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ARTICLE

Performance of Supported Au-Pd Alloy Nano Particles Catalyst for Base-free Synthesis of Imines by Self-coupling of Amine

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Abstract: A series of supported nano particles catalysts, Au/γ-Al_2O_3, Pd/γ-Al_2O_3 and Au-Pd/γ-Al_2O_3, were prepared by the impregnation reduction method. The catalytic performance of these catalysts for direct base-free synthesis of imines by self-coupling of benzylamine was investigated. The results show that the yield of imine could reaches 93% over bimetallic alloy Au-Pd/γ-Al_2O_3 catalyst, much higher than monometallic Au or Pd nano particle catalyst. The used catalyst is recovered and 44% yield of imine could be obtained after 5 recycling use of Au-Pd/γ-Al_2O_3.

Key words: Au-Pd alloy nanoparticle; benzylamine; imine

Imines are important building blocks used in the synthesis of a wide range of biology medicines, agricultural chemicals and fine chemicals [1-3]. The traditional method for imine synthesis is the condensation of amines with carbonyl compounds in the presence of a Lewis acid. Moreover, the electrophilic carbonyl compounds are generally unstable and reactive. Therefore it is highly desirable to produce imines from more stable compounds[4,5]. Given that only one reaction substrate is needed in the direct oxidation of coupling of primary amines, it is considered as an attractive and environmental friendly alternative to traditional method due to its atom-economy and green synthesis route. Some homogenous metal catalysts, such as Cu and Pd, have shown to be highly active for this reaction. However, some of them suffer from high temperature, high pressure, additional base or oxidation reagent [6-9]. Therefore it is very appealing to develop the imine synthesis route under ambient and environmental friendly conditions.

In recent years, nano gold particles have been applied for many reactions, such as hydrocarbon oxidation, dehydrogenation activation, and selective liquid phase oxidation because of their outstanding performances [10-12]. In particular, the addition of palladium to form Au-Pd alloy particles leads to an enhancement in activity for many reactions compared with the gold-only and palladium-only catalysts[13-18]. The significant enhancement of catalytic performance could be explained by synergistic interaction between Au and Pd nanoparticles (NPs)[19]. However, there are few reports about bimetallic Au-Pd catalysts for the direct base-free synthesis of imines by self-coupling of benzylamine. In this work, Au, Pd and Au-Pd nanoparticles supported on γ-Al_2O_3 have been prepared and used as catalysts for this challenging reaction.

1 Experiment

1.1 Catalyst preparation

All the catalysts with total Au-Pd loading of 3 wt% were

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prepared by the impregnation reduction method and the synthesis process was as follows. Typically, 1.0 g γ-Al_2O_3 powder was dispersed into 100 mL aqueous solution containing a certain amount of $HAuCl_4$ and $PdCl_2$. Lysine (0.53 mol/L, 8 mL) was then added to the mixture under vigorous stirring for 30 min. An aqueous solution of $NaBH_4$ (0.35 mol/L, 4 mL) was added gradually to the suspension during about 10 min, followed by hydrochloric acid (0.3 mol/L, 3 mL). The mixture was aged for 24 h and then the solid in the suspension was separated by centrifugation, washed with deionized water for four times and ethanol twice and dried at 60 °C. The dried sample was 3 wt% Au-Pd/γ-Al_2O_3 catalyst and used directly for catalytic test and characterization. In order to compare the effect of Au/Pd molar ratio on the activity, a series of catalysts with 3 wt% total metal loading including Au_2-Pd_1/γ-Al_2O_3, Au_1-Pd_1/γ-Al_2O_3, Au_1-Pd_2/γ-Al_2O_3 as well as Au/γ-Al_2O_3, Pd/γ-Al_2O_3 were prepared.

1.2 Catalyst characterization

The UV-visible spectra of the samples were recorded on a Shimadzu UV-2550 spectrophotometer in the range of 200~800 nm at room temperature with $BaSO_4$ as the reference. TEM images were recorded with a FEI Tecnai G2 F20 S-Twin transmission electron microscope employing an accelerating voltage of 200 kV. The specimens were fine powders deposited onto a copper microgrid coated with a holey carbon film. The composition of some samples was determined by the energy-dispersive X-ray spectroscopy attachment of an FEI Quanta 200 scanning electron microscope. The actual loadings of Au and Pd were analyzed by the Beijing Purkinje General Instrument Limited Liability Company's TAS-990 Purkinje General Atomic Absorption spectrophotometer. Lamp current is 6 mA and wavelengths are 242.8 and 244.8 nm. XPS spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source ($h\nu$=1486.6 eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). An aperture slot of 300 μm×700 μm was used during XPS analysis. Survey spectra were recorded with a pass energy of 80 eV, and high resolution spectra with a pass energy of 40 eV. In order to subtract the surface charging effect, the C 1s peak has been fixed at a binding energy of 284.6 eV.

1.3 Activity test

The reaction of synthesis of N-benzylidenebenzylamine was carried out in a 25 mL reaction tube. In a typical reaction, 0.25 mmol benzylamine, 5 mL toluene and 25 mg catalyst were added into the reaction tube. Then the reaction was conducted at 70 °C for 36 h in a water bath under magnetically stirring if not specified.

After reactions, the suspension was filtered. The filtrate was analyzed by a Shimadzu GC-2014 with a HP-5 capillary column (50 m of length, 0.25 mm of internal diameter, and 0.25 μm of film thickness). The temperature of column was increased from 100 to 120 °C with a heating rate 2 °C/min, then risen to 230 °C (15 °C/min) and maintained for 5 min. The injector and flame ionization detector temperatures were kept at 300 and 310 °C for product analysis, respectively. The products were further identified by GC-MS and ^{1}HNMR.

1.4 Catalysts recycle experiment

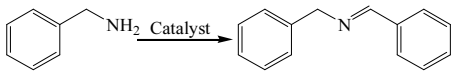
After each reaction cycle, the mixture of the solvent, substrate, and products were separated with the catalyst by centrifugation. The used catalyst was washed thoroughly with ethanol solution and distilled water, followed by centrifugal separation and drying at 80 °C for 12 h. The recovered catalyst was used for the next cycle.

2 Results and Discussion

2.1 Activity of catalysts

The activity for the base-free synthesis of N-benzyl-1-phenylmethanimine on different catalysts was investigated and shown in Table 1. It could be found that in the presence of 3 wt% Pd/γ-Al_2O_3, the conversion of benzylamine is 50%, and Au/γ-Al_2O_3 is mostly inactive to the reaction (entries 1, 2). It should be pointed out that Au_1-Pd_2/γ-Al_2O_3 alloy nanoparticles catalysts exhibit higher activity than the monometallic Pd/γ-Al_2O_3 catalyst (entries 3). This result confirms the hypothesis that the synergistic interaction between Au and Pd NPs could enhance the catalytic performance of Pd NPs. In order to investigate the effect of Au/Pd molar ratio on the catalyst activity, Au_2-Pd_1/γ-Al_2O_3 and Au_1-Pd_1/γ-Al_2O_3 were also evaluated for this reaction. The Au_1-Pd_1/γ-Al_2O_3 catalyst shows the highest catalytic activity with 99% conversion of benzylamine and 94% selectivity of N-benzyl-1-phenylmethanimine (entries 4, 5). It is noteworthy that no reaction is observed in a blank experiment conducted with γ-Al_2O_3 powder instead of Au-Pd/γ-Al_2O_3 alloy nanoparticles catalysts under identical conditions (entry 6).

Table 1 Catalytic activities of catalysts for direct synthesis of N-benzylidene benzylamine[a]



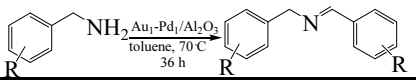
Entry	Catalyst	Conversion/%	Selectivity /%
1	Pd/γ-Al_2O_3	50	95
2	Au/γ-Al_2O_3	<5	100
3	Au_1-Pd_2/γ-Al_2O_3	74	93
4	Au_1-Pd_1/γ-Al_2O_3	99	94
5	Au_2-Pd_1/γ-Al_2O_3	93	96
6	γ-Al_2O_3	-	-

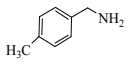
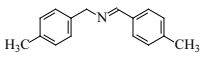
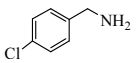
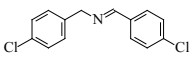
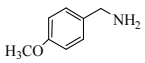
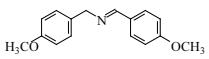
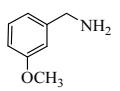
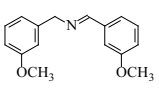
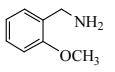
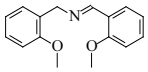
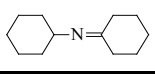
[a]: reaction conditions: 0.25 mmol benzylamine, 5 mL toluene, 25 mg catalyst, temperature 70 °C, time 36 h; (the reaction conversion and selectivity are calculated based on benzylamine, determined by GC)

The scope of the methodology for synthesizing a broad range of imines was investigated with a variety of derivatives over the best catalyst (Au_1-Pd_1/γ-Al_2O_3) for N-benzylidenebenzylamine synthesis. As shown in Table 2, every substituted benzylamine, including *o*, *m*, *p*-methoxybenzylamines, *p*-chlorobenzylamine and *p*-methylbenzyl amine, can be converted to the corresponding imines with a yield of 62%~86%. It is well known that the reactivity of all the substituted benzylamines is lower than benzylamine and the catalytic reaction is not affected by electronic effect of substrates. Furthermore, comparison of *o*, *m*, *p*-methoxybenzylamines shows that the *o*-position substituent group hinders the self-coupling reaction (entries 3~5). Likewise, when greater steric hindrance amine, 1-phenylethan-1-amine, is used as the substrate, no desired product is obtained (entry 6). When cyclohexanamine is used as the substrate, only trace amount of product is detected by GC. This result indicates that the benzyl group is essential for Au-Pd/γ-Al_2O_3 catalyzed self-coupling reaction of amine.

One of the important advantages of using heterogeneous catalyst is its recyclability. We found that the catalytic activity of recycling the Au_1-Pd_1/γ-Al_2O_3 catalyst in the reaction of imine decreases with recycling times, but it is still held above 44% after recycling 5 times. This result shows the potential of heterogeneous bimetallic Au-Pd catalyst for direct imine synthesis.

Table 2 Substrate scope of the self-coupling of amines



Entry	Substrate	Product	Yield/%
1			83
2			69
3			76
4			86
5			62
6			No product
7			Trace

Note: reaction conditions: 0.25 mmol benzylamine, 25 mg catalyst, 5 mL toluene, 70 °C, 36 h, the yield determined by GC

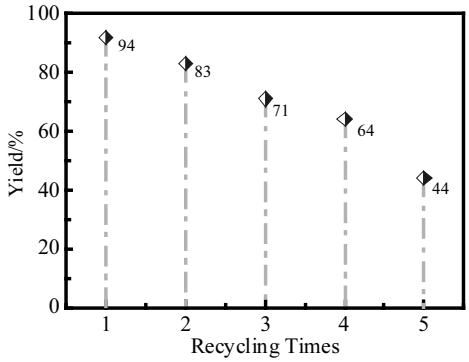


Fig.1 Recyclability of catalyst

2.2 Characterization of catalysts

2.2.1 UV-visible spectra

The diffuse reflectance UV-Visible spectra of catalysts are presented in Fig.2. An absorption peak at ~520 nm is observed for Au/γ-Al_2O_3 catalyst, which is due to surface Plasmon resonance (SPR) effect, a distinguishing feature of the gold nanoparticles[20]. However, no apparent absorption is observed over bimetallic Au-Pd catalysts in the visible light zone, implying the formation of Au-Pd alloy nanoparticles rather than individual monometallic Au and Pd particles

2.2.2 Transmission electron microscope

Fig.3 and Fig.4 show TEM images and particles size distribution of catalysts. The metallic particles are well dispersed on γ-Al_2O_3 support. And the particle sizes are in range of 2~7 nm with mean diameter of about 4.4 nm for 3 wt% Au/γ-Al_2O_3, 4.6 nm for 3 wt% Pd/γ-Al_2O_3 and 3.9 nm for 3 wt% Au-Pd/γ-Al_2O_3. From the TEM images of 3 wt% Au_1-Pd_1/γ-Al_2O_3 catalyst after recycling 5 times, the slight aggregation of metal was found and the mean size increases to 4.4 nm.

2.2.3 Atomic absorption spectroscopy

The composition Au_1-Pd_1/γ-Al_2O_3 of catalysts listed in Table 3 illustrates that the actual loading is slightly lower than the nominal loading of 3 wt%. It is mostly notable

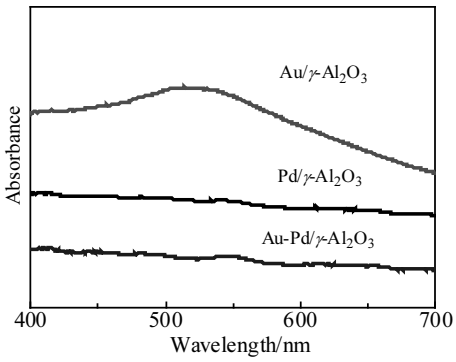


Fig.2 UV-Visible absorption spectra of different catalysts

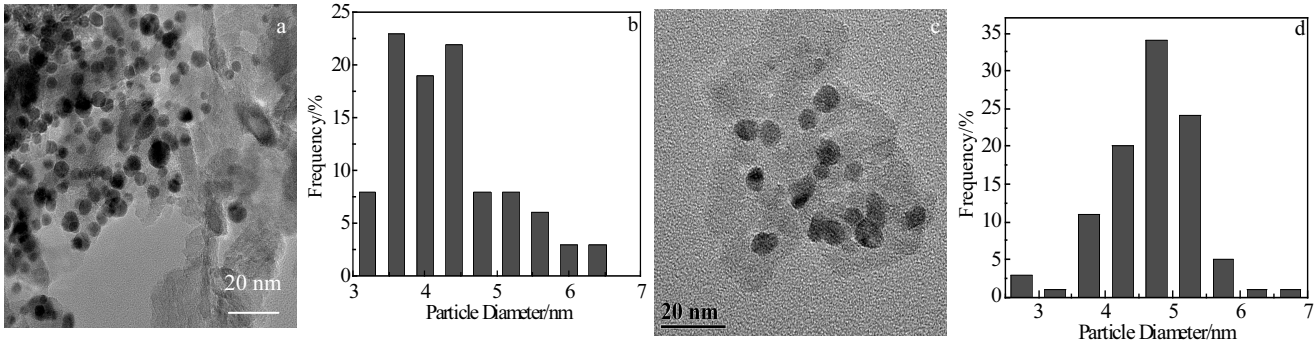


Fig.3 TEM images (a, c) and particles size distribution (b, d) of catalysts Au/γ-Al_2O_3 (a, b) and Pd/γ-Al_2O_3 (c, d)

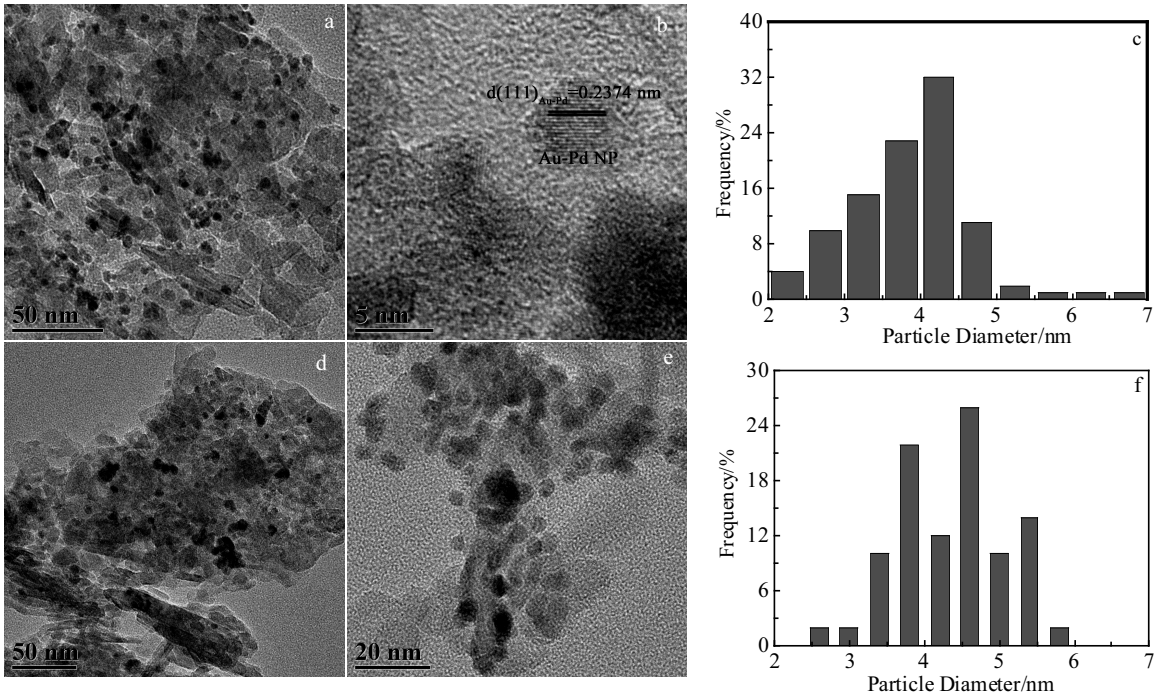


Fig.4 TEM images (a, b, d, e) and particles size distribution (c, f) of fresh Au_1-Pd_1/γ-Al_2O_3 catalyst (a, b, c) and recycled Au_1-Pd_1/γ-Al_2O_3 catalyst (d, e, f) after 5 times

Table 3 Actual loading of Au_1-Pd_1/γ-Al_2O_3 catalyst

Catalysts	Theoretical loading/wt%	Actual loading/wt%	Au/Pd molar ratio
Catalyst	3	2.6	1:1
Recycled catalyst	3	1.0	4.7:1

the decrease of the total loading and the change of Au/Pd ratio after 5 times recycling. The total metal loading decreases to 1 wt% and Au/Pd changes to 4.7, implying the serious leaching of Pd. The decrease of catalytic activity after 5 times might be due to the metal loss of the catalyst.

2.2.4 X-ray photoelectron spectroscopy

The XPS spectra of Au/γ-Al_2O_3, Pd/γ-Al_2O_3 and Au-Pd/γ-Al_2O_3, Au_1-Pd_1/γ-Al_2O_3 catalysts are shown in Fig.5. Compared with monometallic Au/γ-Al_2O_3 catalyst, the negative shift of Au $4f_{7/2}$ and Au $4f_{5/2}$ is observed for Au_1-Pd_1/γ-Al_2O_3 (Fig.5a). However, The Pd $3d_{3/2}$ peaks of the Au_1-Pd_1/γ-Al_2O_3 shift to higher binding energy when compared with that in Pd/γ-Al_2O_3 (Fig.5b). This synergistic effect between Pd and Au further alludes to the formation of an Au-Pd alloy, which is beneficial for the activity enhancement

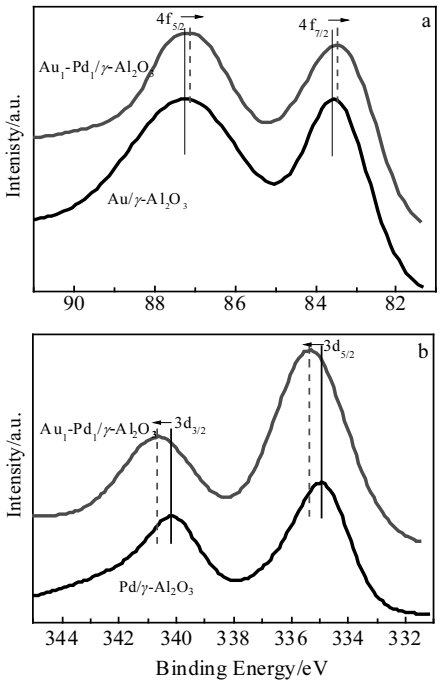


Fig.5 X-ray photoelectron spectra of catalysts: (a) Au_1-Pd_1/ γ-Al_2O_3, Au/γ-Al_2O_3; (b) Au_1-Pd_1/γ-Al_2O_3, Pd/γ-Al_2O_3

3 Conclusions

1) Bimetallic Au_1-Pd_1/γ-Al_2O_3 catalyst shows high activity for the base-free synthesis of N-benzylidene benzylamine by self-coupling. 99% benzylamine conversion and 94% selectivity to N-benzylidene benzylamine is obtained over Au_1-Pd_1/ γ-Al_2O_3 catalyst at temperature of 70 °C.

2) The catalyst could be readily recovered and recycled. After 5 recycling use, the yield decreases to 44%.

3) The aggregation of nanoparticle and leaching of active metal, especially Pd are found over Au_1-Pd_1/γ-Al_2O_3 catalyst after 5 recycling use, which could be attributed to the decrease of activity during recycling runs.

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负载纳米 Au-Pd 合金催化剂对苄胺氧化偶联合成亚胺的研究

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摘 要：采用浸渍还原法制备了 Au/γ-Al_2O_3, Pd/γ-Al_2O_3 和 Au-Pd/γ-Al_2O_3 系列纳米催化剂，考察了催化剂对无碱条件下苄胺自身氧化偶联合成亚胺的反应性能。结果显示 3% Au-Pd/γ-Al_2O_3 (质量分数) 催化剂对伯苄胺自身氧化偶联合成亚胺的反应表现出较好的催化活性，在 70 ℃、常压条件下，不加氧化剂和碱时，亚胺收率可达 93%。催化剂能够回收利用，使用循环 5 次后的催化剂，产物亚胺的收率降到 44%。

关键词：Au-Pd 纳米合金；苄胺；亚胺

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