| Pd−MCM-41        | no      | 373                      | 1                    | 6049                        | 28.6      | 96.6    | 1730           | 35  |
| Pd−MgAl−MMO      | no      | 373                      | 1                    | 6395                        | 66.5      | 99.5    | 4253           | this work |
| Pd−SBA-15        | no      | 393                      | 3                    | 5000                        | 42.0      | 85.0    | 700            | 36  |
| Pd−TiO$_2$NM     | no      | 393                      | 7                    | 40000                       | 57.6      | 74.1    | 3291           | 37  |
| PdO@SNP          | toluene | 363                      | 6                    | 30                          | 99.0      | 92.0    | 5              | 38  |

Table 5. Catalytic Performances of Pd−MgAl−MMO for the Oxidation of Other Alcohols (Reaction Temperature: 373 K)

| alcohol            | reaction duration (h) | conv. (%) | sel. (%) | TOF (h$^{-1}$) |
|--------------------|-----------------------|-----------|----------|----------------|
| 4-methoxybenzyl alcohol | 1                      | 58.4      | 98.1     | 4656           |
| 2-naphthalenemethanol     | 3                      | 68.7      | 95.8     | 1826           |

Figure 6. TEM images of Ag (a) and Au (b) nanoparticles supported on MgAl−MMO. Histograms of particle size distribution for Ag (c) and Au (d) nanoparticles.
MgAl–MMO at room temperature. Alcohols with an α-hydrogen atom acted as the solvent and reducing agent. It has been demonstrated that successful immobilization of Pd nanoparticles on other powder supports (which would react with the byproduced acid, e.g., LDH with different Mg/Al ratio, MgO, and Al2O3) would be realized through this methodology. Both the mean particle size and loading amount of Pd nanoparticles were highly adjustable. The mean diameter increased from 1.1 to 4.9 nm when the loading amount varied from 6.4 to 42.3 mg/g. Noble metal nanoparticles with high stand electrode potentials in the immobilization mode could also be prepared through the in situ strategy. For instance, supported Ag and Au were obtained and their mean particle sizes were 5.6 and 4.7 nm, respectively. The as-prepared supported Pd nanoparticles showed high catalytic activity for oxidation of benzyl alcohol. By using the catalyst with the Pd content of 6.4 mg/g, a conversion of 60.3% and a selectivity of 99.2% were obtained with a TOF of 4807 h\(^{-1}\). More research on the effect of support on the catalytic activity and the shape control of the metal nanoparticles would be carried out in the future.

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