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Short Communication

High-performance gold-promoted palladium catalyst towards the hydrogenation of phenol with mesoporous hollow spheres as support

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1. Introduction

Catalytic hydrogenation of phenol is of commercial and environmental significance because cyclohexanone is an important intermediate for the manufacture of dyestuffs, pharmaceutical products, etc., and is especially significant as the key raw material to produce both caprolactam for Nylon 6 and adipic acid for Nylon 66 [1]. Therefore, selective hydrogenation of phenol for cyclohexanone is an important chemical process that has been studied extensively to date [2-13]. A broad range of catalysts, such as raney Ni [7], Pd-based film/chamber [8.9], amorphous alloy [10], bimetal catalysts [11] and supported catalvsts [12,13], have been developed for this purpose. According to the literatures, issues arising from relatively low catalytic efficiency and severe conditions (>150 °C in the vapor phase [4,5,11,14] or >10 MPa in sc-CO₂ medium [15,16]) may be the main obstacles to achieving practical application. Notably, an excellent study reported by Han [17] disclosed complete phenol conversion with >99.9% selectivity to cyclohexanone under mild conditions based on a dualsupported Pd-Lewis acid catalyst. This may be the most exciting result for phenol hydrogenation up to now.

Inspired by this previously reported work, we attempted to prepare gold promoted Pd catalyst with mesoporous hollow silica spheres as support (PdAu/MHSS) and obtained exciting results. The catalyst shows excellent activity and selectivity towards the hydrogenation of phenol under mild conditions. For PdAu/MHSS with an Au:

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ABSTRACT

A high-performance, gold-promoted Pd catalyst with mesoporous hollow silica spheres as support, PdAu/ MHSS, was prepared using an impregnation–reduction approach. The catalyst showed 10 times higher activity than commercial Pd/C catalyst and 6 times higher activity than Pd/MHSS catalyst. The conversion of phenol was 100% within 30 min of reaction at 80 °C. The catalyst was characterized by XRD, XPS, and TEM, which revealed that its high performance may result from both the high dispersion of active components on the MHSS, caused by the addition of gold, and the interaction between palladium and gold.

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Pd atomic ratio of 1:10, the activity is 10 and 6 times higher than that of Pd/C and Pd/MHSS catalysts, respectively, at a reaction temperature of 50 $^{\circ}$ C and 1 MPa of hydrogen pressure.

2. Experimental

2.1. Preparation of catalyst

Mesoporous hollow silica spheres (MHSS) were synthesized by a one-pot route previously reported by our group [18].

The PdAu/MHSS catalyst was prepared by a co-impregnation method, in which lab-synthesized MHSS were impregnated with an ethanol solution containing PdCl₂ and HAuCl₄ (the molar ratio of Pd/Au was 10/1), then were dried and reduced with hydrogen at 200 °C. The palladium and gold loadings of the catalyst were 2 wt.% and 0.37 wt.%, respectively. For comparison, a commercial Pd/C catalyst with Pd content of 5 wt.% was purchased from ZhongKe Kaidi Catalyst (Lanzhou, China), and Pd/MHSS and Au/MHSS catalysts were prepared using the same procedures as for the PdAu/MHSS catalyst. The general properties of the catalysts are given in Table 1.

2.2. Evaluation of catalysts

Hydrogenation of phenol was used to evaluate the catalyst; the reaction was carried out in a stainless-steel autoclave equipped with a magnified stirrer and thermostat. A reaction mixture containing 1.0 g of phenol, 0.5-1.25 g of catalyst (typically containing 0.025 g of Pd), and 10 ml of CH₂Cl₂ as solvent was introduced into the autoclave. Before the reaction, the system was purged with pure hydrogen

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30 Table 1

Specifications of several catalysts with various compositions.				
Catalyst	Metal loading (wt.%)	Metal particle size (nm)/ ^a	Surface area $(m^2 g^{-1})$	Pore size (nm)
Pd/C	5.0 (4.9) ^b	-	252	-
Au/MHSS	2.0 (1.9)	-	872	3.2
Pd/MHSS	2.0 (1.8)	10-20	854 (41) ^c	3.8
PdAu/MHSS	Pd, 2.0 (1.8)	2-3	766 (166)	4.0
	Au, 0.32 (0.30)			

^a Observed from TEM images.

^b The recipe metal content and the content measured by atomic absorption spectroscopy (in brackets).

^c The BET surface area of the catalyst and the surface area of the metal components (calculated from TEM images, in brackets).

(99.99%) for 5 min to remove air. The evaluation was conducted at 50 °C and 1.0 MPa of hydrogen pressure for all catalysts, unless otherwise mentioned.

The products were analyzed using a gas chromatograph (Agilent 6840N, USA) equipped with a flame ionization detector. A GC-MS (Shimadzu GCMS-QP5050A, Japan) equipped with a 0.25 mm \times 30 m DB-WAX capillary column was used to identify cyclohexanone and cyclohexanol. The column oven temperature was programmed from 120 °C (held for 1 min) to 280 °C at a rate of 20 °C min⁻¹.

2.3. Catalyst characterizations

X-ray diffraction (XRD) patterns were obtained with a D/MAX-IIIA X-ray diffractometer (Rigaku, Japan) using Cu K α radiation. Atomic absorption analysis was performed with a SpectrAA-220Z (Varian, USA). Transmission electron microscopy (TEM) was carried out on a JEOL JEM2010 microscope (JEOL, Japan) using an accelerating voltage of 200 kV. N₂ adsorption–desorption isotherms were measured with a Tristar 3010 isothermal nitrogen sorption analyzer (Micromeritics, USA) using a continuous adsorption procedure. X-ray photoelectron spectroscopy (XPS) with an AXIS Ultra DLD (Kratos, Britain) was used to examine the electronic properties of the catalysts. The binding energy was calibrated using a C 1s binding energy of 284.8 eV. Hydrogen temperature-programmed reduction (H₂-TPR) was performed on a FineSorb 3010 adsorption system (Finetec, China).

3. Results and discussion

For both the Pd/MHSS and the PdAu/MHSS, a well-defined diffraction peak occurred at 2-3° (see XRD patterns in Fig. 1a), demonstrating the well-preserved, wormhole-like mesoporous structure of the MHSS support after metal loading. As shown in the magnified, wide-angle XRD pattern inset in Fig. 1a, the supported palladium catalysts, including Pd/C (not shown, for simplicity) and Pd/MHSS exhibit three obvious, sharp diffraction peaks corresponding to the (111), (200), and (220) planes of the face-centered cubic structure of palladium, confirming metallic palladium loading on the support after hydrogen reduction. The PdAu/MHSS catalyst exhibited comparable broad peaks, as featured in the (111) plane (see Fig. 1b). Generally, the broadened peaks may be caused by high dispersion and small particle size, or the amorphous structure of the sample. For our PdAu/MHSS catalyst, however, we attributed the broadened peaks to the high dispersion and small particle size of PdAu on the PdAu/MHSS catalyst, caused by the addition of gold; this is further proved by the TEM images. It should be pointed out that the diffraction peaks of gold cannot be observed in the XRD pattern, while the peak (111) of palladium is shifted slightly to the left. We suggest that traces of gold may have entered the palladium lattice, or were outside the detection limits of XRD.



Fig. 1. XRD patterns of (a) Pd/MHSS and (b) PdAu/MHSS catalysts. Inset shows the corresponding magnified, wide-angle XRD.

The average particle sizes of Pd nanoparticles in Pd/MHSS and PdAu nanoparticles in PdAu/MHSS were 12 nm and 3.5 nm, respectively, calculated from the Scherrer equation. It appears that the addition of gold enhanced the dispersion of the active components in the catalyst.

The high-resolution TEM images in Fig. 2 reveal the dispersion of the loading metal on the silica support. For Pd/MHSS (Fig. 2a and b), relatively dark coloration was found at the silica shell; energydispersive X-ray spectroscopy confirmed this cloud-like aggregation to be Pd, which was in agreement with the sharp reflection peaks observed in the XRD pattern. Notably, the PdAu/MHSS catalyst exhibited high dispersion of metal nanoparticles that had a narrow size range of 2.0-4.0 nm (Fig. 2c and d), further confirming that the addition of gold promoted the dispersion of palladium. The data for several catalysts, shown in Table 1, also clearly reveal the superiority of the MHSS support and the promotion of gold for the dispersion of active components. For the PdAu/MHSS catalyst, the high dispersion of its active components as observed by TEM is guite consistent with the results from XRD and the Scherrer equation. But for the Pd/ MHSS, the situation is different: the particle size obtained by XRD is smaller than that observed by TEM, indicating aggregation of the primary particles of palladium in Pd/MHSS, because the particle size given by XRD and the Scherrer equation is the average particle size of primary particles of palladium.

Actually, some researchers have previously recognized and reported the difficulty of achieving high dispersion of pure palladium, and the fact that dispersion can be promoted by additives [19–21].



Fig. 2. TEM images of (a, b) Pd/MHSS and (c, d) PdAu/MHSS.



Fig. 3. XPS spectra of (a) Pd and (b) Au in PdAu/MHSS, (c) Pd in Pd/MHSS, and (d) Au in Au/MHSS.

Table 2			
Hydrogenation of	phenol catalyzed	with different	catalysts.

Entry	Catalyst	Time	Conversion	Selectivity (%)	
		(h)	(%)	C==0	C-OH
1	Au/MHSS	20	Trace	-	-
2	Pd/C	0.75	9.1	95.2	4.8
3	Pd/MHSS	0.75	15.0	94.6	5.4
4	PdAu/MHSS	0.75	97.5	96.6	3.4
5 ^a	PdAu/MHSS ^{3rd}	0.75	95.0	96.5	3.5
6 ^a	PdAu/MHSS ^{5th}	0.75	93.7	97.0	3.0

 6^{a} PdAu/MHSS³⁴¹ 0.75 93.7 97.0 3.0 Reaction conditions: mass ratio M_{phenol} : M_{Pd} = 1:0.025; 10 ml CH₂Cl₂; 50 °C, 1 MPa of H₂ pressure; stirring speed 1000 rpm.

^a Recycle usability test, 3rd/5th denotes number of times catalyst tested.



Fig. 4. Relationship of conversion to reaction temperature for catalysts Pd/MHSS and PdAu/MHSS; mass ratio of phenol to catalyst 1:0.01, reaction time 30 min.

Fig. 3 shows the XPS spectra of Pd and Au in the PdAu/MHSS catalyst; the spectra were calibrated using the C 1s peak energy of 284.8 eV. As shown in Fig. 3a, the binding energies of palladium in the catalyst were 341.0 eV (Pd $3d_{3/2}$) and 335.8 eV (Pd $3d_{5/2}$), which can be assigned to the Pd⁰ species. Compared with 340.3 eV (Pd 3d_{3/2}) and 335.1 eV (Pd 3d_{5/2}) for the Pd/MHSS catalyst (Fig. 3c), the shift toward a higher binding energy could be an indication of charge transfer from Pd to Au in the PdAu/MHSS catalyst, which would suggest Pd-Au alloy formation [22,23]. No obvious binding energy shift can be observed for Au (see Fig. 3b and d). We also investigated the interaction between palladium and gold by temperature-programmed reduction (TPR); after the addition of gold, the reduction peak is shifted toward high temperature with an increasing range of 30 °C, which supports the suggestion of a strong interaction or the formation of an alloy between the palladium and the gold [24,25].

It is noteworthy that the addition of gold greatly enhanced the performance of the catalyst towards the hydrogenation of phenol, as shown in Table 2. The Au/MHSS catalyst showed almost no activity toward the reaction, while under the same reaction conditions, Pd/C and Pd/MHSS showed conversions of 9.1% and 15.0%, respectively. However, PdAu/MHSS exhibited an excellent conversion of 97.5% with a high selectivity of 96.6% for cyclohexanone, clearly indicating that the addition of gold significantly improved the performance of the catalyst. The exceptional promotion may be attributed to high dispersion of the active components and interactions between the gold and palladium. Furthermore, the catalyst showed good stability, with almost no degradation in activity or observable selectivity after 5 tests. We were not able to prepare a Pd/MHSS catalyst with the same smaller particle size as PdAu/MHSS using the same metal loading, in the absence of gold.

Fig. 4 shows the relationship of conversion to reaction temperature. To make a clear comparison, we increased the mass ratio of M_{phenol} : M_{Pd}

 Table 3

 The catalytic activities and selectivity of PdAu/MHSS catalyst towards hydrogenation of several aromatic derivatives.

 Entry
 Substrate
 Temperature (°C)
 Conversion (%)

Entry	Substrate	Temperature (°C)	Conversion (%)	Selectivity (%)
1	ОН	50	>99	↓ 0 96; ↓ 0Н 4
2	ОН	50	>99	96; OH 4
3	ОН	50	>99	97; OH 3
4	но	50	>99	H0 95; H0 5
5	ОН	50	>99	>99
6	NO ₂	50	>99	NH2 >99
7	ОН	100	22	ОН >99

Reaction conditions: mass ratio: $M_{substrate}$: M_{Pd} = 1:0.025; hydrogen pressure, 1 MPa; impeller speed, 1000 rpm; and reaction time 1 h.

to 1:0.01. For both Pd/MHSS and PdAu/MHSS, conversion increased sharply as the reaction temperature rose. However, PdAu/MHSS exhibited much higher temperature sensitivity than Pd/MHSS. At 80 °C, the conversion of phenol was almost 100% within 30 min. To the best of our knowledge, this is the highest activity achieved for this reaction under such mild conditions (1 MPa, <100 °C).

Intrigued by the above exciting results, we further investigated the catalysis of PdAu/MHSS for the hydrogenation of other aromatic derivatives. We found that PdAu/MHSS also possesses high activity for the hydrogenation of phenol derivatives, nitrobenzene, naphthol, and benzoic acid (see Table 3), revealing this catalyst's extensive capacity for hydrogenation of aromatic derivatives.

4. Conclusions

In conclusion, a high-performance hydrogenation catalyst for phenol and aromatic derivatives was successfully prepared, consisting of gold and palladium supported on mesoporous hollow silica spheres. The addition of gold improved the dispersion of the active components and greatly enhanced the activity of PdAu/MHSS. This catalyst's ultra-high performance and high selectivity may make it a promising candidate for phenol hydrogenation in industrial applications.

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