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Supported Au nanoparticles as efficient catalysts for aerobic homocoupling of phenylboronic acid†

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Au nanoparticles with small sizes (1–4 nm) were effectively formed on Mg–Al mixed oxides (Au/MAO), which showed superior catalytic performances and good recyclability in aerobic homocoupling of phenylboronic acid.

One of the most important discoveries in the field of synthetic organic chemistry is the coupling reactions for the formation of carbon to carbon bonds, because the coupling products of biaryls are widely applied for the production of pharmaceutical and fine chemicals.[1–7] Particularly, homocoupling of phenylboronic acid has been attracting much attention recently.[4–7] Normally, this reaction is catalyzed by Pd^{2+} species.[4] But in recent years, Au catalysts, which are currently a hot topic in catalysis,[5–17] have performed well in homocoupling of phenylboronic acid.[5–8] For example, Corma and co-workers reported that Au^{3+} cations supported on CeO_2 show excellent catalytic performances in homocoupling of phenylboronic acid;[5] Primo and co-workers showed that Au nanoparticles rich in Au^{3+} and Au^+ are effective catalysts for this reaction.[7] In these cases, gold cations are catalytically active sites for the homocouplings.[5–8]

Additionally, Tsukuda and co-workers also reported water-soluble Au nanoparticles as homogeneous-like catalysts exhibiting excellent catalytic properties in the homocoupling of phenylboronic acid.[8] Here, we demonstrate that Au nanoparticles formed on Mg–Al mixed oxides (Au/MAO, molar ratio of Mg/Al of 3) as efficient heterogeneous catalysts are highly active in homocoupling of phenylboronic acid. Importantly, the Au/MAO has excellent recyclability and a new mechanism has been proposed.

The Au/MAO catalyst was prepared by anion-exchange of $AuCl_4^-$, followed by calcination at 400 °C for the formation of Au nanoparticles. In order to completely eliminate Au^+ or Au^{3+} species, the Au/MAO was treated in $NaBH_4$ solution (see ESI†). The Au loading is 0.7 wt% as analyzed by inductively coupled plasma spectroscopy (ICP). Fig. 1 shows typical transmission electron microscopy (TEM) images of Au/MAO, where the Au nanoparticles are highly dispersed on
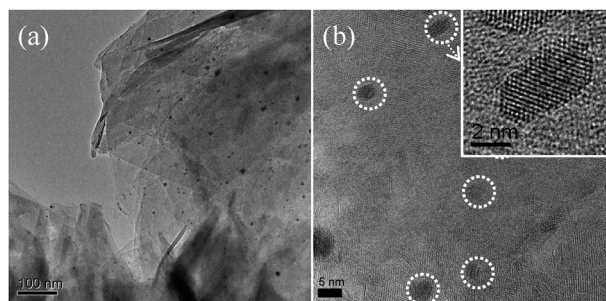
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Fig. 1 TEM images of Au/MAO. Inset: enlarged TEM image.

a MAO support, with narrow size distribution of 1.0–4.0 nm. The high-resolution TEM images of Au nanoparticles show obvious Au lattices, with a lattice spacing of 0.239 nm, associated with {111} Au (Fig. 1b).[9c] These results indicate that the Au species are present as metallic Au nanoparticles on the MAO support. Additionally, in comparison with the XRD patterns of the MAO support, Au/MAO gives additional peaks at 38.7°, 64.7°, and 77.7°, which are associated with (111), (220) and (311) incidences of metallic Au (Fig. S1, ESI†).[15a] The XRD results are in good agreement with the results obtained by TEM, confirming that Au nanoparticles are successfully formed on the MAO support. Fig. 2 shows Au4f XPS spectra of the Au/MAO samples with various treatments. The as-synthesized Au/MAO gives a binding energy of $Au4f_{7/2}$ of 84.5 eV (Fig. 2a), with a shift of 0.5 eV from the typical Au^0 (84.0 eV).[15,16] This shift is reasonably attributed to the interaction between Au nanoparticles and the MAO support.[15,16]
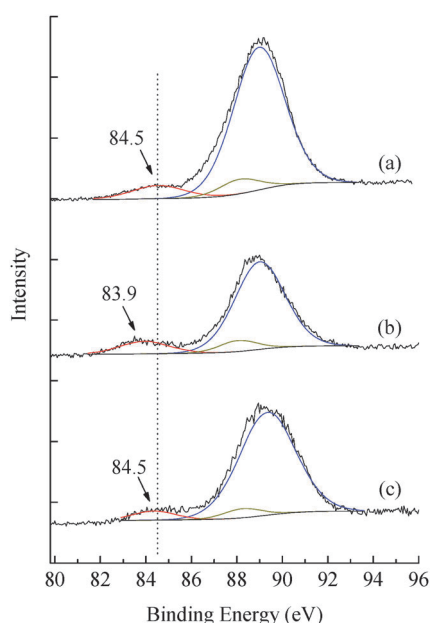
Table 1 presents catalytic activities and selectivities of various Au catalysts in homocoupling of phenylboronic acid. Generally, an inorganic base (*e.g.* K_2CO_3) is necessary to activate the phenylboronic acid.[5–8] However, the Au/MAO catalyst shows very high activities under base-free conditions (Table 1, entries 1–4), and the MAO support is completely inactive in this homocoupling under the same reaction conditions (Table 1, entry 12). For example, Au/MAO gives the conversion of phenylboronic acid higher than 99.5% with diphenyl yields of 88.0–90.0% in MeOH or EtOH solvent (Table 1, entries 1 and 2). These results indicate that the Au/MAO catalyst is very efficient. In addition, the Au/MAO catalyst is very stable, and the Au leaching was negligible in the reaction. For example, after treating Au/MAO in MeOH for 12 h and filtrating the solid catalyst, the Au concentration in the liquor is less than 5 ppb

Fig. 2 Au4f XPS spectra of (a) as-synthesized Au/MAO, (b) Au/MAO treated with phenylboronic acid in the absence of oxygen, (c) after (b), exposure to molecular oxygen.
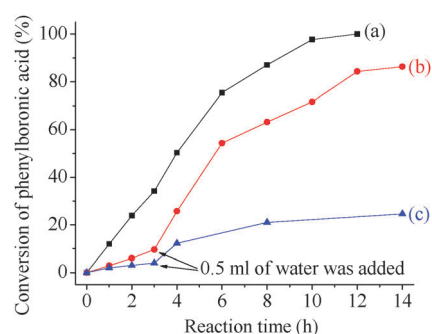
Table 1 Homocoupling of phenylboronic acid on Au catalysts[a]

Entry	Catalyst	Solvent	Yield[b] (%)		Conversion of Ph–B(OH)$_2$[c] (%)
			Ph–Ph	Ph–OH	
1	Au/MAO	MeOH	90.0	10.0	>99.5
2	Au/MAO	EtOH	88.0	12.0	>99.5
3	Au/MAO	Toluene	88.7	6.4	95.1
4	Au/MAO	H$_2$O[d]	53.4	44.6	98.0
5[e]	Au/MAO	MeOH	90.4	9.6	>99.5
6[f]	Au/MAO	MeOH	85.0	12.9	97.9
7[g]	Au/MAO	Deoxidized MeOH	Trace	Trace	<1.0
8	Au/MAO	Anhydrous toluene	22.6	1.6	24.2
9	Au/SiO$_2$	MeOH	2.5	Trace	2.5
10	Au/Al$_2$O$_3$	MeOH	12.3	3.5	15.8
11	Au/TiO$_2$	MeOH	7.0	0.3	7.3
12	MAO	MeOH	—[h]	—[h]	—[h]

[a] Reaction conditions: 1 mmol of phenylboronic acid, 6 mL of solvent, 30 mg of Au catalyst, 1.5 MPa of O$_2$, 100 °C for 12 h, dodecane as internal standard. [b] GC yields. [c] Conversion of Ph–B(OH)$_2$ for the yield of products. [d] The mixture stirred at room temperature for 1 h before reaction. [e] Reused. [f] Recycled 4 times. [g] N$_2$ instead of O$_2$. [h] Undetectable.

by ICP analysis. Very interestingly, after recycling 4 times, the Au/MAO catalyst is still very active, giving the conversion of 97.9% (Table 1, entries 5 and 6). These results indicate that the Au/MAO catalyst has excellent recyclability.

To understand the role of oxygen in the reaction, oxygen was replaced by nitrogen. As a result, no products were detected in the homocoupling (Table 1, entry 7). This result suggests that oxygen is necessary for this reaction. It is worth mentioning that when treated in deoxidized toluene containing phenylboronic acid in the absence of oxygen, the Au/MAO showed an Au4f$_{7/2}$ binding energy of 83.9 eV, with a shift of


Fig. 3 Dependences of catalytic conversion on time in homocoupling of phenylboronic acid over (a) Au/MAO catalyst in toluene solvent, (b) Au/MAO catalyst in anhydrous toluene solvent, (c) Au/MAO catalyst poisoned by triethoxyethylsilane in anhydrous toluene solvent. The reaction conditions were the same as those given in Table 1.

0.6 eV from that of the as-synthesized Au/MAO (Fig. 2b). This shift might be attributed to the interaction between Au nanoparticles and phenylboronic acid such that the boronic acid groups were transmetalated by Au nanoparticles.[17] Interestingly, when molecular oxygen was introduced into the reaction system, the Au/MAO gave an Au4f$_{7/2}$ binding energy of 84.5 eV (Fig. 2c) again. These results confirm that the molecular oxygen should interact with Au nanoparticles.

Notably, there are H$_2$O molecules[18] and hydroxyl groups on the MAO support in the reaction system. To investigate the necessity of H$_2$O molecules for the reaction, catalytic conversion over the Au/MAO catalyst in the presence of anhydrous toluene was tested. As shown in Fig. 3, when the reaction time reached 3 h, the Au/MAO catalyst with anhydrous toluene gave a conversion of 9.6% (Fig. 3b), which is much lower than that (34.1%, Fig. 3a) of the Au/MAO catalyst with conventional toluene. Upon addition of 0.5 mL of water to the reaction system, the high conversion of phenylboronic acid (86.3%) on Au/MAO could be obtained after reaction for 11 h (Fig. 3b). These results suggest that a small amount of water is necessary for the homocoupling. Additionally, the product distribution influenced by H$_2$O molecules in the reaction system was also investigated. In conventional toluene solvent, the molar ratio of biphenyl and phenol in the products was 13.9 (88.7%/6.4%, Table 1, entry 3), which is very similar to the value of 14.1 (22.6%/1.6%, Table 1, entry 8) in anhydrous toluene solvent, suggesting that a small amount of H$_2$O in the reaction system almost does not influence the product distribution. However, when the water solvent was used, the molar ratio of biphenyl and phenol in the products was 1.2 (53.4%/44.6%, Table 1, entry 4), suggesting that a large amount of water strongly influences the phenol selectivity. This phenomenon might be assigned to that more hydroxyls are favorable for the formation of phenols by a side-reaction (step 2, Scheme S2, ESI†). In contrast, when the Au/MAO catalyst was poisoned by triethoxyethylsilane (Scheme S1 and Fig. S2, ESI†) to remove most of the surface hydroxyl groups, it still gave relatively low conversion (24.6%) even if water was introduced and the reaction time was long enough (Fig. 3c). These results suggest that hydroxyl groups on Au/MAO play a critical role in the homocoupling.

Based on the experimental evidence and the suggested mechanism in the literature,[4,5,8,14a,17] we proposed the homocoupling of phenylboronic acid over the Au/MAO catalyst as
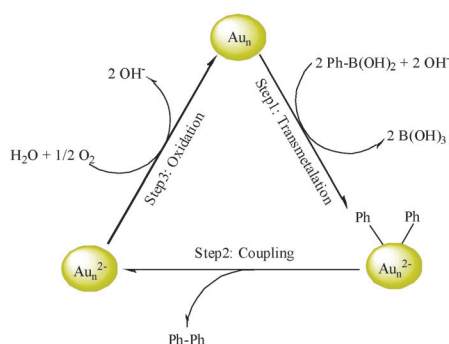
Scheme 1 The proposed new mechanism for aerobic homocoupling of phenylboronic acid over a Au/MAO catalyst.

follows (Scheme 1): (1) the phenylboronic acids should interact with the surface hydroxyl groups of MAO to form boric acid and phenyl species on Au nanoparticles with negative charge (Au_n^{2-}, Au4f XPS in Fig. 2b); (2) the phenyl species on the Au nanoparticles interact with each other to form a biphenyl product, where the homocoupling occurs. However, if the phenyl species on the Au nanoparticles interact with hydroxyl groups, a by-product of phenol would be formed (Scheme S2, ESI†); (3) the negatively charged Au nanoparticles (Au_n^{2-}) formed in step 1 could be oxidized by molecular oxygen in the presence of H_2O, forming the active Au nanoparticles (Fig. 2c, Au_n) and hydroxyls (OH^-). It is mentioned that this mechanism based on the Au/MAO catalyst with only metallic Au^0 is quite different from that involving cationic gold, which was proposed for a Au/CeO_2 catalyst, a system containing cationic Au^{3+} and Au^+ sites, where the reduced Au^+ ions could be oxidized by H^+, forming H_2.[5] When the Au_n^{2-} species return to the active Au_n, the catalytic reaction is recyclable, and the overall homocoupling reaction could be described as follows:

$$2Ph\text{–}B(OH)_2 + H_2O + 1/2O_2 \rightarrow Ph\text{–}Ph + 2B(OH)_3$$
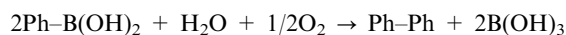
Furthermore, Au nanoparticles formed on SiO_2, Al_2O_3 and TiO_2 with similar Au loadings were prepared, but they show much lower conversions of phenylboronic acid (2.5–15.8%, Table 1, entries 9–11) than Au/MAO, which possibly are due to the difference in Au particle sizes and hydroxyl groups. These works are currently under investigation. Moreover, various substituted phenylboronic acids were employed in the homo-coupling over Au/MAO. As shown in Table S1 (ESI†), the catalyst worked well with different substrates, giving the desired coupling products with high conversion (83.7–99.5%).

In summary, we prepared Au nanoparticles on MAO, which shows high activities and excellent recyclability in aerobic coupling of phenylboronic acid under base-free conditions. Catalytic tests and XPS characterizations show that molecular oxygen, hydroxyls on MAO, and H_2O in a reaction system play important roles in this reaction, therefore a possible mechanism is proposed. Considering the importance of hetero-geneous nanosized Au catalysts and homocouplings, it is expected that this work could have great potential for the production of pharmaceutical and fine chemicals that need further exploration.

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