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Preparing highly-dispersed noble metal supported mesoporous silica catalysts by reductive amphiphilic molecules⁺

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We present an in-situ reduction strategy to prepare mesoporous silica supported with highly-dispersed noble metals. First, an amphiphilic molecule with ferrocenyl as a reductive hydrophobic terminal group was designed and synthesized. Next, we used it as a structure-directing agent to self-assemble into mesoporous silica. Then the amphiphile remained in the mesoporous channels could in-situ reduce gold or palladium salts into corresponding metal nanoparticles. Finally, the amphiphile was removed through calcination. Through XRD and TEM the mesoporous structure and the highly-dispersed Au or Pd nanoparticles were confirmed. The reducibility of the amphiphile was proved by XPS, and was further verified by cyclic voltammetry and thermodynamic calculation. BET analysis showed that the mesoporous catalysts have a specific surface area above 900 m²/g. The catalysts showed significantly higher catalytic activities to the reduction of 4-nitrophenol traditional and Suzuki reaction than the ones prepared via the impregnation methods.

Introduction

Mesoporous materials, known as porous materials whose pore diameters are from 2 nm to 50 nm,¹ have been attaching considerable attention to the chemists since they were born for their large specific surface area as well as the controllable pore diameters and pore structures. They have been widely applied in diverse fields including catalysis,²⁻⁷ adsorption,⁸⁻¹⁰ sensors,¹¹⁻¹⁴ cells^{15, 16} and sustained drug-release^{17, 18} etc. Mesoporous materials are mainly prepared by the self-assembly of surfactants, which act as the structure-directing agent to construct nano-scale channels.¹⁹ Usually after the inorganic framework was formed, the surfactants will be removed through calcination, solvent extraction or other techniques.

In general, the functionalization of mesoporous materials is carried out by doping other elements to the frameworks or by modifying the pore surface structures. For example, noble metals are traditionally loaded in the mesoporous channels as catalysts through impregnation^{20, 21}. In this method, it is a common problem that the noble metal nanoparticles may grow larger than expected, consequently leading to less dispersion. Specific control to the pore structure and the impregnation process will often be necessary,²² without which it will be difficult to realize the high-dispersion of the metal nanoparticles via normal methods. There are also other methods to load noble metals in mesoporous silica, for

example post-synthetic functionalization or self-assembly functionalization²³ before loading noble metal ions, but some of them are quite complicated.

In this paper, we synthesized an amphiphilic molecule with a reductive hydrophobic terminal group (ferrocenyl) to serve as the structure-directing agent, which can co-hydrolyze with silicate ester to form mesoporous silica materials similar to that formed from traditional quaternary ammonium salts (Scheme 1). Then, the reductive amphiphile can in-situ reduce gold or palladium salts into corresponding metal nanoparticles that could be loaded in the mesoporous channels. The catalysts, i.e. mesoporous silica supported with high-dispersed noble metal nanoparticles, were finally obtained through calcination. Compared with the ones prepared by the traditional impregnation methods, our catalysts show significantly higher catalytic activity to the reduction of 4nitrophenol and Suzuki reaction.



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<code>+Electronic Supplementary Information (ESI) available: [Measurement of the critical micellar concentration (CMC) of the amphiphile FcC11PyBr, Analysis of the redox reaction between [PdCl₄]²⁻ and FcC11PyBr, and The characterization data for FcC11Br for FcC11Br and FcC11PyBr]. See DOI: 10.1039/x0xx00000x</code>

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Experiment Section

Materials

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acid, Ferrocenecarboxylic 11-bromo-1-undecanol, N.Ndicyclohexylcarbodimide (DCC), 4-dimethylaminopyridine (DMAP), pyridine, methanol, petroleum ether, ethyl acetate, dichloromethane, acetonitrile, tetraethoxysilicane (TEOS), hydrochloric acid (36%~38%), sodium hydroxide, ammonia solution (25%~28%), hexadecyltrimethylammonium Bromide (CTAB) and 95% ethanol were purchased from Sinopharm Chemical Reagent Co.,Ltd. Chloroauric acid, palladium chloride, 4-nitrophenol, sodium borohydride, bromobenzene, iodobenzene, phenylboronic acid and biphenyl were purchased from the Shanghai Aladdin Bio-chem Technology Corporation. All reagents were used without further purification.



Synthesis of 11-bromoundecyl ferrocenecarboxylate (FcC₁₁Br)

The compound was synthesized according to the literature²⁴. Ferrocenecarboxylic acid (0.48 g, 2.1 mmol) and 11-bromo-1undecanol were dissolved in 50mL anhydrous dichloromethane (dried with molecular sieves) and stirred for 0.5 h at 0 $^{\circ}$ C, then catalytic amount of DMAP (0.05 g, 0.4 mmol) was added to the mixture. Next, DCC (0.43 g, 2.1 mmol) was dissolved in 50 ml anhydrous dichloromethane, and the solution was added to the mixture dropwise. The solution was stirred at room temperature for 2 days. The mixture was then filtered and the filtrate was collected. The solvents were removed under reduced pressure. The crude product was purified with column chromatography (Eluent: petroleum ether: ethyl acetate = 20: 1, the ratio is by volume).

The product is an orange crystal. Yield 50%.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 4.82 (s, 2H), 4.40 (s, 2H), 4.16 (m, 7H), 3.41 (t, 2H), 1.92 – 1.79 (5, 2H), 1.77 – 1.64 (5, 2H), 1.49 – 1.22 (m, 14H).

¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 77.37, 77.05, 76.74, 71.31, 70.19, 69.81, 64.29, 34.06, 32.84, 29.54, 29.47, 29.41, 29.28, 28.92, 28.76, 28.17, 26.07.

HRMS: m/z = 463.0925

Synthesis of N-(11-(ferrocenecarboxyloxy)undecyl)pyridinium bromide (FcC₁₁PyBr)

 $FcC_{11}Br$ (0.46 g, 1 mmol) was dissolved in 50 mL acetonitrile. Then pyridine (0.14 g, 2 mmol) was added dropwise to the solution under vigorous stirring. The mixture was refluxed for 24 h. After the reflux the acetonitrile was removed by rotary evaporator. The final product was obtained through chromatography (Eluent: petroleum ether: ethyl acetate = 20: 1, the ratio is by volume).

The product is a viscous dark orange liquid. Yield 80%. ¹H NMR (400 MHz, CDCl₃) : δ (ppm) = 9.47 (s, 2H), 8.50 (s, 1H), 8.12 (s, 2H), 5.03 (s, 2H), 4.81 (s, 2H), 4.40 (s, 2H), 4.21 (m, 7H), 2.09 (m, 2H), 1.83 – 1.60 (m, 2H), 1.54 – 1.19 (m, 14H). ¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 171.76, 145.30, 144.71, 128.43, 77.91, 77.59, 77.27, 71.16, 71.08, 69.84, 69.54, 64.09, 61.75, 49.63, 31.66, 29.23, 29.16, 29.06, 28.96, 28.79, 28.62, 25.79.

HRMS: m/z = 462.2090

Synthesis of the mesoporous silica material (MS)

0.5 g FcC₁₁PyBr was dissolved in a mixture of 4.18 g ammonia solution and 13.74 g deionized water, then 1.60 g TEOS was added dropwise under vigorous stirring. The mole ratio of the compounds is TEOS: FcC₁₁PyBr: NH₃: H₂O=1:0.12:8:122. The mixture was further stirred for 2h under room temperature. Then it was transferred into a stainless autoclave with polytetrafluoroethylene equipment liner and left for 3 days at 80 °C. When the hydrothermal treatment was complete, the solids were separated through filtration and washed with deionized water for several times. Finally, the solids were dried in a vacuum desiccator.

The obtained mesoporous material (MS) is a brown solid.

As a control experiment, MCM-41 was prepared with the following procedure: 2.4 g CTAB, 50 mL water, 50 mL 95% ethanol, 13 mL ammonia solution and 3.5 mL TEOS was added into a flask and stirred at room temperature for 2 h. Then the solids were filtered and dried in a vacuum desiccator.

Synthesis of Au-supported (or Pd-supported) mesoporous silica material (Au@MS or Pd@MS)

The reduction part in the procedure is according to the literature. $^{25} \ensuremath{$

A solution of 10 mg chloroauric acid (dissolved in 4 ml solvent consisting of methanol: dichloromethane=3:1) was added dropwise carefully to 100 mg MS (dispersed in 1ml dichloromethane) at 0 degree Celsius. The mixture was further stirred for 30 min. The solid gradually turned dark brown. After the reaction was complete, the mixture was filtered and the solids were washed with the solvents (methanol: dichloromethane=3:1) for several times. Then the solids were transferred into a quartz boat for calcination. The temperature of the furnace was raised at the rate of 5 °C /min, and maintained at 300 °C for 6h. Finally, the temperature was slowly cooled down to room temperature and the mesoporous material Au@MS was obtained.

Pd@MS was synthesized with a similar procedure. 6.5 mg PdCl₂ was dissolved in 35 μ l hydrochloric acid in advance because of the insolubility of palladium chloride. Moreover, the reaction was carried out at room temperature for 1 h.

As a control experiment, MCM-41 was treated with the same procedure to obtain Au@MCM-41 and Pd@MCM-41.

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Catalytic tests

1) Catalytic reduction of 4-nitrophenol (4-NP)

0.14 g 4-NP was dissolved in water and diluted into 100 ml. 0.4 g NaBH₄ was dissolved in 20 ml deionized water. Then 10 mg Au@MS and 1000 μ l 4-NP solution were added to the NaBH₄ solution. The mixture was kept stirred and the reaction was monitored with a UV-Vis spectrophotometer at 400 nm. The reference cell of spectrophotometer was deionized water.

2) Catalysis of Suzuki reaction

The procedure is according to the literature.²⁶

Phenylboronic acid (0.6 mmol, 74 mg) and sodium hydroxide (2 mmol, 80 mg) was dissolved in 10 ml deionized water. Then 0.5 mmol bromobenzene (or iodobenzene) and 10 mg Pd@MS were added to the mixture. The reaction was refluxed at 80 °C for 5 h. After the reflux, mixture was diluted with methanol until a homogeneous liquid phase was formed. The catalysts were recycled through centrifuge. The remaining liquid was sampled and the yield was further analyzed by HPLC.

3) The calculation of turnover frequency (TOF)

Because of the complexity of the heterogeneous reaction in liquid phase, the TOF is simplified and calculated by the following formula according to the literature²⁷:

$$\text{TOF} = \frac{n}{n_{\text{cat}} \cdot t}$$

In the formular, n is the moles of the consumed reactant in time t, and n_{cat} is the total moles of the noble metals, which is determined by ICP.

Characterization

The ¹H NMR and ¹³C NMR spectra were measured on PerkinElmer Bruker Avance II 400 NMR spectrometer with chemical shifts reported in ppm (CDCl₃ as solvent, TMS as internal standard). The HRMS spectra were obained on Agilent G6224A Liquid Chromatography & Time-of-Flight Mass Spectrometer. The Fourier transform infrared spectoscopy (FT-IR) spectra were obtained on a Nicolet Avatar 360 FT-IR spectrometer with the wavenumbers ranging from 4000 cm⁻¹ to 500 cm⁻¹, and the test samples were prepared though KBr pellet pressing method. The X-ray powder diffraction (XRD) patters were collected on a Rigaku D/max-2400 X-ray powder diffractometer, using Cu K α (λ = 1.5405 Å) radiation. The smallangle XRD data were collected from $2\theta=0.9^{\circ}$ to 10° , and the wide-angle XRD data were collected from $2\theta=5^{\circ}$ to 80° . The transmission electron microscopy (TEM) images were obtained on a FEI Tecnai F30 transmission electron microscope with a working voltage of 300kV. The TEM samples were prepared by depositing a drop of the suspension (containing the samples suspended in anhydrous ethanol and sonicated for 30 minutes) on a copper grid coated with a carbon film and followed with drying. The nitrogen adsorption and desorption isotherms was measured at 77 K on an ASAP 2010 analyzer (Micromeritics Co. td.). The samples were degassed under vacuum at 473 K for 2 h. The specific surface areas were calculated using Brunauer-Emmett-Teller (BET) method. The pore size and pore volume distributions were calculated from the desorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model. The X-ray photoelectron spectroscopy (XPS) data were obtained on a Shimadzu KROTAS AMICUS X-ray photoelectron spectrometer. The cyclic voltammetry (CV) curve was measured on a CHI 660D electrochemical workstation. A Pt electrode was used as the working electrode referenced by a saturated calomel electrode, and 0.1 mol/L KCl was used as the supporting electrolyte. Before the scan, the solution was bubbled with pure argon for 10 min to remove the dissolved oxygen. The ultraviolet-visible (UV-Vis) spectra were collected on a Purkinje TU-1900 UV-visible spectrophotometer. The high performance liquid chromatography (HPLC) tests were run on a Shimadzu LC-20A high-performance liquid chromatograph using 90% methanol/10% water as the mobile phase. The inductive coupled plasma emission spectroscopy (ICP) tests were analyzed on a PerkinElmer Optima 2000DV spectrometer. The critical micellar concentration (CMC) of the amphiphile was measured by the surface tension method. The surface tension was measured on a Kruss100C surface tension meter.

Results and Discussion

As the structure-directing agent, the hydrophilic group and hydrophobic group are necessary. Herein, ferrocenyl is chosen as the hydrophobic terminal and N-alkylpyridinium ion is chosen as the hydrophilic terminal. To ensure we can assemble the amphiphile into micellar, the self-assembly need to be carried out above the critical micellar concentration (CMC) of the amphiphile. Therefore, we determined the CMC of FcC₁₁PyBr under experimental condition (Fig. S1). From the measurement we can infer that the CMC of FcC₁₁PyBr is 0.001mol/L, while the experimental concentration is 0.06mol/L, indicating that the amphiphile did form micellar during the assembly process.





Fig. 1 is the FT-IR spectra of the amphiphile and the as synthesized mesoporous silica (MS). It can be noticed that the absorption at 2930 cm⁻¹, 2860 cm⁻¹, 1460 cm⁻¹ and 1710 cm⁻¹ (corresponding to the C–H and C=N bond vibration of FcC₁₁PyBr) also appears in the FT-IR of MS. And the absorption at 1070 cm⁻¹ is the vibration of the Si-O-Si bond, which

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indicates that the amphiphile and the silica formed a composite system. From the small angle XRD patterns of the mesoporous material in Fig. 2a, a strong peak at 2.260°, and two weaker peaks at 3.921° and 4.500° are observed. These XRD results are basically identical to the XRD patterns of MCM-41, suggesting a hexagonal channel mesoporous structure. The peaks remained after the treatment of the noble metal salts as well as calcination, which indicates the mesoporous material is stable enough to endure both the noble metal ions and calcination.



Fig. 2. (a) The small-angle XRD patterns of the mesoporous silica materials; (b) The wide-angle XRD patterns of the mesoporous silica materials.

The further wide angle XRD patterns show no apparent Au or Pd diffraction peaks in Fig. 2b. Au@MS showed tiny diffraction peaks at 38.079° and 44.167°, corresponding to the (111) and (200) crystal plane. The peaks can be observed both before and after the calcination, which implies that metal gold has already existed in Au@MS before calcination, and also implies the reducibility of the surfactant, i.e. to reduce Au(III) salts into metal Au. While the diffraction peaks of Pd are almost unobservable, suggesting that Pd has formed smaller clusters than the Au nanoparticles. To sum up, the XRD curves of the mesoporous materials indicate that no large crystals of the metals exist in the mesoporous materials.



Fig. 3. The XPS patterns of (a) Au@MS (the scan of Fe2p) (b) Au@MS (the scan of Au4f) (c) Pd@MS (the scan of Pd3d). The patterns of $Fe2O_{3,k}^{28, 29}$ metal Au,³⁰ Cs[AuCl₄],³¹ metal Pd^{32, 33} and PdCl₂^{34, 35} are stimulated according to the data from National Institute of Standards and Technology (NIST) XPS Database

The XPS results can further confirm this conclusion. As is shown in Fig. 3a, after the treatment of HAuCl₄, the $2p_{3/2}$ peak of Fe appears at 711.14 eV, suggesting that the valance of iron is +3. The observed data are consistent with the iron(III) compounds in the literature²⁸. However, it is commonly

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recognized that the valance of iron in ferrocene is +2. Thisindicates that the iron(II) does have been oxidized. The valance of iron has no apparently change after calcination. On the other hand, the valance of gold turned zero after the treatment, and a peak at 82.75 eV was observed. There is also no obvious change in the valance of gold after calcination. This proves that Au(III) has already been reduced to metal gold and no Au(III) was remained in Au@MS before calcination. Moreover, the calcination process also did not change the valance of gold. These results can further verify that there does be a redox reaction between the metal ions and the surfactants containing ferrocenyl group. As a control experiment, uncalcined Au@MCM-41 did not show Au peaks due to the low content of gold, indicating that amphiphile such as ferrocenyl cannot reduce Au(III) salts. Similar results can be observed on Pd@MS, revealing that Pd salts can also be reduced into simple substance supported on the mesoporous silica



In addition, we investigated the redox potential of the amphiphile by cyclic voltammetry as is shown in Fig. 4. After converting the potential vs SCE to the potential vs NHE, the standard electrode potential of $FcC_{11}Py^{2+}/FcC_{11}Py^{+}$ is 0.687 V, while the standard electrode potentials of $[AuCl_4]^{-}/Au$ and $[PdCl_4]^{2-}/Pd$ are 1.002 V³⁶ and 0.591 V³⁷ respectively. Obviously, [AuCl₄]⁻ can oxidize FcC₁₁PyBr. For palladium, [PdCl₄]²⁻ cannot oxidize FcC₁₁PyBr at standard state. However, owing to the small difference between the two electrode potentials, it can be inferred that the reaction of [PdCl₄]²⁻ and FcC11PyBr may reach an equilibrium with sufficient metal palladium formed. According to a calculation given by the Nernst Equation (the details are in the supporting information), the electrode potential of [PdCl₄]²⁻/Pd will increase to 0.655 V under the experimental conditions. On the other hand, the electrode potential of $FcC_{11}Py^{2+}/FcC_{11}Py^{+}$ is 0.629 V when we terminated the reaction. Thus, it is explainable that $[PdCl_4]^{2-}$ can oxidize $FcC_{11}PyBr$ under experimental conditions. The calculation also agrees with several facts in our experiments. First, Pd@MS was synthesized at room temperature for 1h. However, if Au@MS was prepared under the same condition, the percentage of Au in Au@MS can reach 6.612%wt and the dispersion of the Au nanoparticles will be very poor. Secondly, even though we optimized the condition to reduce HAuCl₄ (0 °C for 15 min to

30 min), the Au nanoparticles in the obtained Au@MS is still larger than the Pd nanoparticles in Pd@MS. To conclude this part, it is completely feasible to use ferrocenyl-grafted amphiphile to act as both a structure-directing agent and the

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The nitrogen absorption-desorption isotherms (Fig. 5a) show a typical type-IV curve defined by IUPAC, suggesting an ordered mesoporous structure of silica similar to MCM-41. After loaded with noble metals, both the materials have a specific surface area above 900 m²/g (Table 1), providing more contacting positions for the reaction. The pore diameter is around 3.2nm, which is far bigger than the normal small molecules. Meanwhile, the narrow distribution of pore diameters indicates that a formation of uniform mesopores, which can reduce the clog during the diffusion and make the substances go in and out of the channels smoothly through the catalytic process.

reductant to load noble metal nanoparticles on mesoporous



Fig. 5. (a) The nitrogen adsorption-desorption isotherms (inset: pore size distribution) (b) the mesoporous structure of MS in the TEM image

Table 1. The BET analysis results of the as-synthesized mesoporous silica (MS) and MS loaded with noble metals

Samples	Surface area	Pore volume	Pore
	/m²⋅g⁻¹	/mL·g ⁻¹	diameter/nm
Au@MS	920.9152	0.9000	3.13
Pd@MS	924.4732	1.0335	3.14



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Fig. 6. The TEM images of (a) Au@MS (b) the Au nanoparticles in Au@MS (c) Pd@MS (d) the Pd nanoparticles in Pd@MS

The TEM images of the mesoporous materials loaded with noble metal nanoparticles (Fig. 5b) reveal the uniform hexagonal channels, most of which are ordered structure and a little few of which are worm-like structure. Furthermore, the fine structure of the Au and Pd nanoparticles can be clearly observed in the HRTEM images (Fig. 6). The nanoparticles have a size below 10nm, showing excellent lattice structure and dispersion. It also can be inferred from the TEM results that the size of the metal nanoparticles will increase as the reaction time extends (Fig. 7). Consequently, the reduction time should be controlled no longer than 30 minutes for Au@MS. Larger nanoparticles usually will decrease the dispersion of the catalysts and further affect the catalytic activities.



Fig. 7. The TEM images of the Au nanoparticles in Au@MS obtained by different reaction time: (a) 72h (b) 14h (c) 6h (d) 3h (e) 30min (f) 15min

The catalytic performance of the supported Au and Pd nanoparticles are investigated through the hydrogenation of 4nitrophenol (4-NP) and Suzuki reaction respectively. For Au@MS, excellent catalytic activity has been observed. As we can see in Table 2, 4-NP can be completely reduced in 90 seconds (Table 2, Entry 2), whereas no reduction can be observed without the presence of Au (Table 2, Entry 1). On the other hand, Au@MCM-41, i.e. MCM-41 loaded with Au through traditional impregnation method, was prepared to compare the catalytic ability with Au@MS. It turns out that more than an hour is required to consume all the 4-NP under the same reaction conditions, and the yield in 90 seconds is only 17.6% (Table 2, Entry 3). To further confirm that the experimental phenomena were caused by the catalysis of Au nanoparticles rather than simple physisorption, we measured the full-spectra scan during the reaction (Fig. 8a). From the spectrogram we can naturally see the absorption of 4-NP decrease at 400 nm. Besides, a new absorption peak gradually appears at 300nm simultaneously, corresponding to the reduction product 4-aminophenol, excluding the possibility of the simple physisorption of 4-NP by the mesoporous materials. For Pd@MS, we choose Suzuki reaction to investigate the catalytic activities. From the experiments we found good catalytic activities for both bromobenzene or iodobenzene to react with phenylboronic acid and form the product biphenyl. The yield can be both over 90%. The TOF of the reaction is relatively high (Table 2, Entry 4), which is due to the low percentage of palladium in the mesoporous material (0.32%). For bromobenzene, the TOP is 308 h⁻¹. However, for Pd@MCM-41, which is obtained by traditional impregnation method, the yield is only 6.184% (Table 2, Entry 5), less than one tenth of Pd@MS. The results also prove that through insitu reduction the obtained mesoporous silica loaded with Pd nanoparticles showed high catalytic activities. The cycle experiments indicate that the yield maintained around 70% after 3 cycles (Fig. 8b). What caused the yield to decrease should be the damage of silica framework in basic condition, which further caused the leaching of the Pd nanoparticles. The reason may also be the small particle size and the small dosage of the catalysts leading to the unavoidable loss through the centrifuge.



Fig. 8. (a) The UV-vis spectra of 4-nitrophenol solution in presence of Au@MS and NaBH₄. To make the reaction monitored by the full-spectra scan more easily, the amount of 4-NP was increased. (b) The catalyst recycling test of Pd@MS for the Suzuki reaction of PhBr and phenylboronic acid

 Table 2 The catalytic performance of the synthesized mesoporous silica catalysts

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Entries	Samples	Noble metal percentage (wt%)	Yield (%)	TOF(h ⁻¹)
1	MS(calcined)	0	0 ^{a,b}	0
2	Au@MS	0.2727	100.0^{a}	3039
3	Au@MCM-41	0.0613	17.60^{a}	2380
4	Pd@MS	0.3231	90.55 [♭]	300
5	Pd@MCM-41	trace ^c	6.184 ^b	-

a) Catalytic reduction of 4-nitrophenol for 90 seconds.

b) Suzuki reaction of PhI and phenylboronic acid for 5 hours.

c) Not detected by ICP.

Conclusion

In this work, we designed and synthesized amphiphile with ferrocenyl as the hydrophobic group. The synthesized molecule can act as structure-directing agent to synthesize mesoporous silica with highly ordered hexagonal channels; Meanwhile, the surfactants remained in the channels, and the ferrocenyl group in the surfactants can reduce Au(III) and Pd(II) salts into corresponding metal nanoparticles. Through this method, the prepared catalysts contain noble metal nanoparticles of a small size as well as a high dispersion in the mesoporous channels. The catalysts further show higher catalytic activities for the catalytic hydrogenation of 4nitrophenol and Suzuki reaction compared with those obtained by the traditional impregnation method. To conclude, this is an idea to realize fabricating high performance catalysts by molecule design. On the one hand, through the idea we may fully utilize different properties of the designed molecules to achieve atom economy; On the other hand, the idea may help noble nanoparticles form highly dispersed system in mesoporous channels, which will promote the catalytic process. In addition, this is also an idea to prepare catalytic materials via supramolecular assembly and reaction process in confined space, providing a reference when synthesizing other new catalytic materials.

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