

# Strong Metal–Support Interactions between Gold Nanoparticles and Nonoxides

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## Supporting Information

**ABSTRACT:** The strong metal–support interaction (SMSI) is of great importance for supported catalysts in heterogeneous catalysis. We report the first example of SMSI between Au nanoparticles (NPs) and hydroxyapatite (HAP), a nonoxide. The reversible encapsulation of Au NPs by HAP support, electron transfer, and changes in CO adsorption are identical to the classic SMSI except that the SMSI of Au/HAP occurred under oxidative condition; the opposite condition for the classical SMSI. The SMSI of Au/HAP not only enhanced the sintering resistance of Au NPs upon calcination but also improved their selectivity and reusability in liquid-phase reaction. It was found that the SMSI between Au and HAP is general and could be extended to other phosphate-supported Au systems such as Au/LaPO<sub>4</sub>. This new discovery may open a new way to design and develop highly stable supported Au catalysts with controllable activity and selectivity.

Metal nanoparticles (NPs) dispersed on high-surface-area support materials are one of the most important classes of heterogeneous catalysts and are widely employed in the chemical industry and environmental protection.<sup>1</sup> The interactions between metals and supports, i.e., metal–support interactions, are of great importance in determining their catalytic performance.<sup>1b,2</sup> Specially, the strong metal–support interaction (SMSI) was first coined by Tauster et al. to explain the phenomenon that the adsorption of H<sub>2</sub> and CO was dramatically suppressed on TiO<sub>2</sub>-supported VIII group metals after high-temperature reduction in H<sub>2</sub>.<sup>3</sup> Since then the studies on SMSI have been performed extensively, and the understanding of them has been developed continually. The support was expanded to many other transition-metal oxides (TiO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, etc.) which are easily reduced,<sup>4</sup> and the encapsulation of metals by supports was clearly observed.<sup>5</sup> It has now been realized that two major factors, i.e., the electronic and geometric, contribute to the SMSI state.<sup>6</sup> The formation of SMSI was found to significantly alter the catalytic properties.<sup>6b</sup> On the basis of these developments, reaction mechanisms could be identified,<sup>7</sup> and new catalysts with high activity were developed.<sup>7a,8</sup> Therefore, any new findings or new understanding of SMSI may have significant influence on

supported catalysts and may further lead to an innovation in catalyst development and application.

In the past decades, supported Au catalysts have drawn extensive and ever increasing attention due to their unique catalytic performance for numerous types of important chemical reactions.<sup>9</sup> However, the practical application of supported Au catalysts faces great challenges, and one of the major issues is the poor stability of Au NPs which tend to sinter easily under reaction and lose their activities.<sup>10</sup> Thus, it is of great importance to develop stable Au catalysts.<sup>11</sup> Development of supported Au catalyst with SMSI is obviously helpful to stabilize the Au NPs on support. However, it has long been considered that Au cannot manifest SMSI behavior due to its lower work function and surface energy.<sup>12</sup> Recently, it was, for the first time, found that Au NPs supported on ZnO nanorods could form SMSI, providing a new way to control the interaction between Au and the support as well as catalytic activity, although the origin of this SMSI is still unclear.<sup>13</sup> Here we report the SMSI between Au NPs and hydroxyapatite (HAP), a phosphate rather than an oxide. Further study shows that this phenomenon is general, and the support could be extended to other phosphates such as LaPO<sub>4</sub>. This is the first time to discover that SMSI could be formed between metal NPs and nonoxide supports. This discovery not only explains the excellent stability and strong antisintering property of the Au catalysts in previous reports<sup>11b,14</sup> but also provides a new way to fabricate highly stable Au catalysts with controllable catalytic performance.

The HAP was synthesized by a chemical precipitation method and further calcined at 400 °C.<sup>11b,15</sup> The Au precursor species was introduced on the HAP by a deposition–precipitation method<sup>11b,16</sup> with an actual Au loading of 2.8 wt % and calcined at various temperatures from 200 to 600 °C in air for 3 h, denoted as Au/H-X (H: HAP; X: the calcination temperature). The catalyst without calcination was also heated under N<sub>2</sub> flow at 500 °C for 3 h and denoted as Au/H-500N. For comparison, the Au/H-500 catalyst was further reduced under H<sub>2</sub> gas at 500 °C for 2 h and denoted as Au/H-500-H<sub>2</sub>. Details of the synthesis procedures of HAP and Au/H catalysts are presented in the Supporting Information (SI).

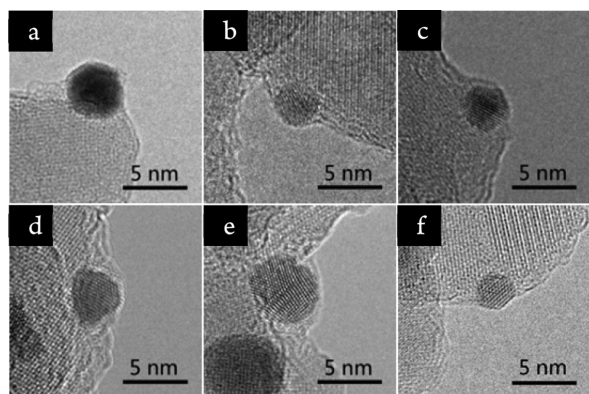
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As shown in Figure S1, besides the HAP patterns, diffuse diffraction peaks of Au (111), located at  $2\theta = 38.2^\circ$ , are observed for all samples (Figure S1b). Interestingly, it clearly shows that the diffraction peaks of Au (111) for Au/H-200 and Au/H-600 are more pronounced than that of the other catalysts, suggesting that the Au NPs on these two samples are bigger. It is not surprising that Au/H-600 catalyst has larger Au NPs, as this catalyst had been calcined at temperature as high as 600 °C. However, it is difficult to understand that Au/H-200 catalyst has larger Au NPs than Au/H catalysts calcined at higher temperatures (i.e., 300, 400, and 500 °C) since it is generally believed that higher-temperature calcination would result in larger Au NPs.

To confirm this unusual phenomenon derived from XRD results, we further examined the samples by transmission electron microscopy (TEM). The representative images and corresponding size distribution of Au NPs are presented in Figure S2. It shows clearly that the mean size of Au/H-200, 3.6 nm, is similar to that of Au/H-600 sample (~3.7 nm) while much larger than that of Au/H-300–500 catalysts with mean size of 2.6, 2.9, and 3.0 nm, respectively, although it contains a small amount of very tiny Au clusters which were not found in other samples (Figure S3). The TEM results are consistent with the XRD results, confirming the unusual size distribution of Au NPs on the series Au/H catalysts.

To figure out how the unusual situation occurred, high-resolution transmission electron microscopy (HRTEM) was further employed to examine the samples. The typical images are presented in Figure 1. To our surprise, it shows that the Au NPs

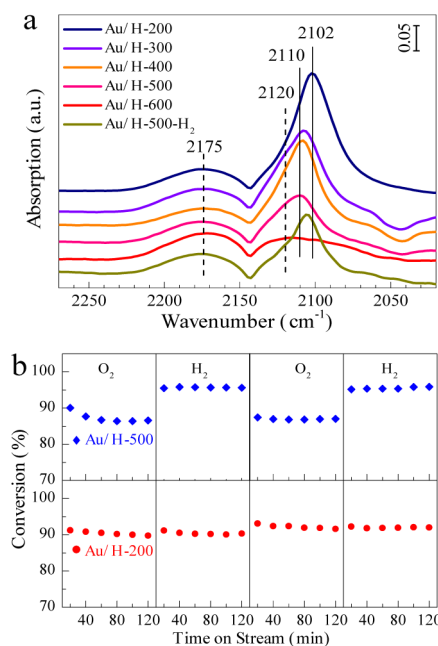


**Figure 1.** HRTEM images of (a) Au/H-200, (b) Au/H-300, (c) Au/H-400, (d) Au/H-500, (e) Au/H-600, and (f) Au/H-500-H<sub>2</sub>.

on all samples are covered by a thin layer except that on the Au/H-200 sample. In addition, the coverage is different and closely depends on the calcination temperature. The surface of Au NPs would not be covered by the thin layer until the calcination temperature  $\geq 300$  °C, and the coverage increased gradually as the calcination temperature increased to 600 °C, where the Au NPs are almost completely covered (Figure 1e). To recognize the composition of the cover layer, selected sample Au/H-600 was further examined by electron energy loss spectroscopy. The result presented in Figure S4 shows that this layer composed of P, suggesting that the coating layer originated from the HAP support. It is most likely due to the migration of HAP onto the surfaces of the Au NPs during calcination.

The encapsulation of metal by support layer in oxide supported metal catalysts is a typical characteristic of SMSI phenomenon. Therefore, the (partial) cover of Au NPs by HAP

layer might imply the formation of SMSI in our Au/HAP catalysts. The SMSI usually results in the suppression of adsorption of small molecules such as CO and H<sub>2</sub> along with the electron transfer between metal and support. The suppression of adsorption is generally regarded as a result of the physical coverage of adsorption sites by the support layer. To detect whether there is any adsorption change and/or electron transfer, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements of CO adsorption were performed. This technique is sensitive to both adsorption and electronic property of a metal surface with suitable probe molecule.<sup>18</sup> As shown in Figure 2a, two bands are detected on the



**Figure 2.** (a) *In situ* DRIFT spectra of CO adsorption on Au/H-X and Au/H-500-H<sub>2</sub>. (b) CO conversions with time on stream at 100 °C on Au/HAP-500 and Au/H-200 with alternative treatment of O<sub>2</sub> and H<sub>2</sub> flow; 40 mg and 50 mg catalysts were used for Au/H-200 and Au/H-500, respectively. Gas flow: 1 vol % CO + 1 vol % O<sub>2</sub> balanced with He, 33.3 mL min<sup>-1</sup>.

Au/H-200 at 2175 and 2102 cm<sup>-1</sup>. The former is attributed to gaseous CO rather than CO adsorption on Au<sup>+</sup> because it decreased rapidly in intensity and disappeared completely under purge with He, Figure S5, which is in contrast to the CO adsorption on Au<sup>+</sup> (CO-Au<sup>+</sup>).<sup>19</sup> The later attributed to CO adsorbed on metallic Au (CO-Au<sup>0</sup>).<sup>20</sup> As the calcination temperature increased, the 2102 cm<sup>-1</sup> band is blue-shifted gradually to 2010 cm<sup>-1</sup> accompanied by a gradual decrease in intensity. The blue-shift of CO adsorption band is an indicator of positively charged surface Au species,<sup>21</sup> implying an electron transfer from Au NPs to HAP support. The intensity decrease can be ascribed to the lower CO coverage mainly caused by the gradual encapsulation of Au NPs by HAP rather than the size increase of Au NPs since the mean size of Au NPs is only slightly increased for Au/H-300–600 (2.6–3.7 nm, Figure S2). This conclusion is further confirmed by the fact that the intensity of the CO-Au<sup>0</sup> band of Au/H-500N on which no encapsulation was observed is far stronger than that of Au/H-500 (Figure S6), although the Au NP size is slightly larger (3.4 nm, Figure S7). Specially, for the Au/H-600 catalyst, no CO adsorption band was detected except the gaseous CO bands (2175 and 2120 cm<sup>-1</sup>), in

agreement with the HRTEM result that Au NPs were almost completely covered (Figure 1e).

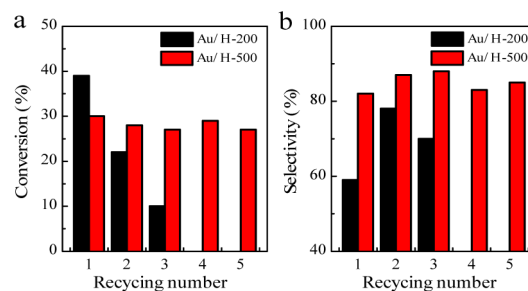
Another feature of SMSI is that the encapsulation of metal is reversible under opposite treatment condition. To verify whether the encapsulation of Au NPs in our case is reversible, we treated the Au/H-500 sample under pure H<sub>2</sub> at 500 °C for 2 h. The HRTEM image (Figure 1f) shows that the coating layer retreated completely. Also, the DRIFT spectrum shows that the CO adsorption band is red-shifted to 2105 cm<sup>-1</sup> accompanied by an obvious increase in intensity, Figure 2a. The red-shift of the band indicates a weakened electron transfer. The intensity increase is a result of the increase of exposed Au surface. The change of surface adsorption sites usually results in the change of activity since these surface adsorption sites are generally the active sites.<sup>13</sup> To confirm this, we further tested the CO oxidation on both Au/H-200 and Au/H-500 with alternative O<sub>2</sub> and H<sub>2</sub> treatments. As shown in Figure 2b, Au/H-500 sample shows an obvious treatment-dependent activity with O<sub>2</sub> and H<sub>2</sub>. Under O<sub>2</sub> treatment, the activity is lower than that under H<sub>2</sub> treatment, consistent with the HRTEM and DRIFT results that O<sub>2</sub> treatment causes encapsulation of Au, while H<sub>2</sub> treatment recovers the original Au surface. On the other hand, the Au/H-200 sample is not sensitive to the treatment conditions with almost identical CO conversion under the redox treatment cycle. This is expected since there is no encapsulation of Au NPs as suggested by the HRTEM and DRIFT examinations (Figures 1a and 2a).

The above results indicate clearly that the HAP-supported Au catalyst involves two reversible progresses under gas treatments, i.e., the encapsulation of Au NPs by a support layer under oxidative gas atmosphere and a retreat of the layer under reductive gas atmosphere along with the electron transfer between Au and HAP. These observations fit the classical description of SMSI on reducible oxides supported Pt-group metal catalysts, except that the mass transport takes place under oxidative condition and retreats under reductive condition; the opposite conditions needed for the classical SMSI, as shown in Table S1.<sup>3,5,22</sup> It also differed from the Au/ZnO system where SMSI occurred in both oxidative and reductive treatment conditions.<sup>13</sup>

It is important to note that the SMSI between Au and HAP which involves the encapsulation of Au NPs by HAP would suppress the growth of Au NPs effectively, as the mean sizes of Au NPs on Au/H-300-600 are very small. The effect of SMSI and Au NPs size was further investigated by using CO oxidation as probe reaction. As shown in Figure S8, for the Au/H-300-600, with the calcination temperature increasing, the catalytic activity decreased gradually which may be mainly ascribed to the decrease of active Au sites caused by the gradual encapsulation of Au NPs by HAP rather than by the change in size of Au NPs. This conjecture was further proved by the increased activity of the Au/H-500-H<sub>2</sub> with larger, uncovered Au NPs. In this regard, the encapsulation of Au NPs by HAP is considered to have a detrimental effect on catalytic activity. However, the catalytic activity of Au/H-200 on which Au NPs are uncovered is significantly lower than that of Au/H-300 and Au/H-400 with partially covered Au NPs. The lower activity is clearly due to the relatively larger Au NPs. The activity test results suggested that although the formation of SMSI could be helpful to stabilize Au NPs against sintering at elevated temperatures, the over encapsulation of Au NPs would also deactivate the catalysts by covering the active sites. It is therefore necessary to find out the appropriate state of the SMSI for special reactions to obtain

stable Au catalysts with high activity. On the other hand, the change of coverage extent also provides a potential way to tune the catalytic performance, for both activity and selectivity.<sup>23</sup> Nonoxide generally could not provide the active site for O<sub>2</sub> activation. In our previous work,<sup>24</sup> a competitive Langmuir–Hinshelwood (L-H) mechanism that both CO and O<sub>2</sub> were activated on Au over Au/HAP catalyst had been confirmed. However, recently Dai et al. proved the coexistence of redox mechanism and L-H mechanism on a FePO<sub>4</sub> supported Au catalyst.<sup>25</sup> Considering that HAP is a type of phosphate, the redox mechanism might also occur partially on our Au/HAP.

Besides the benefit of being able to enhance the sintering resistance of metal NPs and to adjust the catalytic performance, the formation of SMSI, i.e., the (partial) encapsulation of metal NPs might have another potential advantage in application in heterogeneous liquid-phase reactions.<sup>26</sup> When supported metal catalysts are used in liquid-phase reactions, the active metal species might be leached into the liquid-phase which would not only deactivate the catalysts but also cause the contamination of the products.<sup>27</sup> Furthermore, the leaching of metal species into liquid-phase may also change the reaction selectivity since the sizes, and probably the shapes, of the original metal NPs can be significantly modified due to leaching. The encapsulation of metal NPs, however, may restrain the leaching of metal into liquid-phase. To verify this, we tested the recycle performance of Au/H-200 and Au/H-500 in solvent-free selective oxidation of benzyl alcohol. This reaction is important for both fundamental study and commercial application,<sup>28</sup> and Au catalysts were found to be promising with high activity and selectivity.<sup>29</sup> As shown in Figure 3, the Au/H-200 generated ~40% benzyl alcohol



**Figure 3.** (a) Conversion and (b) selectivity of benzyl alcohol over Au/H-200 and Au/H-500. Reaction conditions: 50 mg catalyst, 1.5 g benzyl alcohol,  $P_{O_2} = 1$  MPa, 150 °C, 7 h.

conversion with ~60% benzaldehyde selectivity in the first cycle. However, the conversion decreased dramatically in the second and third cycles, suggesting a serious deactivation. The changes in selectivity may suggest the modification of the active sites in different cycles. The analysis of the used catalyst shows that the loading of Au decreased from 2.8 to 2.3 wt % and the Au NPs sintered seriously. In contrast, the Au/H-500 shows a relative low conversion (30%) but much higher selectivity (~85%) in the first cycle, possibly due to the coverage of active site by the support. However, both conversion and selectivity remain almost unchanged for five cycles, suggesting a much better reusability. The Au loading after 5 cycles is still 2.8%, suggesting that, as expected, there was no detectable Au loss during the reaction cycles.

The above results unambiguously demonstrated the occurrence of SMSI between Au NPs and HAP support. Since HAP is a phosphate we hypothesized that the observed phenomenon is

probably general and could be extended to other phosphate supports. We therefore synthesized a  $\text{LaPO}_4^{30}$  and prepared a Au/ $\text{LaPO}_4$ -500 catalyst (XRD patterns, TEM images shown in Figure S9), which was proved to be sintering resistant.<sup>14a</sup> The HRTEM images in Figure S10 show that the Au NPs are encapsulated by a support layer, similar to that of Au/HAP. The DRIFT spectra of CO adsorption, Figure S11, suggest that both encapsulation and the electron transfer are reversible under  $\text{O}_2$  and  $\text{H}_2$  treatments, suggesting a similar SMSI to that of the Au/HAP system. The origination and mechanism of this SMSI are not clear at present. We believe the underlying reason, and the nature driving force, is to minimize the surface energy, and this process is related to the  $\text{PO}_4^{3-}$  species since the change of cation did not affect the occurrence of SMSI. However, a detailed mechanism needs further investigation.

In summary, we have discovered that the SMSI between Au and HAP took place under oxidative conditions. We found that the Au NPs were encapsulated by the HAP and the degree of encapsulation depended on the calcination temperature. The encapsulation of Au NPs not only enhanced their sintering resistance upon high-temperature calcination but also significantly improved their reusability in liquid-phase catalysis. Furthermore, it was found that this SMSI is general and could be extended to other phosphate-supported Au catalysts such as Au/ $\text{LaPO}_4$ . To our knowledge, this is the first time to report that SMSI occurs between metal and nonoxide supports. Considering the wide variety of phosphates and the structural designability of HAP, this new finding may provide a new way to design and develop highly stable supported Au catalysts with controllable activity and selectivity.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11306.

Experimental details and data (PDF)

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### Notes

The authors declare no competing financial interest.

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