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## The synergistic effect of nanoporous AuPd alloy catalysts on highly chemoselective 1,4-hydrosilylation of conjugated cyclic enones†

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The nanoporous AuPd (AuPdNPore) alloy catalyst showed superior chemoselectivity and high catalytic activity for the direct 1,4-hydrosilylation of the conjugated cyclic enones with hydrosilane in comparison with the monometallic nanoporous Au and Pd catalysts. The enhanced catalytic properties of AuPdNPore arise mainly from the nanoporous structure and the synergistic effect of the AuPd alloy.

Heterogeneous catalysis is widely used in chemical industrial processes and environmental protection, which overcomes the problems of homogeneous catalysis, and therefore considerable efforts have been made to develop new nanostructured metals as powerful green catalysts.<sup>1</sup> Particularly, among the nanoparticle catalysts, the bimetallic alloy catalysts exhibit enhanced stability, activity, and selectivity in various chemical reactions compared with the monometallic counterparts,<sup>2</sup> which are mainly attributed to ensemble and ligand effects.<sup>2b</sup> Although much progress has been made in the synthesis of such nanoparticulate catalysts, it is still difficult to control their composition, particle size, and geometry simultaneously to attain optimal catalytic performances.<sup>2</sup>

Recently, we and other groups have demonstrated that nanoporous metals having a 3D nanoporous structure are promising green heterogeneous catalysts for various chemical/electrochemical reactions in terms of high catalytic activities, selectivities, and recyclability.<sup>3–7</sup> Importantly, the nanoporous alloys display enhanced electrocatalytic performances and stability in electrochemical reactions compared with the monometallic nanoporous metals owing to the alloy effect.<sup>8</sup> The selective etching of a less noble element from suitable precursor alloys possessing a homogeneous single phase is one of the most efficient routes to fabricate nanoporous metals and alloys with uniform nanoporous structures.<sup>9</sup> However, so far the nanoporous alloy catalysts have never been demonstrated to show such an alloy effect toward the selective organic transformations. Here, we report superior chemoselectivity and high catalytic activity of the nanoporous AuPd alloy (AuPdNPore) catalysts for the direct 1,4-hydrosilylation of conjugated cyclic enones with hydrosilane, which cannot be achieved by using monometallic nanoporous Au (AuNPore) and Pd (PdNPore) catalysts. The 1,4-hydrosilylation of conjugated cyclic enones is one of the direct methods for preparing the synthetically useful intermediates of silyl enol ethers.<sup>10</sup> Although a number of stoichiometric and homogeneous catalytic methodologies have been reported,<sup>11</sup> the catalytic protocol using a reusable heterogeneous catalyst has never been reported to date.<sup>12</sup>

In this study, the AuPdNPore-1 alloy catalyst was fabricated by the selective etching of Al from the Au<sub>20</sub>Pd<sub>10</sub>Al<sub>70</sub> (at%) ternary alloy, which was prepared using a high-frequency induction furnace, using NaOH (20%) as the electrolyte at room temperature for 36 h. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the as-dealloyed AuPdNPore-1 (Fig. 1) catalyst showed a bicontinuous nanoporous structure and the curved metallic ligaments with an average size of ~8 nm. The composition of AuPdNPore-1 was Au<sub>58</sub>Pd<sub>27</sub>Al<sub>15</sub> (at%) determined by energy dispersive X-ray (EDX) analysis. The AuPdNPore-1 catalyst surface area was measured by the BET method to be 28.5 m<sup>2</sup> g<sup>-1</sup>. For comparison, AuPdNPore-2 (Au<sub>75</sub>Pd<sub>16</sub>Al<sub>9</sub>) and AuPdNPore-3 (Au<sub>35</sub>Pd<sub>47</sub>Al<sub>17</sub>) were fabricated using the same dealloying method from the corresponding ternary alloys of Au<sub>25</sub>Pd<sub>5</sub>Al<sub>70</sub> and



Fig. 1 SEM (a) and TEM (b) images of the AuPdNPore-1 catalyst.

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Table 1 Screening of various nanoporous metal catalysts<sup>a</sup>

Ĺ	$\begin{array}{c} 0 \\ \hline \\ + \text{ HSiEt}_3 \\ \hline \\ 100 ^{\circ}\text{C, neat} \\ 1a \\ 4.12 \text{ h} \end{array}$	OSiEt <sub>3</sub> + ( 2a	OSiEt <sub>3</sub> + ( 3a	OSiEt <sub>3</sub>
Entry	Catalyst (precursor alloy)	$2\mathbf{a}^{b}$ (%)	$3a^b$ (%)	) $4a^{b}$ (%)
1	PdNPore-1 (PdAl)	14	0	23
2	PdNPore-2 (PdNiP)	75	0	12
3	AuNPore-1 (AuAl)	56	44	0
4	AuNPore-2 (AuAg)	48	51	0
5	AuPdNPore-1 (Au <sub>20</sub> Pd <sub>10</sub> Al <sub>70</sub> )	92 (89, 87	$r)^{c} = 0$	4
6	AuNPore-1 + PdNPore-1	70	20	6
7	Au <sub>20</sub> Pd <sub>10</sub> Al <sub>70</sub> alloy	0	0	0
8	None	0	0	0
9	AuPdNPore-2 (Au <sub>25</sub> Pd <sub>5</sub> Al <sub>70</sub> )	87	0	5
10	AuPdNPore-3 $(Au_{10}Pd_{20}Al_{70})$	46	0	13
$11^d$	AuPdNPs on TiO <sub>2</sub>	47	6	4

<sup>*a*</sup> Reaction conditions: **1a** (2.0 mmol), HSiEt<sub>3</sub> (2.0 mmol), and nanoporous catalyst (2.5 mol%) at 100 °C without solvents. <sup>*b*</sup> <sup>1</sup>H NMR yields determined using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>*c*</sup> The yields of second (10 h) and third (24 h) uses. <sup>*d*</sup> 1 mol% of the AuPdNPs catalyst was used.

 $Au_{10}Pd_{20}Al_{70}$ , respectively (Fig. S1, ESI<sup>†</sup> for TEM images). The monometallic nanoporous Pd (PdNPore) and Au (AuNPore) catalysts were fabricated following our reported methods.<sup>3</sup>

Initially, we investigated the catalytic activity and selectivity of nanoporous metals and alloys for the 1,4-hydrosilylation of 2-cyclohexene-1one (1a) with triethylsilane at 100 °C (Table 1). The PdNPore-1 prepared from a PdAl alloy and the PdNPore-2 prepared from a PdNiP metallic glass produced the corresponding 1.4-adduct 2a in 14% and 75% yields, respectively, along with the by-product of phenoxysilane (4a) in comparable yields (entries 1 and 2, Scheme S2 in ESI<sup>+</sup>).<sup>3*j*,*k*</sup> The use of AuNPore-1 and AuNPore-2 catalysts, which were prepared from a AuAl alloy and a AuAg alloy, respectively, completely suppressed the formation of 4a, while the 1,2-adduct 3a was obtained as a by-product together with the desired 1,4-adduct 2a (entries 3 and 4). Interestingly, unlike those monometallic nanoporous catalysts, the AuPdNPore-1 alloy catalyst exhibited a high catalytic activity and chemoselectivity for the 1,4-hydrosilylation, affording the 1,4-adduct 2a in 92% <sup>1</sup>H NMR yield and only a small amount of 4a (4%) was obtained without producing the 1,2-adduct 3a (entry 5). It should be noted that the combined catalysts of AuNPore-1 and PdNPore-1 afforded a mixture of 2a, 3a, and 4a (entry 6), implying the remarkable alloy effect of the AuPdNPore-1 catalyst on the selective formation of 2a. It was noted that the reaction did not proceed with the precursor alloy Au<sub>20</sub>Pd<sub>10</sub>Al<sub>70</sub> as a catalyst or without catalysts (entries 7 and 8). We also found that the composition ratio of AuPdNPore alloys influences the catalytic properties. For example, although the AuPdNPore-2 catalyst containing a higher amount of Au atom than Pd atom showed a comparable catalytic performance to AuPdNPore-1, the AuPdNPore-3 catalyst having a lower amount of Au atom than Pd atom showed dramatically decreased catalytic activity and selectivity (entries 9 and 10). The Au-Pd nanoparticles (AuPdNPs) catalyst exhibited low activity and selectivity in the present hydrosilylation, producing 2a as a major product together with 3a and 4a as minor products (entry 11).<sup>13</sup>

The nanoporous skeleton catalyst can be readily recoverable by a simple filtration of the skeleton catalyst from the reaction mixture without cumbersome work-up procedures. The recovered AuPdNPore-1 catalyst was further reused 2 times without a significant decrease of yield and selectivity of **2a** (entry 5). In addition, the inductively coupled plasma (ICP-MS) analysis showed that no detectable Au and Pd atoms were observed from the reaction solution at the ppb level. These results together with the leaching experiments (Scheme S1 in ESI<sup>†</sup>) indicate that no Au and Pd catalysts were leached into the reaction solution and the present hydrosilylation was catalysed by the solid state of AuPdNPore catalysts.

The surface chemistry of the AuPdNPore-1 alloy was investigated using STEM-energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) to understand the alloy effect on chemoselectivity. The STEM-EDS mapping of AuPdNPore-1 did not show detectable surface segregation of Pd, Au, and Al atoms, indicating the uniform distribution of those atoms in the ligaments of the nanoporous alloy (Fig. S2 in ESI<sup>+</sup>). The XPS characterization showed that the binding energy of Pd 3d5/2 for AuPdNPore-1 is 336.2 eV, which is more positively shifted than that of PdNPore-1 (336 eV) (Fig. S3a in ESI<sup>†</sup>). Meanwhile, the binding energy of Au 4f<sub>7/2</sub> for AuPdNPore-1 is 83.9 eV, which is visibly lower than that of AuNPore-1 (84.0 eV) (Fig. S3b in ESI<sup>†</sup>). With regard to the change in binding energy, the negative shift of the Au atom and the positive shift of the Pd atom in AuPdNPore-1 indicate that the charge is transferred from Pd to Au due to the higher electronegativity of Au. According to the catalyst characterization and catalytic properties of AuPdNPore-1, we assumed that the more negative hydride in organosilane preferred to chemisorb on the electron poor Pd atom compared with the PdNPore catalyst and the more positive Si in organosilane chemisorbed on the electron rich Au atom, which eliminated the possibility of the adsorption of hydride on the Au atom, resulting in suppression of the formation of the 1,2-adduct 3a. Moreover, we found that both PdNPore-1 and AuPdNPore-1 were able to catalyse the disproportionation reaction of 1a to give a mixture of phenol and cyclohexanone products in the absence of organosilane (Scheme S4 in ESI<sup>+</sup>). In sharp contrast, high chemoselectivity was achieved for the 1,4-hydrosilvlation of 1a with the AuPdNPore-1 catalyst in the presence of organosilane (Table 1, entry 5). These results strongly support the preferred chemisorption of hydride on the Pd atom in AuPdNPore-1, which sufficiently diminished the formation of the by-product 4a.

On the basis of the catalyst characterization and properties, the proposed mechanism is shown in Scheme 1. The dissociation of  $HSiEt_3$  on the uniformly distributed AuPdNPore-1 catalyst was promoted by the chemisorption of hydride on the Pd atom and Si on the Au atom (Schemes S3 and S4 in ESI†). The high affinity of Si for carbonyl oxygen of **1a**, which chemisorbed on the AuPdNPore catalyst, induced the selective addition of hydride to the  $\beta$ -position of **1a**, affording the desired product **2a**. Although the role of Al is unclear in the present hydrosilylation, we thought that the remaining Al atoms in the AuPdAl alloy catalyst should modify the electronic and



Scheme 1 Proposed mechanism for the selective 1,4-hydrosilylation of 1a.

Table 21.4-Hydrosilylation of various conjugated cyclic enones using theAuPdNPore-1 catalysta,b



<sup>*a*</sup> Reaction conditions: conjugated cyclic enones 1 (2.0 mmol), HSiEt<sub>3</sub> (2.0 mmol), and AuPdNPore-1 (2.5 mol%) at 100 °C without solvents. <sup>*b*</sup> Isolated yields of products 2. <sup>*c*</sup> 3-Methylcyclohex-2-enone was used as a starting substance.

geometric structures of the nanoporous catalyst, but Al itself may not directly incorporate in the catalysis as an active catalyst species as indicated in entries 1–4 in Table 1.

The catalytic properties of AuPdNPore-1 were further examined by the reaction with various conjugated cyclic enones (Table 2). The monomethyl- and dimethyl-substituted cyclohexen-2-ones were compatible with the present heterogeneous catalytic systems, giving the desired silyl ethers in high yields, while both 3-methyl- and 5-methylcyclohex-2-enones produced a mixture of regioisomers **2b** and **2c**. The 1,2-addition by-products **3** have never been observed and only a less than 4% of the phenol silyl ethers **4** were observed in the case of **2a–d**. The cyclopenten-2-one and cyclohepten-2-one also underwent selective **1**,4-hydrosilylation sufficiently, affording the corresponding silyl ethers in good to high yields.

In conclusion, we have demonstrated for the first time that the uniformly distributed nanoporous AuPd alloy catalysts showed a remarkable synergistic effect for the heterogeneous 1,4-hydrosilylation of conjugated cyclic enones with organosilane in comparison with nanoporous monometallic catalysts. The catalytic performances and characterization disclose that the alloy effect of AuPdNPore plays a crucial role in the reaction efficiency and product selectivity. Further investigation of the underlying mechanism and application to new synthetic methodologies are in progress.

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