

# Identity of the active site in gold nanoparticle-catalyzed Sonogashira coupling of phenylacetylene and iodobenzene

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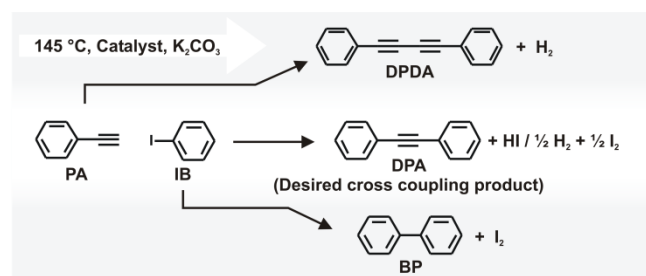
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## ABSTRACT

XPS, TEM and reaction studies were used to examine the catalytic behavior of gold species deposited on lanthana towards the cross-coupling of phenylacetylene and iodobenzene. Atomically dispersed Au<sup>I</sup> and Au<sup>III</sup> were catalytically inert, whereas metallic Au<sup>0</sup> nanoparticles were both active and very selective. Thus it is metallic gold and not ionic gold that provides the catalytically active sites. Au<sup>0</sup> nanoparticles supported on silica,  $\gamma$ -alumina and BaO were active but relatively unselective; however, as with lanthana, ceria-supported Au<sup>0</sup> nanoparticles showed high selectivity. This strong promoting effect of the lanthanide oxide supports on Sonogashira selectivity cannot be accounted for in terms of acid/base, redox or SMSI effects; it may be tentatively ascribed to metal  $\rightarrow$  support hydrogen spillover.

Metal-catalyzed coupling reactions that result in formation of new C-C bonds are strategically important in organic synthesis and metal nanoparticles suspended in solution are often used to provide the catalytic agent.<sup>1-4</sup> Sonogashira coupling is an important example of such chemistry, a prototypical case being the cross-coupling of phenylacetylene with iodobenzene (Scheme 1). When catalyzed by silica-supported Au nanoparticles, detailed evaluation of reaction data and quantitative analysis of the solid and solution phases by XPS and ICP-MS, respectively, led to the conclusion that the reaction was overwhelmingly a heterogeneous process with Au(0) metal clusters providing the active sites.<sup>5</sup> This view was also consistent with the pronounced metal particle size effects that were observed<sup>5</sup> and with the results of recent single crystal observations of the same reaction carried out on an extended Au(111) surface.<sup>6</sup>

**Scheme 1** Coupling reactions of iodobenzene and phenylacetylene to yield both the desired Sonogashira cross-coupling product diphenylacetylene (DPA) and the two homo-coupling side products diphenyldiacetylene and biphenyl.



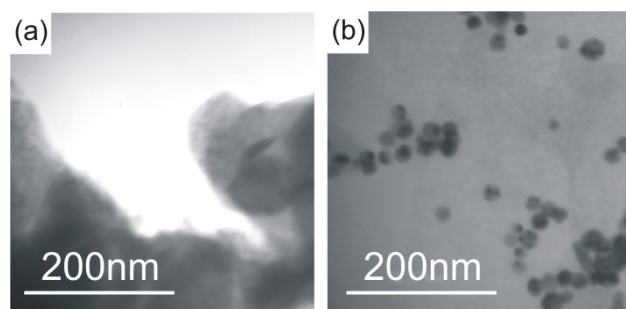
Recently Gonzalez-Arellano *et al.* reported on a new type of gold-ceria nanomaterial that was highly selective as a heterogeneous catalyst for this same reaction, which they attributed to the ability of nanocrystalline ceria to stabilize a small

amount of the gold as Au<sup>I</sup> although Au<sup>0</sup> and Au<sup>III</sup> were the predominant components of the solid catalyst.<sup>7</sup> Their conclusion was based on a comparison of the catalytic behaviour of their Au/ceria material with that of three Au-containing Schiff base complexes that were used as reference homogeneous catalysts. It was found that only the Au<sup>I</sup> complex was an effective homogeneous catalyst, leading to the view that the active agent in the Au/ceria catalyst was Au<sup>I</sup>. (In passing we note that the homogeneous catalysis reference data reported by Gonzalez-Arellano *et al.* have been brought into question because traces of soluble Pd species may actually have been the active agent.<sup>8</sup>) Clearly, this stands in contrast with our recent proposal, as described above.<sup>5</sup> However, our Au/silica catalysts were substantially less selective than the gold-ceria nanomaterial used by Gonzalez-Arellano *et al.*<sup>7</sup> Accordingly, we set out to examine the apparent contradictions regarding the identity of the active site in gold-catalyzed heterogeneous Sonogashira coupling and to investigate the related issue of whether or not rare earth oxide supports do induce higher selectivity. We are led to the conclusion that in all the cases reported here metallic Au<sup>0</sup> nanoparticles are indeed the active agent whereas immobilized Au<sup>I</sup> is not. However, consistent with the results of Gonzalez-Arellano *et al.*, it is found that rare earth oxide supports strongly promote selectivity towards cross-coupling compared to neutral, acidic and basic support materials.

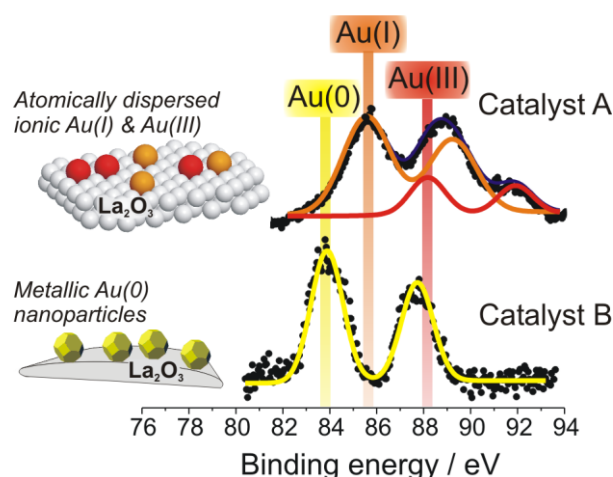
An unambiguous test as to whether gold species in higher oxidation states and immobilized on metal oxides are active Sonogashira catalysts is made possible by the recent discovery by Goguet *et al.* who showed that it is possible to prepare a gold-on-lanthana material in which the metal is present only in the Au<sup>I</sup> and Au<sup>III</sup> oxidation states.<sup>9</sup> On the basis of XANES, XPS, TEM and ISS measurements, these authors concluded that the ionic gold was present as monatomic entities as opposed to multi-atom clusters, and, most importantly for present purposes, *no Au(0) was detectable*. We therefore synthesized this lanthana-based material following a modification of the procedure described by Goguet *et al.*, hereafter designated Catalyst A, and evaluated it for Sonogashira coupling of iodobenzene and phenylacetylene (Scheme 1). For purposes of comparison, using a seeded growth procedure we synthesized Catalyst B, which consisted of ~ 20 nm Au particles with a narrow size dispersion supported on lanthana.

Figure 1 shows the respective morphologies from which it is apparent that whereas the ~ 20 nm Au particles in catalyst B are clearly visible, images of catalyst A were indistinguishable from those of oxide support alone, in good agreement Goguet *et al.*<sup>9</sup> who concluded that Au/La<sub>2</sub>O<sub>3</sub> prepared in this way contained only atomically dispersed gold species. Figure 2 shows the corresponding Au 4f XP spectra. It is clear that Catalyst A contained Au<sup>I</sup> as a majority species and Au<sup>III</sup> as a minority species (Au 4f<sub>7/2</sub> peaks centered at 85.6 and 88.1 eV respectively<sup>10</sup>) *with no detectable Au<sup>0</sup>*. On the other hand, Catalyst B contained only

metallic Au<sup>0</sup> (Au 4f<sub>7/2</sub> peak centered at 83.8 eV<sup>10</sup>), and no detectable ionic gold. Note that the observed binding energy shifts between Catalyst A and Catalyst B (1.8 and 4.3 eV) are substantially greater than the 0.6 – 1.0 eV values typical of metal particle quantum size effects<sup>11,12</sup> and can therefore be reliably ascribed to changes in Au oxidation state. Moreover, the two components in the Au 4f XP spectra of Catalyst A are separated by 2.5 eV, in excellent agreement with reference spectra of Au(I) and Au(III) molecular compounds, which are also separated by 2.5 eV.<sup>10</sup>



**Figure 1.** Representative TEM images of La<sub>2</sub>O<sub>3</sub> supported gold catalysts: (a) Catalyst A containing finely dispersed / mononuclear gold, invisible to TEM, immobilized on a La<sub>2</sub>O<sub>3</sub> support (b) Catalyst B containing 20 nm gold particles (dark features) deposited on a La<sub>2</sub>O<sub>3</sub> support.



**Figure 2.** Au 4f XP Spectra for Catalysts A (top) and B (bottom) showing the different oxidation states of gold present and corresponding to the morphologies shown in the illustration (left).

**Table 1.** Results of catalytic testing of the two Au/La<sub>2</sub>O<sub>3</sub> Catalysts A and B (160 h at 145 °C, 0.5 mmol of IB and PA; 30 mg catalyst; 0.3 mmol base). Also shown for comparison are previously reported results for Au/SiO<sub>2</sub> Catalyst C.<sup>5</sup>

	Selectivity to DPA <sup>[a]</sup>	Final Yield of DPA /mmol	TON <sup>[b]</sup> Molecules of reactant per surface Au atom
<b>Catalyst A</b> Dispersed Au (0.5 wt %)/ La <sub>2</sub> O <sub>3</sub>	Undetectable	Undetectable	<< 10 <sup>[c]</sup>
<b>Catalyst B</b> 20 nm Au (10 wt %)/ La <sub>2</sub> O <sub>3</sub>	82%	0.40	275
<b>Catalyst C</b> <sup>[c]</sup> 20 nm Au (10 wt %)/ SiO <sub>2</sub>	38 %	0.16	158

<sup>[a]</sup> Selectivity is defined as 100% x concentration DPA / concentration of (DPA + BP + DPDA). <sup>[b]</sup> Estimated in number of IB molecules consumed per surface gold atom calculated as described in the supporting information. <sup>[c]</sup> Quoted upper limit based on detection sensitivity. Actual TON likely to be much lower.

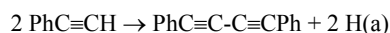
Table 1 summarizes the results obtained with Catalysts A and B after 160 h of reaction carried out at 145 °C in DMF solvent; also shown and for comparison purposes are data reported previously for Catalyst C, a Au/SiO<sub>2</sub> material prepared using exactly the same method as for the Au/La<sub>2</sub>O<sub>3</sub> catalyst B. To enable a direct comparison to be made between Catalysts A,B,C the corresponding turnover numbers (TONs) are shown, calculated on a per surface gold atom basis as explained in the supporting information. It can be seen (Column 4) that Catalyst A, which contained only ionic gold, is *at least* 100 times less active, and possibly *much* less active, towards Sonogashira coupling than the Au<sup>0</sup> nanoparticles present in Catalyst B, which contained no ionic gold. These results amount to very strong evidence that (i) lanthana-stabilized Au<sup>I</sup> species (and indeed Au<sup>III</sup> species) are not the active site whereas (ii) oxide-supported metallic Au nanoparticles are responsible for the observed catalysis. It thus appears that Au<sup>I</sup> immobilized on lanthana does not behave in an analogous way to Au<sup>I</sup> complexes in solution, if the latter are indeed effective for Sonogashira coupling.<sup>7</sup> Notice also the much higher selectivity of La<sub>2</sub>O<sub>3</sub> supported Au nanoparticles (Catalyst B) compared to the silica-supported case (Catalyst C). Interestingly, this effect of a rare earth oxide support in promoting Sonogashira selectivity is consistent with the observations of Gonzalez-Arellano *et al.* who reported 89% selectivity for their Au/nanocrystalline ceria catalyst.<sup>7</sup> We confirmed this selectivity-promoting effect of CeO<sub>2</sub> by preparing and testing Catalyst D using Au impregnated onto ceria,<sup>13</sup> which is a low surface area material. Although the resulting conversion was substantially lower than that achieved by Gonzalez-Arellano *et al.* with their nanocrystalline ceria (15% after 160 h reaction), this likely reflects the much lower active metal area in our case (the ceria surface area was <1 m<sup>2</sup>/g compared to 20 m<sup>2</sup>/g for the La<sub>2</sub>O<sub>3</sub>; see also TEM data in supporting information). The important point is that we too obtained > 85% cross-coupling selectivity, in accord with their findings.

It therefore seems plausible that La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> act in a similar way to enhance selectivity in Au-catalyzed Sonogashira coupling by a mechanism that is not accessible when silica is used as the support. Related to this, it is significant that while Au supported on both lanthana and ceria catalyzed the homocoupling of phenylacetylene to diphenyldiacetylene (DPDA Scheme 1) silica-supported Au did not. Note that both DPDA formation and Sonogashira cross-coupling formally require removal of the acidic hydrogen atom on phenylacetylene. Therefore, in order to examine whether this behavior correlates with the basicity of the support, we synthesized and tested catalysts (see supporting information) consisting of gold supported on a strongly basic support (BaO) and an acidic support (γ-Al<sub>2</sub>O<sub>3</sub>): both gave much lower selectivities, comparable to Au/SiO<sub>2</sub>, and, as with silica, neither produced DPDA. Thus no correlation exists between Sonogashira selectivity (and DPDA formation) and the basicity of the support materials, which falls in the order BaO > CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> > TiO<sub>2</sub>, SiO<sub>2</sub> > γ-Al<sub>2</sub>O<sub>3</sub>.<sup>14,15</sup>

Another possible cause for the exceptional behavior of ceria and lanthana relative to the other supports could be the intervention of redox chemistry, relatively facile in the case of CeO<sub>2</sub>, much less so in the case of La<sub>2</sub>O<sub>3</sub>.<sup>16</sup> Post-reaction XPS of the ceria and lanthana-supported catalysts showed no evidence of

oxide reduction in either case (see supporting information). Given the results of Behm and co-workers<sup>17</sup> who found that Ce<sup>3+</sup> species in partially reduced Au/ceria catalysts survived *ex situ* transfer from reactor to spectrometer, we may tentatively conclude that effects due to oxygen vacancies were not responsible for the observed catalytic behaviour of Au/CeO<sub>2</sub> and Au/La<sub>2</sub>O<sub>3</sub>. Although Au/ceria catalysts can exhibit strong metal support interaction (SMSI),<sup>18</sup> the absence of a high temperature reduction step<sup>19</sup> during the preparation of our catalysts would appear to rule out any such effects as an explanation for Sonogashira selectivity enhancement.

Finally, however, we note that both Sonogashira cross-coupling and phenylacetylene homocoupling may formally be considered to produce hydrogen as product (on a metal surface HI is thermodynamically disfavored relative to  $\frac{1}{2}$  H<sub>2</sub> +  $\frac{1}{2}$  I<sub>2</sub>).<sup>6</sup> Consistent with this, the characteristic orange-brown color of the iodine co-product was observed in every case. Thus:



Additionally, it is known that both ceria- and lanthana-supported catalysts exhibit metal → support hydrogen spillover effects even at room temperature.<sup>20-22</sup> One may therefore speculate that scavenging of hydrogen from the gold by the support acts to promote the above two reactions, but not the homocoupling of iodobenzene to produce biphenyl, in accord with observation.

In summary, the performance of Au/lanthana catalysts, prepared so as to contain to either Au<sup>0</sup> nanoparticles or Au<sup>I</sup> and Au<sup>III</sup>, indicates that it is metallic gold that provides the catalytically active sites. When supported on CeO<sub>2</sub> or La<sub>2</sub>O<sub>3</sub> the Au nanoparticles exhibit strongly enhanced selectivity towards Sonogashira coupling. This behavior cannot be accounted for in terms of redox, acid/base or SMSI effects; it may instead be tentatively ascribed to metal → support hydrogen spillover.

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**Supporting Information Available:** Experimental details of synthesis, catalytic testing and characterization techniques; Additional catalytic data; Ce and La 3d XP Spectra; Representative TEM of Au/CeO<sub>2</sub> Catalyst D.

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