

Unsupported Nanoporous Gold Catalyst for Chemoselective Hydrogenation Reactions under Low Pressure: Effect of Residual Silver on the Reaction

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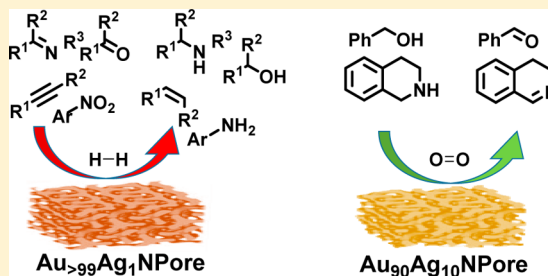
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Supporting Information

ABSTRACT: For the first time, H–H dissociation on an unsupported nanoporous gold (AuNPore) surface is reported for chemoselective hydrogenation of C≡C, C=C, C=N, and C=O bonds under mild conditions (8 atm H₂ pressure, 90 °C). Silver doping in AuNPore, which was inevitable for its preparation through a process of dealloying of Au–Ag alloy, exhibited a remarkable difference in catalytic activity between two catalysts, Au_{>99}Ag₁NPore and Au₉₀Ag₁₀NPore. The former was more active and the latter less active in H₂ hydrogenation, while the reverse tendency was observed for O₂ oxidation. This marked contrast between H₂ reduction and O₂ oxidation is discussed. Further, Au_{>99}Ag₁NPore showed a high chemoselectivity toward reduction of terminal alkynes in the presence of internal alkynes which was not achieved using supported gold nanoparticle catalysts and other previously known methods. Reductive amination, which has great significance in synthesis of amines due to its atom-economical nature, was also realized using Au_{>99}Ag₁NPore, and the Au_{>99}Ag₁NPore/H₂ system showed a preference for the reduction of aldehydes in the presence of imines. In addition to this high chemoselectivity, easy recovery and high reusability of AuNPore make it a promising heterogeneous catalyst for hydrogenation reactions.



INTRODUCTION

Bulk gold is known to be inactive for chemisorption of gases, but pioneering work by Haruta revealed that nanosized gold (particle size <10 nm) possessed extraordinary catalytic activity for low-temperature CO oxidation.¹ Since then, gold has been widely used for a variety of reactions.² Compared to reduction reactions, oxidation reactions have been predominantly reported using gold catalysts.³ Actually, gold shows reduced ability toward hydrogen chemisorption compared to other transition metals due to the less efficient formation of gold–hydride and unstable nature of Au–H,⁴ although attempts had been made to prepare gold–hydride complexes from homogeneous gold salts.⁵ These factors make gold a weak catalyst for hydrogenation reactions. Hence, in most cases, high temperature (100–250 °C) and pressure (>10 atm) are required for hydrogenation, which make it less synthetically applicable.

In general, supported gold nanoparticles (AuNPs) are prepared via reduction of metal salts (from atomic scale to relatively bulkier size), while nanoporous gold (AuNPore) is prepared through the reverse approach in which bulk metal alloys (Au_xAg_y or Au_xAl_y) are converted to nanoskeletal frameworks by an alloying–dealloying method. The advantage of the latter lies in the fact that a self-supported nanoskeletal

framework of gold is formed possessing ligaments and pores, which is robust and mechanically stable. Further, it has been observed that the surface of these ligaments is not smooth but consists of various steps and kinks on which low-coordinated gold atoms are present. These low-coordinated gold atoms are proposed to be the actual reactive site in this catalyst.⁶ Recently, Cao, Hu, et al.⁷ performed a computational study and found that, apart from a Horiuti–Polanyi hydrogenation mechanism,⁸ a non-Horiuti–Polanyi hydrogenation mechanism could also be predominant. Besides, a low-coordinated gold surface was found to promote a non-Horiuti–Polanyi hydrogenation mechanism. A similar type of mechanism cannot be overlooked in the case of AuNPore due to the presence of low-coordinated gold atoms. Nevertheless, the first application of AuNPore in gas-phase reactions appeared for low-temperature CO oxidation.⁹ However, it was found that residual silver or silver impurity which was left from the preparation of AuNPore played a significant role in O₂ activation.¹⁰ Hence, redetermining the importance of different amounts of residual silver in CO oxidation¹¹ as well as methanol oxidation¹² reactions using AuNPore concluded that the reactivity of AuNPore was

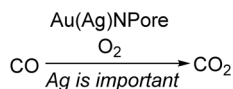
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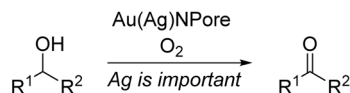
significantly altered with an increase in residual silver (Scheme 1a).

Scheme 1. Effect of Residual Silver Present in AuNPore Catalysts for Oxidation and Reduction Reactions

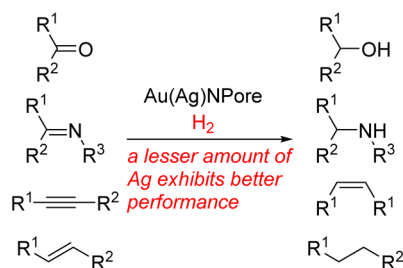
a) Oxidation with O₂^{ref 9}



b) Liquid phase oxidation^{ref 13}



c) Current work, reduction with H₂



In the case of liquid-phase reactions, Asao and co-workers¹³ used AuNPore with 3 atom% Ag (Au₉₇Ag₃NPore) for oxidation of alcohols (Scheme 1b). Here also, Ag impurity was important for efficient oxidation. We have been exploring this heterogeneous gold catalyst, AuNPore, for series of organic transformations due to its promising features.^{14,15} Previously we investigated reduction of various π -bonds using transfer hydrogenating agents such as silanes.¹⁶ Here we report the hydrogenation using AuNPore, and we have experimentally verified that a lesser amount of Ag exhibits more efficient performance, contrary to the trend for oxidation in which larger amounts of Ag show better performance. For example, Au₉₉Ag₁NPore is a more highly efficient catalyst than Au₉₀Ag₁₀NPore for reduction reactions but less efficient for oxidation reactions. In the class of gold catalysts for hydrogenation reactions, it should be mentioned that highly efficient hydrogenation using gold catalysts at pressure lower than 10 atm is scarce.¹⁷ Herein, we describe AuNPore as an efficient and highly chemoselective catalyst for hydrogenation under low pressure, and we show that a lesser amount of silver shows better performance in H₂ hydrogenation, contrary to O₂ oxidation (Scheme 1c).

RESULTS AND DISCUSSION

Reduction under Low H₂ Pressure and Residual Silver Effect. At the start, we carried out a model catalytic reaction using benzaldehyde **1a** (0.5 mmol), 5 mol% Au₉₉Ag₁NPore, and H₂ (8 atm) in ethanol at 90 °C. We were pleased to see that Au₉₉Ag₁NPore was able to catalyze the reaction even at such ambient conditions to give the desired product in 65% yield (Table 1, entry 1). To improve the yield, we screened various solvent (entries 2–5), but ethanol remained the best solvent until we found excellent results (99% yield) using triethylamine (entry 6). Our curiosity about reducing pressure

Table 1. Reduction of Benzaldehyde Using Au Catalysts/H₂^a

entry	Au catalyst	solvent	yield ^b (%) of 2a
1	Au ₉₉ Ag ₁ NPore	ethanol	65
2	Au ₉₉ Ag ₁ NPore	1,4-dioxane	42
3	Au ₉₉ Ag ₁ NPore	tetrahydrofuran	28
4	Au ₉₉ Ag ₁ NPore	acetonitrile	20
5	Au ₉₉ Ag ₁ NPore	toluene	11
6	Au ₉₉ Ag ₁ NPore	triethylamine	99
7	Au ₉₉ Ag ₁ NPore	triethylamine	52 ^c
8	Au ₉₉ Ag ₁ NPore	triethylamine	86 ^d
9	Au/TiO ₂	triethylamine	78
10	AuClPPh ₃	triethylamine	NR ^e

^aReaction conditions unless otherwise mentioned: 5 mol% Au cat., 0.5 mmol **1a**, H₂ (8 atm) in respective solvent at 90 °C for 24 h. ^bYield determined by NMR using CH₂Br₂ as an internal standard. ^cYield at 2 atm H₂ pressure. ^dYield at 4 atm H₂ pressure. ^eNR = no reaction.

down to 2 and 4 atm also resulted in 52% and 86% yields of the desired product, respectively (entries 7 and 8). Finally, two gold catalysts, heterogeneous gold nanoparticles (Au/TiO₂) and homogeneous gold salt (AuClPPh₃), were tested under the optimized conditions. Au/TiO₂ resulted in 78% yield (entry 9), while AuClPPh₃ was unreactive under our conditions (entry 10).

As it has been believed that residual silver is important for oxidation reaction, we applied two catalysts (Au₉₉Ag₁NPore and Au₉₀Ag₁₀NPore) for reduction of aldehydes to check if such silver effect could be observed in the case of reduction. Three representative examples were tested for reduction under the above optimized conditions using these two AuNPore catalysts, and the results are summarized in Table 2. For

Table 2. Residual Silver Effect on Reduction of Aldehydes Using AuNPore/H₂^a

entry	AuNPore	R; 1	yield ^b (%) of 2
1	Au ₉₉ Ag ₁ NPore	H; 1a	99
2		CH ₃ ; 1b	98
3		Cl; 1c	96
4	Au ₉₀ Ag ₁₀ NPore	H; 1a	51
5		CH ₃ ; 1b	32
6		Cl; 1c	73

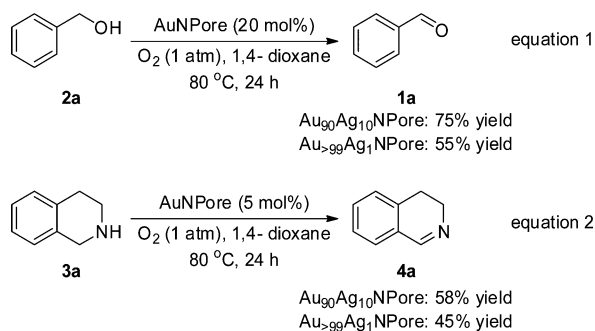
^aReaction conditions: 5 mol% AuNPore, 0.5 mmol **1**, and H₂ (8 atm) in triethylamine at 90 °C for 24 h. ^bYield determined by NMR using CH₂Br₂ as an internal standard. In the cases where the yields of **2** were low (for example, entries 4–6), **1** was recovered in ca. 30–60% yields.

example, when benzaldehyde **1a** was subjected to reduction, Au₉₉Ag₁NPore showed exceptionally high activity, leading to the formation of an excellent yield of benzyl alcohol **2a** (entry 1), while Au₉₀Ag₁₀NPore resulted in a poor yield of benzyl alcohol (entry 4). This reactivity pattern was again confirmed by performing reaction of electronically poor **1b** (entries 2 and 5) as well as electronically rich aldehyde **1c** (entry 3 and 6). In

both cases, $Au_{>99}Ag_1NPore$ showed better performance than $Au_{90}Ag_{10}NPore$.

Oxidation with O_2 and the Effect of Residual Silver. Although previously it was proposed that residual silver helped in oxidation, we tested $Au_{90}Ag_{10}NPore$ and $Au_{>99}Ag_1NPore$ by performing two oxidation reactions. First, benzyl alcohol **2a** was stirred with 20 mol% $AuNPore$ in the presence of oxygen atmosphere at 80 °C. The expected effect of residual silver was observed: $Au_{90}Ag_{10}NPore$ resulted in a comparatively higher yield of the desired benzaldehyde **1a** than $Au_{>99}Ag_1NPore$ with composition of $Au_{>99}Ag_1$ atom% (Scheme 2, eq 1). Second,

Scheme 2. Effect of Residual Silver on Oxidation of Benzyl Alcohol and Tetrahydroisoquinoline^a



^aReaction conditions: 5 mol% $AuNPore$, 0.5 mmol **2a** or **3a**, dioxane (1 mL), 80 °C, O_2 (1 atm).

tetrahydroisoquinoline **3a** was subjected for oxidation using 5 mol% of either $Au_{90}Ag_{10}NPore$ or $Au_{>99}Ag_1NPore$. Even in this case, a higher yield of the desired dihydroisoquinoline product **4a** was achieved using $Au_{90}Ag_{10}NPore$ (Scheme 2, eq 2). These results clearly indicate that residual silver played a significant role for the oxidation reaction, in which $Au_{90}Ag_{10}NPore$ showed enhanced reactivity compared to $Au_{>99}Ag_1NPore$ in both cases.

SEM and XPS of the Two Catalysts. The effect of residual silver on reduction and oxidation reactions was very contradictory. To clarify this interesting contrast between the two catalysts, we investigated their differences in structure and electronic states by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM images of two catalysts showed different morphologies. $Au_{>99}Ag_1NPore$ exhibited a pore size of nearly 25–40 nm (Figure 1a), while $Au_{90}Ag_{10}NPore$ exhibited bigger pores as well as ligament sizes (50–75 nm) (Figure 1b). Due to the presence of a larger amount of silver, $Au_{90}Ag_{10}NPore$ showed a larger pore and ligament size than $Au_{>99}Ag_1NPore$. Au 4f XPS spectra of a pristine sample $Au_{>99}Ag_1NPore$ (blue curve in Figure 1c) showed that the oxidation state of Au in the sample is very close to $Au(0)$.¹⁸ On the other hand, Au 4f XPS spectra of a pristine sample of $Au_{90}Ag_{10}NPore$ (green curve in Figure 1c) showed a shoulder peaks around 85.0 and 89.0 eV due to Au^{x+} .¹⁹ This means that electron transfer from Au to Ag took place, leading to a partial positive charge on Au and negative charge on Ag. The work function (WF) of Au metal is higher than that of Ag metal; however, the formation of the nanoparticles increases the WF of Ag.¹⁹ Thus, electron transfer from Au to Ag at contacting sites takes place. Ag 3d XPS spectra (Figure 1d and 1e) clearly indicate that $Au_{90}Ag_{10}$ contains a relatively higher negative charge on Ag than $Au_{>99}Ag_1$.

XPS Investigation of $AuNPore$ Catalysts under Hydrogenation Conditions. Au 4f XPS spectra of the two catalysts

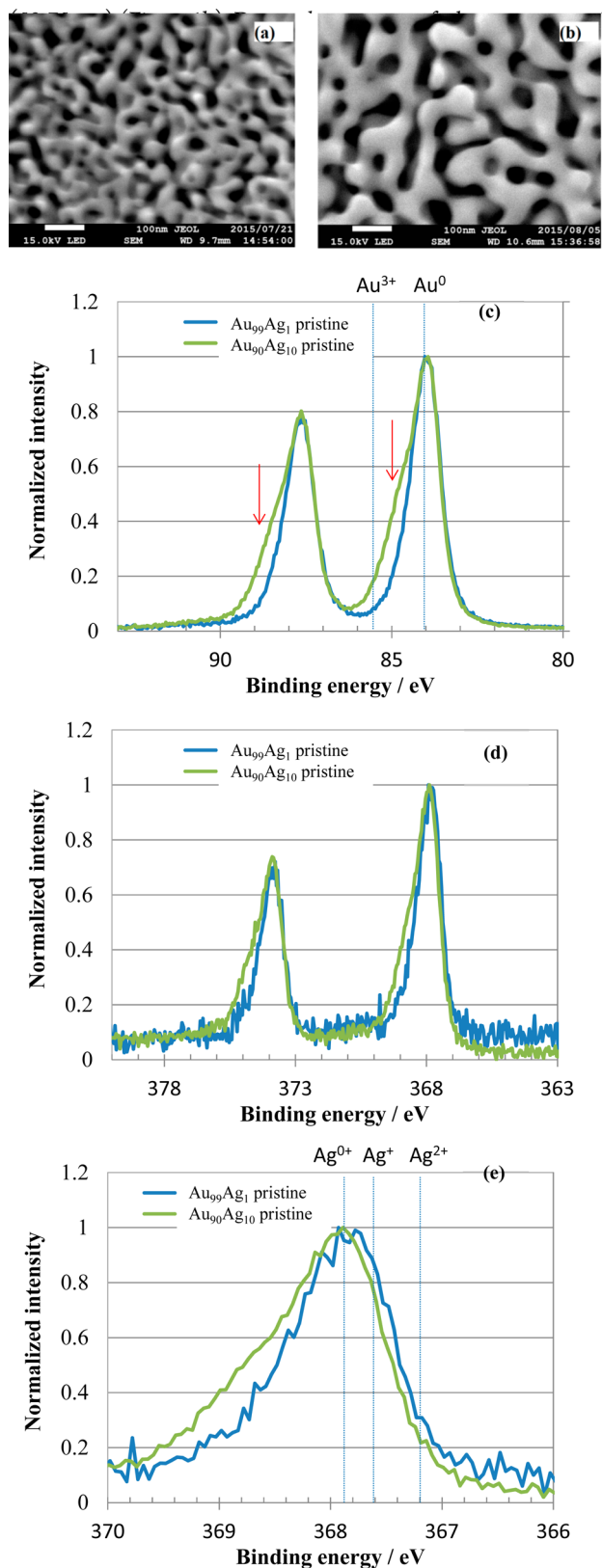


Figure 1. SEM images of (a) $Au_{>99}Ag_1NPore$ and (b) $Au_{90}Ag_{10}NPore$. (c) Au 4f and (d) Ag 3d XPS spectra of the two catalysts. (e) Ag 3d 5/2 XPS spectra of two catalysts, where a shift to higher/lower binding energy of Ag 3d spectra is caused by negative/positive charge in Ag.¹⁸

after treatment with benzaldehyde are shown in Figure 2. It is clear that in both cases ($Au_{>99}Ag_1$ and $Au_{90}Ag_{10}$) shoulder

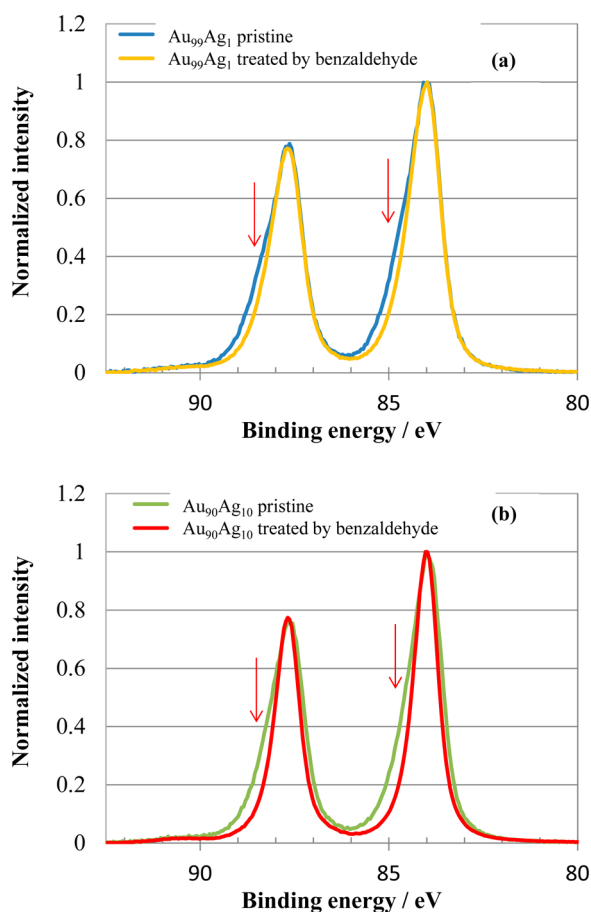


Figure 2. Au 4f XPS spectra of (a) Au₉₉Ag₁NPore and (b) Au₉₀Ag₁₀NPore before (blue and green) and after (orange and red) treatment with benzaldehyde for 10 min.

peaks around 85.0 and 89.0 eV due to Au⁺ were decreased after treatment with benzaldehyde. This suggests that positively charged Au species decreased, which is reasonable since coordination of the oxygen atom of benzaldehyde must decrease positively charged species. Au 4f XPS spectra indicated that there was no apparent change after treatments with H₂ (Figure S3). Ag 3d XPS spectra showed very slight shifts to higher binding energy (BE) after H₂ treatments (Figure S4). Au 4f and Ag 3d XPS spectra after treatments with triethylamine are shown in Figures S5 and S6; in both cases there was no obvious change in the spectra after treatment with triethylamine. In conclusion, no significant difference between the two catalysts was observed in the presence of substrates and H₂. Accordingly, the catalytic activity difference in H₂ reduction is presumably due to the surface structural difference; ligament size is bigger in Au₉₀Ag₁₀, and hence reactivity is lower for reduction because larger ligaments mean smaller defects.⁶

XPS Investigation of AuNPore Catalysts under Oxidation Conditions. Very similarly, Au 4f XPS spectra of both catalysts in the presence of benzyl alcohol were investigated (Figure 3). No significant change was observed in the case of Au₉₉Ag₁, but the intensity of the shoulder peaks around 85.0 and 89.0 eV in the spectra of Au₉₀Ag₁₀ was slightly decreased (Figure 3b), indicating that the amount of positively charged Au species decreased, as observed in Figure 2b. Ag 3d XPS spectra of both catalysts after treatments with benzyl alcohol did not show significant change (Figure S7). Au 4f XPS spectra after treatments with O₂ indicated an interesting

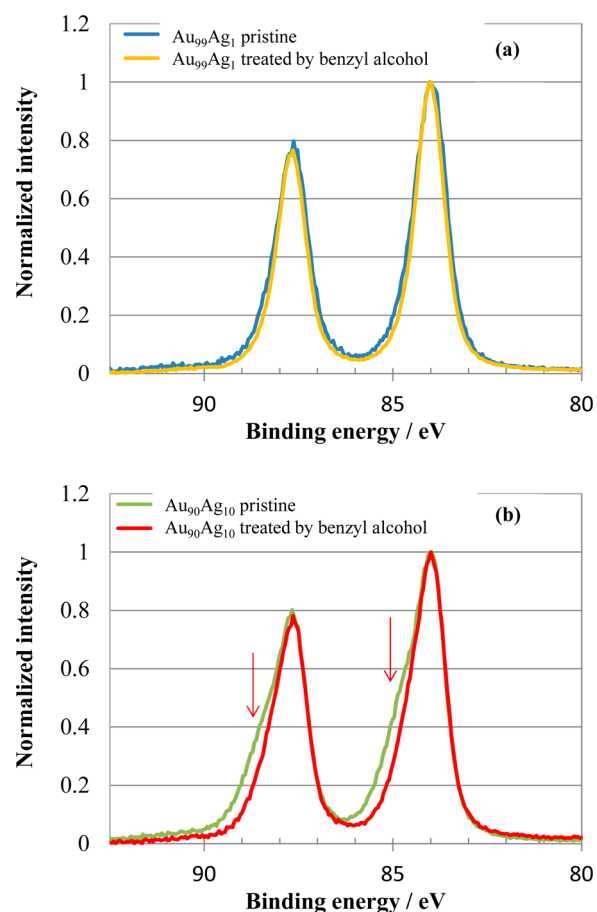


Figure 3. Au 4f XPS spectra of (a) Au₉₉Ag₁NPore and (b) Au₉₀Ag₁₀NPore before (blue and green) and after (orange and red) treatments with benzyl alcohol for 10 min.

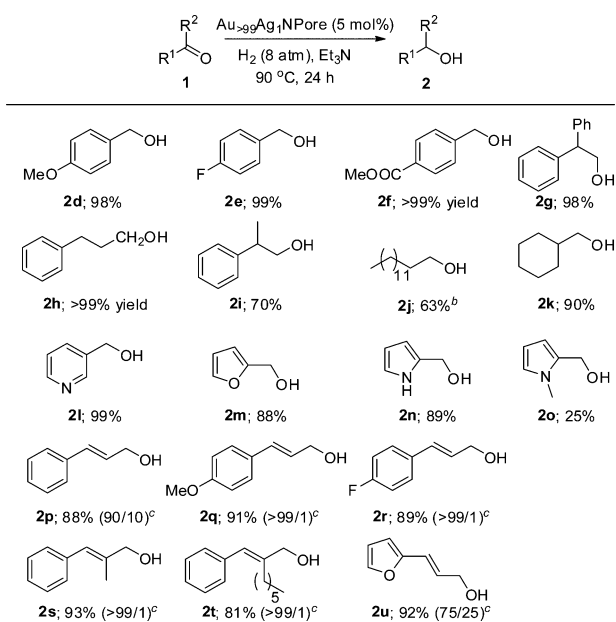
difference: no change was observed in the case of Au₉₉Ag₁, while the shoulder peaks at 85.0 and 89.0 eV in the spectra of Au₉₀Ag₁₀ were increased, suggesting the amount of positively charged Au species increased slightly (Figure S8). Ag 3d XPS spectra after treatments with O₂ showed a similar trend: there was no change in the case of Au₉₉Ag₁, while the spectra of Au₉₀Ag₁₀ were shifted slightly to higher BE, indicating that Ag contains slight negative charge (Figure S9).

Contrary to the above observations, the interaction of dioxane with the catalyst Au₉₉Ag₁ was much stronger than that with Au₉₀Ag₁₀. Au 4f XPS spectra of Au₉₉Ag₁ clearly showed that Au⁺ species significantly increased in comparison with the case of Au₉₀Ag₁₀ (Figure S10), and further Ag 3d XPS spectra showed that negatively charged Ag species significantly increased in the case of Au₉₉Ag₁, while there was no significant change in the case of Au₉₀Ag₁₀ (Figure S11). In conclusion, it may be said that the interaction of the catalyst Au₉₉Ag₁ with O₂ is weaker, but the interaction with a solvent, dioxane, is stronger; this stronger interaction would diminish to some extent the catalytic activity of Au₉₉Ag₁. On the other hand, the interaction of the catalyst, Au₉₀Ag₁₀, with O₂ (and also benzyl alcohol) was observed, suggesting that the progress of the oxidation reaction was enhanced, compared to the case of Au₉₉Ag₁ catalysis.

Reduction of Carbonyl Compounds. After it was found that Au₉₉Ag₁NPore is an excellent catalyst for reduction reaction, we turned our attention to exploring the substrate scope for reduction of aldehydes using Au₉₉Ag₁NPore and H₂

gas (Table 3). Aryl aldehydes substituted with either electron-donating or electron-withdrawing groups resulted in good to

Table 3. Reduction of Carbonyl Compounds Using Au₉₉Ag₁NPore/H₂^a



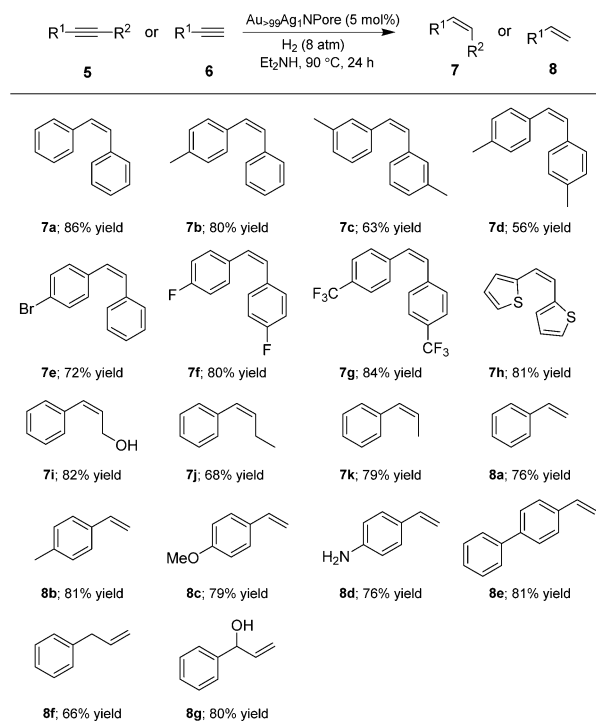
^aReaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol **1**, H₂ (8 atm) in triethylamine at 90 °C for 24 h. ^bIsolated yields are shown. ^cRatio of 1,2/total reduction is shown in parentheses.

excellent yields of the desired alcohols (2d–2f). Not only aromatic but also aliphatic and alicyclic aldehydes were reduced to the corresponding alcohols in high chemical yields (2g–2k). Heterocyclic aldehydes were exclusively reduced to the corresponding alcohols without reduction of the heteraryl ring (2l, 2o). Reduction of unsaturated aldehydes has been widely investigated due to the importance of final products (allylic alcohols)²⁰ and selectivity issues. We subjected selected unsaturated aldehydes to the Au₉₉Ag₁NPore/H₂ system, and in almost all cases, good yields with excellent selectivities toward allylic alcohols were obtained. Both electron-donating and electron-withdrawing groups on the aryl ring resulted in high chemical yields (2p–2r). Alpha-substituted unsaturated aldehydes were also reduced selectively to the corresponding allylic alcohols (2s, 2t). Furan-2-acrolein also resulted in selective reduction of the aldehyde group to an alcohol (entry 2u).

Reduction of Alkynes. Very recently, Kaneda and co-workers²¹ reported chemoselective reduction of internal alkynes with high H₂ pressure (30–50 atm) using core–shell AuNPs. Although they achieved high yields, the rather high hydrogen pressure required for the reaction hinders its application. Hence, we were curious to see if alkynes could be reduced using milder conditions (<10 atm H₂ pressure). To examine highly chemoselective reduction of internal as well as terminal alkynes, diphenylacetylene was subjected to hydrogenation using H₂ gas (8 atm) in the presence of 5 mol% Au₉₉Ag₁NPore in diethylamine as a solvent. After the mixture was stirred for 24 h, 86% yield with >99% selectivity for *cis*-stilbene **7a** was observed. This result encouraged us to apply the present protocol toward reduction of various internal and terminal alkynes.

The results are summarized in Table 4. It should be noted that the reduction of internal alkynes always resulted in *cis*-

Table 4. Reduction of Alkynes Using Au₉₉Ag₁NPore/H₂^{a,b}



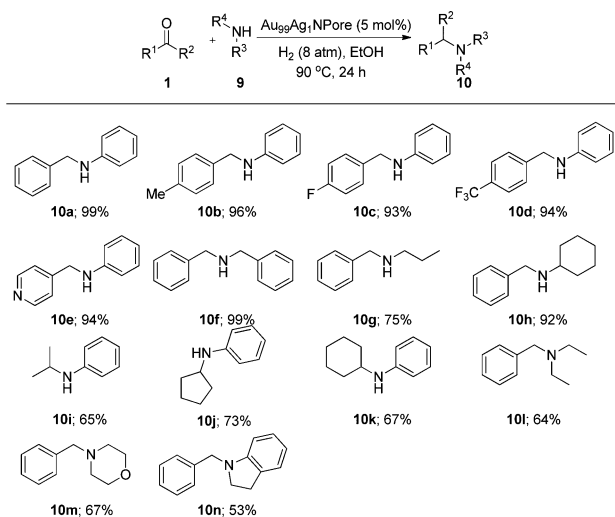
^aReaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol **5** or **6**, H₂ (8 atm) in diethylamine at 90 °C for 24 h. ^bIsolated yields are shown.

semi-hydrogenated products with >99% selectivity; further reduction of the double bond was not observed. This remarkable reactivity was also obtained in the case of terminal alkynes. For example, treatment of terminal alkynes **6a–6g** with 8 atm H₂ pressure in the presence of Au₉₉Ag₁NPore resulted in the desired products in moderate to good chemical yields (**8a–8g**). Whenever a quantitative yield of the desired products was not obtained, significant amounts of the starting materials were recovered without the formation of over-reduced products.

Reductive Amination of Carbonyls. Reductive amination is considered as one of the important and atom economical methods to prepare amines.²² Traditional methods which use an equal amount of inorganic hydrides are not atom economical,²³ but the use of transition metals along with hydrogen gas is considered as an atom-economical approach.²⁴ Nevertheless, this type of reaction is similar to the reaction via a two-step, one-pot procedure; hence, formation of series of byproducts is an unavoidable issue. To this end, development of highly selective catalyst is important. Recently, we used stoichiometric organic silanes along with AuNPore for selective reductive amination reaction.^{16c} However, the formation of imine intermediate was not efficient in those conditions, which was depicted by weak reaction scope and the formation of lower yields of the desired products. Additionally, the necessity of an equivalent amount of organosilanes prevented this method from being atom economical. Reduction of alkynes and aldehydes with H₂ gas had been already in hand, we thought that Au₉₉Ag₁NPore/H₂ system would be atom-economical and would overcome the drawbacks of previously reported methods. Subsequently, benzaldehyde **1a** (R¹ = Ph, R² = H)

was heated at 90 °C with aniline **9a** ($R^3 = \text{Ph}$, $R^4 = \text{H}$) and hydrogen gas (8 atm) in the presence of 5 mol% $\text{Au}_{0.99}\text{Ag}_1\text{NPore}$ in ethanol as a solvent. Gratifyingly, >99% yield of the desired amine **10a** was obtained. Initially, we selected a variety of aldehydes **1** and tested for reductive amination using aniline **9a**. The reactions proceeded very well to give the desired products in excellent yields (Table 5, **10a**–

Table 5. Reductive Amination of Aldehydes and Ketones Using $\text{Au}_{0.99}\text{Ag}_1\text{NPore}/\text{H}_2$ ^a



^aReaction conditions: 5 mol% $\text{Au}_{0.99}\text{Ag}_1\text{NPore}$, 0.5 mmol **1**, 0.5 mmol **9**, H_2 (8 atm) in ethanol at 90 °C for 24 h. ^bIsolated yields are shown.

10e). Either electronically poor or rich benzaldehydes had no influence on the reactivity, and all of them resulted in excellent yields. Heterocyclic aldehyde such as isonicotinic aldehyde smoothly underwent reductive amination with aniline to produce **10e** quantitatively. Similarly, the use of aliphatic and alicyclic primary amines **9f**–**9h** resulted in good to excellent yields in reductive amination of benzaldehyde **1a** (**10f**–**10h**). It is noteworthy that ketones, which are known for sluggishness in reductive amination, were also found to give the desired products in 65–73% yields (**10i**–**10k**). Not only primary amines but also secondary amines facilitated reductive amination of benzaldehyde to give the desired amines in moderate yields (**10l**–**10n**).

Selectivity Studies on Aldehydes vs Aldimines.

Previously we reported successful chemoselective reduction of imines in the presence of aldehydes using a silane system.^{16c} We were interested to know whether a similar kind of reactivity pattern could be observed using H_2 as reducing source. Unexpectedly, the reactivity of $\text{AuNPore}/\text{H}_2$ was different from that of $\text{AuNPore}/\text{Si-H}/\text{H}_2\text{O}$. For example, reduction of a mixture of benzaldehyde **1a** and the corresponding imine **11a** using triethylamine as a solvent resulted in high selectivity toward reduction of benzaldehyde. We believe that, in the case of silane, intervention of an iminium ion intermediate would enhance the electrophilicity of the $\text{C}=\text{N}$ bond, compared to that of the $\text{C}=\text{O}$ bond of aldehydes.^{16c} On the other hand, in the case of hydrogen gas as a reductant, there is no chance for the formation of iminium ions, and therefore the ordinary electrophilicity order, aldehydes > imines, would be reflected. Further, a time-dependent reactivity study was carried out to get further details about the reaction. A 1:1 mixture of aldehyde **1a** and imine **11a** was reduced, and the yields of the desired

products were determined using NMR at different time intervals (Figure 4). It was found that reduction of imine was

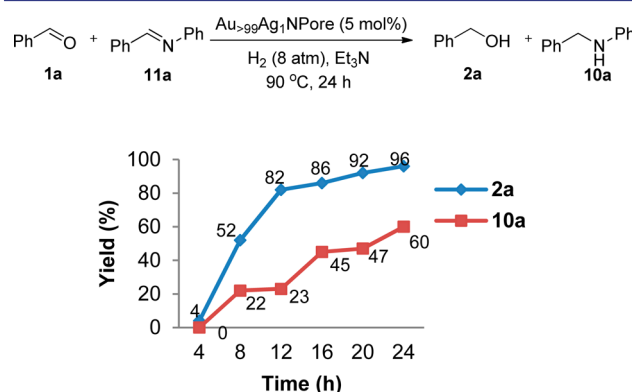


Figure 4. Hydrogenation of aldehyde **1a** and imine **11a** using $\text{Au}_{0.99}\text{Ag}_1\text{NPore}$. Reaction conditions: 5 mol% $\text{Au}_{0.99}\text{Ag}_1\text{NPore}$, 0.5 mmol **1a**, 0.5 mmol **11a**, triethylamine (3 mL), 90 °C, H_2 (8 atm).

never fast at any time. For example, benzaldehyde was reduced to benzyl alcohol in 82% yield after 12 h, while at the same time only 23% yield of the amine **10a** was obtained. From Figure 4, it is clear that the $\text{Au}_{0.99}\text{Ag}_1\text{NPore}/\text{H}_2$ system in triethylamine preferentially reduces aldehydes in the presence of the corresponding imines. On the other hand, the reduction in triethylamine to EtOH gave 56% yield of benzyl alcohol **2a** and >99% yield of the amine **10a**. As suggested in our previous paper,^{16c} iminium ion may be formed in EtOH, and therefore imine **11a** would be reduced more preferentially.

Selectivity Studies on Internal vs Terminal Alkynes.

Although chemoselective reduction of alkynes in the presence of alkenes was obtained previously,²⁰ such chemoselective studies for selective reduction of terminal alkynes in the presence of internal alkynes are rarely reported. We performed hydrogenation of a mixture of terminal alkynes and internal alkynes in the presence of $\text{Au}_{0.99}\text{Ag}_1\text{NPore}/\text{H}_2$ using diethylamine as a solvent. Initially, a 1:1 mixture of diphenylacetylene (**5a**) and phenylacetylene (**6a**) was treated with 8 atm H_2 pressure in the presence of 5 mol% $\text{Au}_{0.99}\text{Ag}_1\text{NPore}$. Consequently, it was observed that only phenylacetylene was reduced to styrene (**8a**) in 75% yield, while diphenylacetylene could not undergo reduction but was recovered quantitatively. Similar cross experiments were carried out by using other internal alkynes and terminal alkynes, and in most of the cases exclusive reduction of terminal alkynes to internal alkenes was observed (Table 6, entries 1–9). It should be noted that treatment of a 1:1 mixture of **5a** and **6a** with supported gold nanoparticles Au/TiO_2 (1 mol%) under similar conditions resulted in reduction of phenylacetylene in 91% yield, while diphenylacetylene was reduced in 51% yield (Table 6, entry 10). Further, the other heterogeneous and homogeneous catalysts, such as Lindlar palladium, Pd/C, and $\text{Pd}(\text{OAc})_2$, were tested, but the chemoselective reduction of terminal alkyne **6a** was not achieved by these traditional catalysts (entries 11–13).

Selectivity Studies on Alkynes vs Alkenes. Although exclusive selectivity for conversion of terminal alkynes to alkenes was observed, we thought that it would be worth to know if selective reduction of phenylalkyne **6a** in the presence of a certain alkene, for example, 4-methylstyrene **8b**, would take

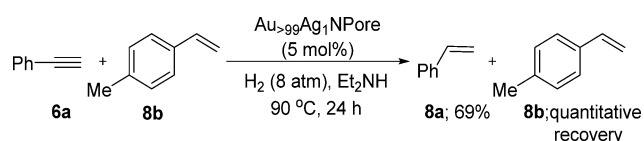
Table 6. Hydrogenation of Terminal Alkynes in the Presence of Internal Alkynes Using Au₉₉Ag₁NPore/H₂^a

$$R^1-C\equiv C-R^2 + R^3-C\equiv C \xrightarrow[H_2 (8 \text{ atm}), Et_2NH, 90^\circ C, 24 \text{ h}]{Au_{99}Ag_1NPore (5 \text{ mol}\%)} R^1-CH=CH-R^2 + R^3-CH=CH + R^3-CH=CH$$

entry	R ¹ /R ² ; 5	R ³ ; 6	yield ^b (%)		
			7	8	8'
1	Ph/Ph; 5a	Ph; 6a	7a , trace	8a , 75	8a' , 0
2	Ph/Ph; 5a	4-MeC ₆ H ₄ ; 6b	7a , 3	8b , 78	8b' , 0
3	Ph/Ph; 5a	4-MeOC ₆ H ₄ ; 6c	7a , trace	8c , 62	8c' , 0
4	Ph/Ph; 5a	4-tBuC ₆ H ₄ ; 6h	7a , 7	8h , 65	8h' , 0
5	Ph/Ph; 5a	4-CNC ₆ H ₄ ; 6i	7a , 4	8i , 52	8i' , 0
6	Ph/4-MeC ₆ H ₄ ; 5b	Ph; 6a	7b , 9	8a , 61	8a' , 0
7	4-CF ₃ C ₆ H ₄ /4-CF ₃ C ₆ H ₄ ; 5g	Ph; 6a	7g , 8	8a , 60	8a' , 0
8	Ph/4-FC ₆ H ₄ ; 5l	Ph; 6a	7l , trace	8a , 81	8a' , 0
9	Ph/4-MeCOC ₆ H ₄ ; 5m	Ph; 6a	7m , 6	8a , 67	8a' , 0
10 ^c	Ph/Ph; 5a	Ph; 6a	7a , 51	8a , 91	8a' , 0
11 ^d	Ph/Ph; 5a	Ph; 6a	7a , 33	8a , 10	8a' , 55
12 ^e	Ph/Ph; 5a	Ph; 6a	7a , 51	8a , 0	8a' , 12
13 ^f	Ph/Ph; 5a	Ph; 6a	7a , 56	8a , 0	8a' , 35

^aReaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol **5**, 0.5 mmol **6**, H₂ (8 atm) in diethylamine at 90 °C for 24 h. ^bYield determined by NMR using CH₂Br₂ as internal standard. ^cReaction was performed using 1 mol% Au/TiO₂ as a catalyst. ^dLindlar palladium catalyst was used as a catalyst. ^ePd/C was used as a catalyst. ^fPd(OAc)₂ was used as a catalyst.

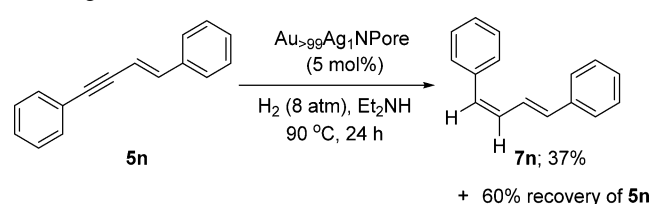
place (Scheme 3). Even in this case, we achieved exclusive selectivity toward reduction of the alkyne; **6a** was reduced to

Scheme 3. Hydrogenation of Alkyne in the Presence of Alkene Using Au₉₉Ag₁NPore^a

^aReaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol **6a**, 0.5 mmol **8b**, diethylamine (3 mL), 90 °C, H₂ (8 atm).

styrene in 69% yield, while **8b** was recovered quantitatively. In addition, enyne **5n** was also tested for chemoselective reduction using Au₉₉Ag₁NPore/H₂ system (Scheme 4). Although the desired partially reduced product **7n** was obtained in a poor yield, further reduction of double bond was not observed. These results indicate that Au₉₉Ag₁NPore is a highly chemoselective catalyst for partial reduction of alkynes.

Hydrogenation of Other π-Bonds. Reduction of aldehydes, alkynes, imines was achieved but it was also important for us to investigate the reactivity of Au₉₉Ag₁NPore toward the reduction of comparatively less reactive organic substrates. Subsequently, a variety of other substrates **12** containing π-bonds were tested. Table 7 summarizes the results obtained by reduction of these organic substrate at com-

Scheme 4. Hydrogenation of Enyne to Diene Using Au₉₉Ag₁NPore^a

^aReaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol **5n**, diethylamine (3 mL), 90 °C, H₂ (8 atm).

paratively higher temperature using Au₉₉Ag₁NPore catalyst in EtOH as a solvent.

Table 7. Hydrogenation of Other Organic Substrates Using Au₉₉Ag₁NPore/H₂^a

entry	Substrate	Au ₉₉ Ag ₁ NPore (5 mol%)	Product	yield ^b (%) of 13
	12	H ₂ (8 atm), EtOH 120 °C, 24 h		
1				21
2				51
3				39
4				67

^aReaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol substrate, H₂ (8 atm) in ethanol at 120 °C for 24 h. ^bIsolated yields. ^cNR: No Reaction.

Reusability and Recovery of Au₉₉Ag₁NPore Catalyst.

The robustness and mechanical stability of Au₉₉Ag₁NPore catalyst were investigated by its reuse for several cycles. It was observed that the catalytic activity remained same in every cycle. The simple recovery of the catalyst using tweezers (Figure 5, inset) makes it a challenging in hydrogenation reactions.

CONCLUSIONS

In summary, although CO, CO₂, and O₂ gaseous systems were widely studied using nanoporous gold catalysts, hydrogen dissociation, which needs comparatively high energy on gold surfaces, was never realized. As described earlier, residual silver shows a promising effect in oxygen activation, and our experimental results agree with this phenomenon, with the reactivity of almost pure AuNPore diminishing in oxidation reactions. On the other hand, almost pure nanoporous gold catalyst Au₉₉Ag₁NPore exhibited much higher catalytic reactivity in hydrogenation than Au₉₀Ag₁₀NPore; this means that a lesser amount of residual silver is more desirable in

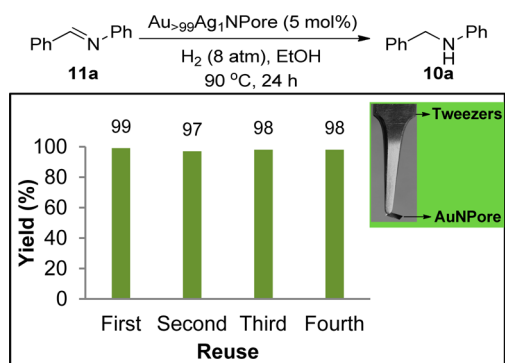


Figure 5. Reusability of Au₉₉Ag₁NPore catalyst in reduction of imine. Reaction conditions: 5 mol% Au₉₉Ag₁NPore, 0.5 mmol **11a**, ethanol (3 mL), 90 °C, H₂ (8 atm).

reduction reactions. The wide applicability of Au₉₉Ag₁NPore was tested for hydrogenation of a variety of functional groups. Wide ranges of aldehydes including unsaturated aldehydes were reduced to the corresponding alcohols in high yields with excellent chemoselectivities. *Cis*-semi-hydrogenations of internal alkynes as well as partial reductions of terminal alkynes were realized with excellent selectivities. Additionally, the selective reduction of terminal alkynes was obtained in the presence of internal alkynes, which otherwise could not be achieved using commercially available supported AuNPs. In a similar manner, reductive amination, which has great significance in the synthesis of amines due to its atom-economical nature, has also been realized using Au₉₉Ag₁NPore. Further, the Au₉₉Ag₁NPore/H₂ system in triethylamine is found to prefer the reduction of an aldehyde in the presence of an imine. Apart from this, less reactive functional groups such as nitro, quinoline, ketone, and alkene could also be reduced to the corresponding products in lower yields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b06569](https://doi.org/10.1021/jacs.6b06569).

Fabrication of AuNPores, their EDX spectra, XPS investigation in the presence of substrates, and hydrogenation reactions (PDF)

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Notes

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