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Positively charged bulk Au particles as an efficient catalyst for oxidation of styrene with molecular oxygen†

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Positively charged bulk Au particles with size of 20–150 nm were formed on amino-modified porous polydivinylbenzene (Au/PN), which showed superior catalytic performance and good recyclability in the aerobic oxidation of styrene.

Since the pioneering work of Hutchings and Haruta *et al.,*[1] Au catalysts have been demonstrated to be active for many important reactions, especially for oxidation by molecular oxygen,[2–7] where a critical factor for determining the catalytic performance is the particle size of the Au catalysts. When the Au particle sizes are over 5 nm, the Au catalysts are normally of low-efficiency.[4a,6,8]

As an important model reaction for the production of fine chemicals and pharmaceuticals, the oxidation of styrene has been widely investigated over various Au catalysts.[2,9–14] For the liquid-phase oxidation of styrene by molecular oxygen, additives (*e.g. t*-butyl hydroperoxide) as the initiator are necessary.[2,11,12] However, when the size of Au particles is extremely small (∼1.4 nm, 55 atoms, or ∼0.9 nm, 25 atoms), the Au catalysts are very active even in the absence of additives.[9,10] In contrast, when the size of Au particles is 2 nm, they become completely inactive. Notably, the synthesis of extremely small Au nanoparticles usually requires precursor ligands in the starting step and the removal of the precursor ligands in the final step, which is expensive and could produce undesirable waste.[8b,9,10] In addition, extremely small Au nanoparticles are unstable in catalytic oxidations due to their aggregation. As a result, their catalytic activity reduces significantly for long

reactions,[9] which strongly limits the wide application of Au nanoparticle catalysts with extremely small particle size.

Here, we demonstrate an alternative catalyst of amino functionalized, porous polydivinylbenzene supported, positively charged bulk Au particles (Au/PN) with particle sizes of 20–150 nm, which are very stable and active in the aerobic oxidation of styrene. This result is quite different from the known fact that only Au particles with a size smaller than 2 nm are catalytically active and stable for the aerobic oxidation of styrene in the absence of initiators.[9,15]

The Au/PN sample is synthesized from the one-pot treatment of amino functionalized porous polydivinylbenzene with HAuCl$_4$ solution. The choice of amino groups is due to our careful investigation of the interaction between the HAuCl$_4$ solution with various amines. Fig. S1 (ESI†) shows the photographs and UV-Visible spectra of mixtures of the HAuCl$_4$ solution with different amines. When the aliphatic amines cyclohexylamine and ethylenediamine were added into the HAuCl$_4$ solution, the mixture still exhibited a yellow color, which was very similar to the color of the pure HAuCl$_4$ solution (Fig. S1A, ESI†). In addition, the mixture of cyclohexylamine and HAuCl$_4$ exhibited a similar UV-Visible spectra (Fig. S1B-c, ESI†) to the pure HAuCl$_4$ (Fig. S1B-a, ESI†), indicating that the valence of Au cations was stable in the mixture of cyclohexylamine with HAuCl$_4$. Interestingly, when aniline was added into the HAuCl$_4$ solution, the color immediately changed to dark brown. In comparison with the UV-Vis spectra of pure HAuCl$_4$ solution (Fig. S1B-a, ESI†) and pure aniline (Fig. S1B-d, ESI†), the dark brown mixture showed clear additional signals in the wavelength of 500–700 nm (Fig. S1B-e, ESI†), which are associated with the presence of metallic Au.[16] These results indicate that metallic Au species could be formed by the interaction between aniline and Au cations.

Based on the interaction between aniline and Au cations, it is suggested that amino-modified porous polydivinylbenzene (PN) should be a suitable support for the formation of metallic Au species as a heterogeneous catalyst (Au/PN). Fig. 1A shows the synthesis scheme of Au/PN where the Au content is about 2.4 wt% (Table S1, ESI†).

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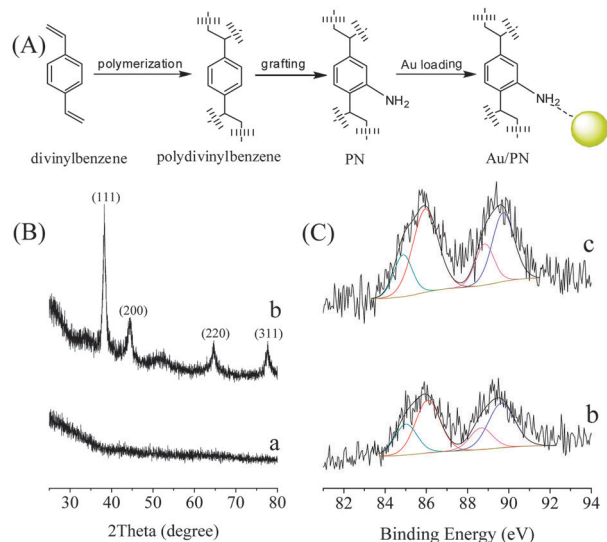
Fig. 1 (A) Scheme, (B) XRD, and (C) Au4f XPS spectra of (a) PN, (b) Au/PN, and (c) Au/PN-R.

The presence of amino groups on polydivinylbenzene was confirmed by IR and N1s XPS techniques (Fig. S2, ESI†). In addition, the XRD pattern of Au/PN shows four obvious peaks at 38.3, 44.5, 64.7, and 77.7°, which are attributed to the (111), (200), (220), and (311) incidences of a typical metallic Au species (Fig. 1B). Notably, these peaks are narrow and sharp, suggesting a relatively large particle size of metallic Au.[16] Furthermore, the UV-Vis spectrum of Au/PN gives an obvious peak at 518 nm (Fig. S3, ESI†), confirming the presence of metallic Au species in the Au/PN sample,[16] in good agreement with the results of the XRD patterns (Fig. 1B).

Fig. 2 shows the microscopic characterization of Au/PN. In the STEM image, the Au particles with large sizes of 20–150 nm are clearly observed on the porous PN support (Fig. 2a and b). The elemental mapping shows that the C and N species are
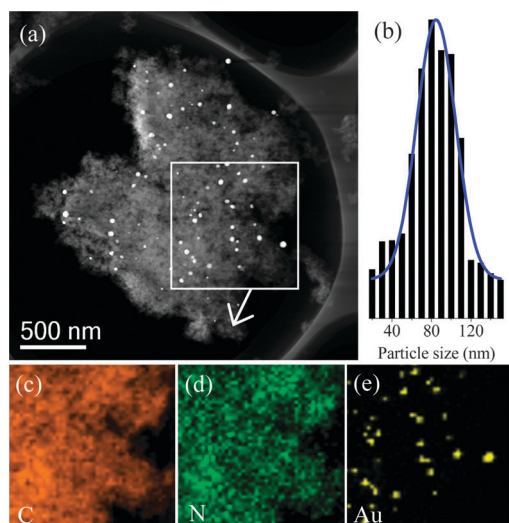
Fig. 2 (a) STEM image, (b) particle size distribution, (c–e) C, N, and Au elemental maps of Au/PN.

homogeneously distributed on the Au/PN sample (Fig. 2c and d). Notably, the distribution of Au particles in the STEM image (the white square in Fig. 2a) is highly consistent with the distribution of Au species in the Au elemental mapping (Fig. 2e). A similar result could also be found in various areas of the Au/PN sample (Fig. S4, ESI†), indicating that the Au species on the Au/PN are present as bulk Au particles. Additionally, the HRTEM images show that extremely small Au nanoparticles could not be detected on the Au/PN (Fig. S5, ESI†), which supports that only bulk Au particles exist in the Au/PN sample.

Although the bulk metallic Au particles have been confirmed on the Au/PN sample, it is still desirable to investigate the electronic properties of the Au species on the surface of the bulk Au. Fig. 1C shows the Au4f XPS spectra of various samples. Interestingly, the Au4f XPS spectrum of Au/PN shows obvious Au4f$_{7/2}$ peaks at 86.0 and 84.9 eV associated with typical Au^{3+} and Au^{+} species, respectively.[17] These results indicate that there are positively charged Au species on the surface of the bulk Au particles (Table S1, ESI†). The EPR spectra show that PN gives the signal at $g = 2.0045$, while Au/PN has an additional strong signal ($g = 2.3262$), which is reasonably assigned to the positively charged Au species (Fig. S6, ESI†) because the pure metallic Au is EPR-silent.[18] In combination of the results obtained from the XPS and EPR techniques, we could conclude that the bulk Au particles of Au/PN are rich in Au cations. Very surprisingly, the Au cations on Au/PN are extremely stable. For example, after reduction of the Au/PN sample by NaBH$_4$, the obtained Au/PN-R still shows similar Au4f XPS (Fig. 1C-c, Table S1, ESI†) and EPR spectra (Fig. S6-c, ESI†) to those of the as-synthesized Au/PN. These results indicate that the Au cations on Au/PN have extraordinarily high stability, which might be related to the interaction between the aniline groups and the Au species.

For comparison, the aliphatic amino functionalized mesoporous silica was synthesized by coating aminopropyltriethoxysilane (KH-550) on the surface of MCM-41 (MCM-N, Scheme S1, ESI†). When the Au species were loaded on MCM-N (Au/MCM-N), the metallic Au nanoparticles were undetectable from the XRD pattern (Fig. S7, ESI†). After reduction with NaBH$_4$, Au^{3+} cations were undetectable on the Au/MCM-N sample, indicating that Au^{3+} cations are unstable in the presence of NaBH$_4$ (Fig. S7–S9, ESI†), which is quite distinguishable from the phenomenon of the Au/PN sample with very stable Au cations.

Table 1 presents the catalytic data of various Au catalysts in the direct aerobic oxidation of styrene. The PN support is completely inactive for this reaction (entry 1 in Table 1). However, the Au/PN catalyst shows high styrene conversion at 27.0%, with selectivity towards styrene epoxide at 30% (entry 2 in Table 1, Fig. S12, ESI†). In comparison, the non-porous supported Au particles (Au/non-porous PN, Table S1, Fig. S10 and S11, ESI†) with similar Au particle sizes and cations, show styrene conversion at 14.2% (entry 5 in Table 1, Table S2, ESI†). The extremely small Au nanoparticles (∼1.4 nm) supported on boron nitride (Au$_{55}$/BN) and SiO$_2$ (Au$_{55}$/SiO$_2$), which were reported as very efficient catalysts for the aerobic oxidation of styrene, show styrene conversion at 19.2 and 25.8, with styrene epoxide selectivity at 12–14% (entries 6 and 7 in Table 1).

Table 1 Catalytic data of various Au catalysts in the aerobic oxidation of styrene[a]

			Product selectivity[b] (%)				
Entry	Catalyst	Conv. (%)	P1	P2	P3	P4	Ref.
1	PN	Inactive					This work
2	Au/PN	27.0	30.0	65.2	2.8	2.0	This work
3[c]	Au/PN	16.4	22.2	67.2	10.6	—	This work
4[d]	Au/PN	24.9	31.2	64.8	2.1	1.9	This work
5	Au/non-porous PN	14.2	29.1	60.2	3.3	7.4	This work
6	Au_{55}/BN	19.2	14.0	82.3	3.9		9
7	Au_{55}/SiO$_2$	25.8	12.0	82.1	5.7		9
8	Au/MCM-N-R	Inactive					This work
9	Au/MCM-N	Inactive					This work
10[e]	HAuCl$_4$	Inactive					This work
11	Au/PN-R	27.1	29.0	65.7	3.1	2.2	This work

[a] Reaction conditions: 100 mg of catalyst, 12 mmol of styrene, 20 mL of toluene, 1.5 bar of O$_2$, 100 °C, 15 h, dodecane as the internal standard. [b] P1 = styrene epoxide, P2 = benzaldehyde, P3 = acetophenone, P4 = phenylacetaldehyde, benzyl alcohol and others. [c] 1.0 bar of O$_2$. [d] 25 mg of catalyst. [e] 1.3 mg of catalyst.

These results indicate that the Au/PN catalyst is very active (Fig. S13, ESI†).

In contrast, the Au/MCM-N-R catalyst with small Au nanoparticles of 2.0–3.4 nm (Fig. S9 and Table S1, ESI†) is completely inactive for this reaction (entry 8 in Table 1).[9] Additionally, both the Au/MCM-N and HAuCl$_4$ catalysts, which have only Au^{3+} cations, are also inactive for this reaction (entries 9 and 10 in Table 1). These results might suggest that the Au^0 on the Au particles (>2 nm) or Au^{3+} sites are not the active centres for the aerobic oxidation of styrene. Based on these results, it might be suggested that the Au$^+$ sites on Au/PN are the active sites for the oxidation of styrene, because the Au$^+$ sites have similar Au4f$_{7/2}$ electron binding energy (85.0 eV) to that of the Au$_{55}$ clusters

(85.1 eV), suggesting their similar electronic properties which might lead to unusual catalytic performances.[9,17,19]

It is very important to point out that there is no leaching for the Au/PN catalyst. For example, after filtrating the used Au/PN catalyst, the Au concentration in the liquor is less than 3 ppb (ICP analysis). More importantly, Au/PN has very excellent recyclability. Even when recycled 7 times, the sample still exhibits very similar activities (Fig. 3). On the contrary, the Au$_{55}$/SiO$_2$ catalyst loses most of its activity after two further cycles under the same reaction conditions (Fig. 3), because the Au$_{55}$ clusters are not stable and aggregate into relatively large nanoparticles during the reaction process.[9]

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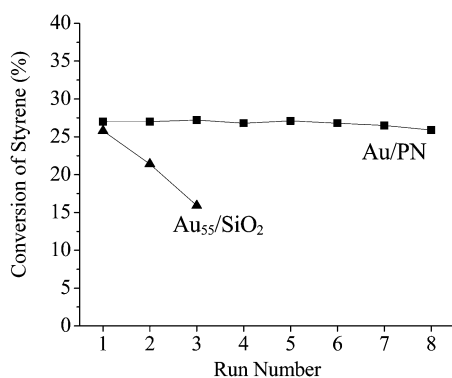
Fig. 3 Aerobic oxidation of styrene using Au/PN and Au$_{55}$/SiO$_2$ catalysts over several cycles. The data for the Au$_{55}$/SiO$_2$ catalyst is from ref. 9.