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Accessing frustrated Lewis pair chemistry through robust Gold@N-doped carbon for selective hydrogenation of alkynes

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ABSTRACT. Pyrolysis of Au(OAc)₃ in the presence of 1,10-phenanthroline over TiO₂ furnishes a highly active and selective Au nanoparticle (NP) catalyst embedded in a nitrogen-doped carbon support, Au@N-doped carbon/TiO₂ catalyst. Parameters such as pyrolysis temperature, type of support and nitrogen ligands and Au:ligand molar ratios were systematically investigated. Highly selective hydrogenation of numerous structurally diverse alkynes proceeded in moderate to excellent yield under mild conditions. The high selectivity toward the industrially important alkene substrates, functional group tolerance and the high recyclability makes the catalytic system unique. Both high activity and selectivity are correlated with a frustrated Lewis pairs interface formed by the combination of gold and nitrogen atoms of N-doped carbon that, according to DFT calculations, can serve as a basic site to promote the heterolytic activation of H₂ under very mild conditions. This "fully heterogeneous" and recyclable gold catalyst makes the selective hydrogenation process environmentally and economically attractive.

KEYWORDS. Gold; N-doped carbon; hydrogenation; alkyne; heterolytic cleavage, frustrated Lewis pairs.

INTRODUCTION

Alkenes have an extensive range of applications from intermediates in the chemicals industry to their primarily use as co-monomers in the production of polymers. High purity alkene feedstocks (alkyne free) for the polymer industry are obtained by a very fine tuned catalytic hydrogenation process; the challenging selective hydrogenation of impurities (alkyne to alkene), while inhibiting the hydrogenation of the alkene to the alkane step and double-bond isomerization.¹ The semihydrogenation of alkynes to alkenes is also known as a valuable

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synthetic strategy for drug design.² Typically, platinum group metal catalysts are very active for hydrogenations, but they usually suffer from the lack of selectivity to alkenes.^{3,4} Approaches to improve the chemoselectivity relied on addition of ligands,^{5,6} usually nitrogen, phosphorus, sulfur or addition of a second less active metal.^{7,8} In the context of hydrogenations, gold was less explored,^{9,10} but is expected to be intrinsically selective for hydrogenation of triple bonds in alkyne-alkene mixtures, because the preferential adsorption of only one of these components, the alkyne.¹¹ Nevertheless, gold-based catalyst still suffer from the lack of activity, mainly due to limited capability to dissociate molecular hydrogen (H_2) , which usually is the rate-limiting step.³ Cooperation between the coordinatively unsaturated Au atoms on the Au NPs and the acid-base pair site on Al₂O₃, 12,13 basic sites on hydroxyapatite^{14,15} and on ceria^{16,17} has been suggested as a strategy for the H_2 dissociation to yield a H^+/H^- pair at the metal-support interface, which is then transferred to the organic moiety. Such heterolytic H₂ splitting has been proposed to occur on pure oxides,¹⁸⁻²⁰ on gold complexes,²¹⁻²³ or due to a cooperation between gold and adsorbed basic ligands.^{24–30} We have recently systematically studied the activation of gold via the heterolytic dissociation of H₂ based on the adsorption of nitrogen-containing bases on gold surfaces.²⁴ The activation of H₂ was proposed to occur at the metal-ligand interface forming a tight ion pair induced by a frustrated Lewis pair (FLP) like structure,^{31–35} which was able to promote the heterolytic activation of H₂, allowing a high activity and selectivity for the hydrogenation of alkynes into alkenes. In the proposed mechanism, identified by DFT, the H_2 molecule splits forming a quaternary N center (amine protonation) and a hydride on the gold surface: both H⁻ and H⁺ were then transferred to the organic moiety in a syn-fashion controlled by electrostatic interactions.

Nitrogen-doped carbon materials affect the catalytic activity and selectivity of transition metals significantly, such as cobalt,^{36,37} nickel,³⁸ palladium,^{39,40} ruthenium,⁴¹ and iron/iron oxide based catalysts.^{42,43} The incorporation of nitrogen atoms in the carbon architecture combined with metal nanoparticles have enabled application in a wide range of catalytic reactions including reductions, oxidations and H₂ generation.^{44,45} N-doped carbon structures have also emerged in a plethora of hydrogenation reactions.^{36,42,46,47} More interestingly, a heterolytic H₂ activation has been invoked to explain the hydrogenation reaction mechanism.^{48,49,50} Although it is not explicit in the previous studies, it is likely that the metal-N-doped carbon interface can be understood as a FLP, with an active participation of the support basic nitrogen atoms in the H₂ activation. Based on our interest in this concept, we decided to explore the synthesis of gold nanoparticles supported on N-doped carbon supports for studies in selective hydrogenations. The main advantage with respect to previous studies²⁴ is to avoid the addition of external ligands, in large excess, for the activation of gold surfaces via FLP, making the whole process environmentally and economically attractive.

RESULTS AND DISCUSSION

We commenced our study by preparing a series of gold catalysts inspired by the method developed by Beller's group for the preparation of Ni, Co and Fe-catalysts.^{36,42,47,51,52} The gold catalysts were prepared by pyrolysis of the gold precursor at different temperatures in the range from 200 to 800 °C in the presence of 1,10-phenantroline (L1) and TiO₂ support under N₂ atmosphere (Figure S1). The thermal behavior TG-DTG of the Au-L1/TiO₂ material under N₂ indicated that the pyrolysis proceeds in a multi-stage fashion (Figure S2). We studied the influence of the pyrolysis temperature on the catalytic activity of the various materials obtained

for the benchmark hydrogenation of phenylacetylene **1a** using molecular hydrogen (H₂) (Table 1). The material pyrolyzed at 200 °C lead to 51% of conversion of **1a** (Table 1, entry 1). The best activity was obtained by performing the pyrolysis at 400 °C (Table 1, entry 2). On increasing the pyrolysis temperature to 600 °C and 800 °C, the activity of the resulting catalyst decreased significantly (Table 1, entry 3 and 4). We next studied the influence of the N-containing ligands on the stabilization and catalytic activity of the various materials obtained after pyrolysis at 400 °C (Table 2).

Table 1. Catalytic activity in the hydrogenation of phenylacetylene of Au@N-doped carbon catalysts obtained from Au-L1/TiO₂ after pyrolysis at different temperatures.^a

la	Au catalyst (2 mol%) EtOH, 100 °C, 6 bar H ₂		2a + (3a		
	Entr	Pyrolysis	Conversion	of 1a	Yield of	2a
	у	temperature (°C)	(%)		(%)	
	1	200	51		>99	
	2	400	100		>99	
	3	600	27		>99	
	4	800	5		65	

^aReaction conditions: 0.14 mmol **1a**, 2 mol% of Au@N-doped catalyst, 2 mL of ethanol, 100 °C, 6 bar H₂, 20 h. ^bDetermined by GC using internal standard technique.

Table 2. Catalytic activity in the hydrogenation of phenylacetylene of Au@N-doped carbon catalysts obtained with different N-containing ligands, after pyrolysis at 400 °C.^a



Entry	Catalyst precursor	Conversion of 1a (%)	Yield of 2 a (%)
1	Au-L1/TiO ₂	100	>99 (95)
2	Au-L2/TiO ₂	47	88
3	Au-L3/TiO ₂	8	79
4	Au-L4/TiO ₂	18	94
5	Au-L5/TiO ₂	65	93
6	Au-L6/TiO ₂	17	89
$7^{\rm c}$	Au-L1/TiO ₂	0	-
8	Au/TiO ₂	4	>99
9	L1/TiO ₂	0	-

^aReaction conditions: 0.14 mmol of **1a**, 2 mol% of Au catalyst, 2 mL of ethanol, 100 °C, 6 bar of H₂, 20 h. ^bDetermined by GC using internal standard technique; numbers in parenthesis refer to isolated yield. ^cCatalyst not pyrolyzed.

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Among the different N-containing ligands tested, 1,10-phenanthroline (L1) was found to give the most-active system (Table 2, entry 1), resulting in a catalyst that exhibited superior reactivity in comparison with those obtained from other ligands such as 2,2'-bipyridine (L2), ethylenediamine (L5), diethylenetriamine (L6) (Table 2, entries 2, 5 and 6). The catalyst obtained using piperazine (L4) showed the lowest activity (Table 2, entry 3). Moreover, the model reaction does not occur to any extent in the presence of the material not submitted to pyrolysis (Table 2, entry 7). Notably, the catalyst prepared without addition of any ligand (Au/TiO₂) showed significant low catalytic activity (Table 2, entry 8), and no conversion was observed with a material obtained via pyrolysis of the support with 1,10-phenantroline (L1/TiO₂) but without the gold precursor (Table 2, entry 9). We further investigated the potential effect of supports (C, CeO₂, MgO, Fe₃O₄, SiO₂ and TiO₂) in the catalytic activity (Table S1). The catalysts based on carbon, cerium oxide, iron oxide and magnesium oxide (Table S1, entries 1-4) showed low conversion ($\leq 10\%$) of **1a**. Although, the catalyst supported on silica reaches 71% of conversion (Table S1, entry 5), the fully hydrogenated product **3a** was formed. Titanium dioxide proved to be the best support (Table S1, entry 6) under the studied conditions. Gold precursor influence in the catalytic activity was also evaluated (Table S2), the catalyst prepared using gold acetate (Table S2, entry 1) show the best result, full conversion of **1a**, a slightly decrease in catalytic activity was noticed when using hydrogen tetrachloroaurate(III) (68% of conversion of **1a**, Table S2, entry 2) or potassium dicyanoaurate(I) (90% of conversion of **1a**, Table S2, entry 3). An increase in the Au:L1 molar ratio from 1:2 to 1:5 or 1:10 lead to complete loss of catalytic activity (Table S3, entries 2 and 3). After a further survey of common reaction parameters (solvent, reaction temperature, molecular hydrogen pressure; for more details, see Tables S4, S5

and S6 at the Supporting Information), the best reaction conditions were ethanol as solvent, 6 bar of H₂ at 100 °C. The most active catalytic material obtained by pyrolysis at 400 °C was characterized in detail. The active catalyst contains 1.1 wt% Au, 0.7 wt% C and 0.2 wt% N, as determined by elemental analysis and FAAS. Images by scanning transmission electron microscopy (STEM) of the material pyrolyzed with the L1 ligand revealed formation of Au NPs with a mean diameter of 4.5 nm, in addition, a few larger particles of 10 nm were observed occasionally (Figure S3a-c). In complete contrast, the catalyst prepared without the presence of the ligand, a significant increase in the gold NPs size was observed, with a mean diameter about 17 nm (Figure S3d-f). UV-Vis diffuse reflectance spectra were recorded for both solids (with and without L1), showing a typical gold SPR band (Figure S4). The X-ray diffraction (XRD) pattern corresponding to Bragg diffractions of Au (200) at 44°, Au (220) at 65°, or Au (311) at 78° , confirmed the metal reductions and anatase as the predominant phase without significant phase conversion after thermal treatment (Figure S5). EDX spectrum imaging (elemental mapping) of the Au-L1/TiO₂ material after pyrolysis at 400 $^{\circ}$ C provided a clear evidence for the presence of carbon deposited on the surface of the Au NPs (Figure 1). No conclusive information on the location of nitrogen in the sample could be obtained, due to the overlap of the majoritarian Ti signal at 0.452 keV with the N signal at 0.392 keV (Figure S6).



Figure 1. (a) Bright field STEM image of a representative area of the Au@N-doped carbon catalyst (Au-L1/TiO₂ material after pyrolysis at 400 °C) and (b) corresponding EDX elemental maps. Carbon appear as the red spots deposited mostly on the yellow gold particles. (c) Au 4f XPS spectra and (d) N 1s XPS spectra for Au-L1/TiO₂ material after pyrolysis at 400 °C.

The type of N-doping was investigated in more detail by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of catalytic material obtained by pyrolysis at 400 °C revealed that the samples surface contains Au, C, Ti, N and O. The Au 4f spectrum exhibit two peaks centered at binding energy 87.0 eV and 83.3 eV, which correspond to the Au⁰ oxidation state^{53,54} (Figure 1c). Valuable information was obtained by analysis of the binding energy peak of the N 1s region (Figure 1d and Figure S7–S9). The N 1s spectrum of the most active Au@N-doped carbon catalyst (pyrolysis at 400 °C) was fitted with three components located at binding

energies of 399.5, 400 and 401.3 eV (Figure 1d). The peak at 401.3 eV can be attributed to graphitic nitrogen, while the peak at 399.5 eV can be attributed to the pyridinic nitrogen species.^{44,55,56} However, the peak at 400 is more difficult to attribute, as it can be both a result of Au-N interaction (see results for Au-L1/TiO₂ (before pyrolysis), Figure S9) or due to pyrrolic nitrogen species, very often present in N-doped carbon systems,⁴⁶ and also present in the XPS N1s spectrum of the sample L1/TiO₂ (without gold) (Figure S7). This component at ca. 400 eV was found in all catalysts prepared by pyrolysis with other ligands (L2–L6) at 400 °C (Figure S8) and for Au/L1-TiO₂ (before pyrolysis) displays two nitrogen species at 399.3 and 399.8 eV (Figure S9), which are tentatively attributed to pyridinic nitrogen atoms of free ligand and of the ligand coordinated and/or adsorbed on gold (Au-N), respectively. The 1,10-phenanthroline ligand adsorbed on TiO₂ (L1/TiO₂ without gold) displays only one nitrogen species at 399.4 eV (Figure S7), typically of a pyridinic nitrogen atom (free ligand).

The kinetic study shown in Figure 2b indicates full conversion of **1a** to **2a** in about 8 hours and suppression of further hydrogenation of **2a** to **3a**, even at long reaction times. This high selectivity for the alkene **2a** is an intrinsic property of our catalyst and it was not observed for the well-known Pd Lindlar catalyst (Pd/CaCO₃ + Pb(OCOCH₃)₂ + quinoline), which produces **3a** at high conversions (Figure S10). It is worth to note that a sixty-fold reaction rate enhancement was observed when comparing the catalytic activity of similar Au catalysts prepared with **L1** (Figure 2b) (reaction rate = 0.273 mmol $g_{cat}^{-1} h^{-1}$) or without any ligand (Figure 2c) (reaction rate = 0.00472 mmol $g_{cat}^{-1} h^{-1}$). In order to further examine the stability as well as recyclability of the "fully heterogeneous" catalytic material, the hydrogenation of **1a** was repeated up to ten times using the same catalysts portion without any further treatment or ligand addition. As depicted in

Figure 2d, the desired product styrene **2a** was obtained in a 99% yield even after ten runs and no significant loss of activity was observed (see also Figure S11). A hot filtration test (Figure 2e) revealed that the obtained activity is not related to any leaching of the catalytically active metal (no remaining activity in the supernatant). ICP AES analysis of the recycling experiments indicated no undesired leaching processes of gold occurred during the course of the catalytic transformation. Furthermore, no aggregation of Au NPs was observed by STEM of the recycled catalyst after the tenth recycle (Figure S12).



Figure 2. (a) Time course of hydrogenation of phenylacetylene 1a catalyzed by (b) Au@Ndoped carbon/TiO₂ catalyst and (c) Au/TiO₂ catalyst; (d) Recycling experiments using the

Au@N-doped carbon/TiO₂ catalyst; (e) Hot filtration test to determine homogeneous catalysis contribution in hydrogenation of **1a**. Reaction conditions: 0.14 mmol of **1a**, 2 mol% of Au, 2 mL of ethanol, 100 °C, 6 bar of H₂.

Since Au@N-doped carbon/TiO₂ catalyst (Au-L1/TiO₂ pyrolyzed at 400 °C) displayed the best activity for the production of styrene, it was explored in the scope study under the optimized conditions. A variety of terminal and internal alkynes was readily hydrogenated to the desired alkene and *cis*-alkene with moderate to excellent yield (Scheme 1) and, notably, different from what occur with other transition metals, without any over-reduction to alkane. cis-Control was also reported to be a consequence of FLP. Moreover, both electron-deficient substituents, such as esters (2ab) and carboxylic acids (2ad) moieties, and electron-rich groups, for example amino (2s and 2t) and methoxy (2c and 2o), were tolerated well. The developed catalyst was even able to reduce only the alkyne unit in molecules with alkene moieties (2k, 2v, 2w and 2x), without any detectable concurrent reduction of the alkene moieties both in the parent and product molecules. The results depicted in Scheme 1 confirmed that a broad range of sensitive and reducible functional groups, including halide (2d, 2e, 2p and 2q), ketones (2u) and aldehydes (2ac), were tolerated in the alkyne hydrogenation process. With an increase in H_2 pressure (10) bar H_2 , (Z)-alkenes were mostly formed from internal alkynes (**2y-2af**). The catalyst system was also applicable for scaled-up conditions, where 5 mmol of 1a (0.51 g) was successfully converted into the alkene 2a (0.49 g, 94%). Considering full conversion, the turnover number (TON) of 1700 was reached, with a TOF of approximately 70 mol mol⁻¹ h⁻¹. Such a TOF value is an order of magnitude higher than the values reported for heterogeneous gold-based catalysts using molecular hydrogen as hydride source and without the use of ligands. Furthermore, this

TOF is also high when taking into account values for system using other sources of hydride and ligands to boost the catalytic activity (Table S7).

Scheme 1. Au@N-doped carbon/TiO₂ catalyst for the semihydrogenation of alkynes to alkenes.^{a,b}



^aReaction conditions: 0.14 mmol of alkyne, 2 mol% of Au-L1/TiO₂ catalyst, 2 mL of ethanol at 100 °C, 6 bar of H₂. ^bGC yields are shown; values in parentheses refer to isolated yields. Selectivity was >99%. ^c8 bar of H₂. ^d80 °C. ^e10 bar of H₂.

To further check the chemoselectivity of the developed catalyst, we performed experiments using **1a** as substrate in the presence of diverse sensitive functionalized molecules (Scheme 2). Total chemoselectivity was observed for the reduction of the model alkyne in the presence of potentially reducible groups such as nitro, aldehydes, epoxides, ketones, nitriles, esters, heteroaromatic *N*-oxides and amide, since not even traces of conversion of these functional groups such as epoxides, nitro, aldehydes, heteroaromatic *N*-oxides and sulfoxides can be efficiently reduced too (Table S8).

Scheme 2. Selective hydrogenation of 1a in the presence of molecules with other reducible functional groups by Au@N-doped carbon/TiO₂ catalyst.^a



^aReaction conditions: 0.14 mmol **1a**, 0.14 mmol of sensitive molecule, 2 mol% of Au catalyst, 2 mL of ethanol, 24 h, 100 °C, 6 bar H₂. Conversion was determined by GC using internal standard technique.

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Based on the experimental results and previous ascertain, we believe that pyridinic, graphitic and pyrrolic N atoms play a pivotal role in boosting the catalytic activity of our gold-based catalyst. The reactivity pattern displayed by the Au@N-doped carbon catalyst, prepared via pyrolysis of Au-L1/TiO₂, allows us to postulate that H₂ activation may proceed by a heterolytic pathway, due to the interaction of Au NPs and the nitrogen atoms of the N-doped carbon around the metallic nanoparticles, following the concept of frustrated Lewis pair (FLP) interface suggested before for Au NPs and externally added N-containing ligands.²⁴ This type of H₂ activation at N-doped carbon supports was previously described for Pd,⁴⁸ boron-nitrogen codoped graphene,⁵⁷ and Co catalyst.⁴⁹ The introduction of N atoms might affect the properties of the supported catalyst, such as tunable acid–base character at the support surface, which could cause a better interaction of metal–support–reactant, as well as charge transfer phenomena at the metal–support junction.⁴⁴

In order to gain more insight into the mechanism of the reaction, we conducted a Hammett correlation study using the developed catalyst and Lindlar catalyst to verify the influence of various *para* substituents on aromatic alkynes. The Hammett plot for the reaction catalyzed by Au@N-doped carbon catalyst reveals that the reaction is sensitive to the substituent (Figure 3). The reaction rate was enhanced in the presence of electron-withdrawing groups and the positive value of ρ ($\rho = +1.73$; R²=0.93) highlights the build-up of negative charge during the catalytic cycle. The value of ρ with Lindlar catalysts was close to 0, which indicates a lack of substituent effect in the hydrogenation reaction, and no charge built or lost during the catalytic cycle. Those results give support to a heterolytic H₂ dissociation mechanism for the Au@N-doped carbon catalyst, in contrast to the homolytic H₂ activation mechanism for Lindlar catalyst. Moreover, theoretical calculation and experimental results have demonstrated that nitrogen doping

structures could also enhance the stability of Au catalyst against sintering, preserving the catalytic activity,^{54,58,59} which explains the high recyclability and lack of particle aggregation.



Figure 3. Hammett plot for the hydrogenation of various para-substituted alkynes catalyzed by $Au@N-doped carbon/TiO_2$ and Lindlar catalyst.

Based on the results described above, we propose that the nitrogen atoms doped on carbon have a major role in the heterolytic activation of H₂ via frustrated Lewis pairs. To support such hypothesis, we present a computational study of the hydrogenation mechanism of alkyne **1a**. Following previous experiments (Table 2, entry 1), we model a Au(111) surface functionalized with phenanthroline L1. Taking into account the high coverage situation of the experiments, the π -system of L1 may adsorb in two main configurations: (i) parallel (flat) to the surface, model **A**, or (ii) perpendicular to it, model **A2**. Model **A** contains one L1 in the supercell, while model **A2** can fit up to three (Figure S13). Both situations present the same adsorption energy (E_{ads}) per ligand, (-0.74 eV and -0.75 eV, respectively, Table S9), with shortest Au····N distances of ca. 3.3 Å and 3.5 Å, respectively. At high coverage situations, the packing predicted in model **A2**

would be expected, and in operando conditions, ligands would be replaced by reactant molecules via 0.75 eV. Such a continuous release of ligand compromises the robustness of the catalyst. After pyrolysis treatment, however, aromatic rings agglomerate to form extended graphene-like sheets. From literature we know that the E_{ads} of benzene on Au(111) is 0.63 eV (experiment)⁶⁰ and 0.48 eV (theory);⁶¹ in other words, ca. 0.08 eV per sp² atom. The E_{ads} of L1 (14 sp² atoms) on Au(111) in model **A** is 0.74 eV or 0.05 eV/sp², somehow smaller than that of benzene. The hypothetical merging of two L1 ligands (28 sp² atoms) would render a new species with a significantly larger E_{ads} of ~1.4 eV. In contrast to free ligand conditions, where ligands can be easily displaced, extended graphene-like sheets anchor to the surface, thus creating a stable and robust system while maintaining the nature of the catalytic active site.

Herein we use model **A** (Figure 4 inset) to properly mimic the N-doped (pyridinic) graphenelike sheets experimentally observed after pyrolysis. The proposed reaction mechanism is shown in Figure 4. Firstly, the alkyne **1a** interacts with the surface **A** with an energy of -0.69 eV (**B**). Although subsequent H₂ adsorption (**C**) is slightly endothermic by 0.23 eV, the N-assisted heterolytic H₂ activation (**TS-C**) is essentially barrierless, with a relative energy barrier of 0.07 eV above **C** (0.30 eV above **B**). Moreover, the formation of **D** is significantly exothermic by 0.71 eV. These results are in sharp contrast with the H₂ dissociation on pristine Au(111), where the energy barrier is 1.45 eV and the reaction energy is endothermic by 0.69 eV.²⁴ The absence of a direct interaction between the lone pair of the nitrogen and the gold surface (Au····N distances of ca. 3.3 Å) creates a unique interface that promotes the heterolytic cleavage. In that sense, we can relate this behavior to gold-based FLP chemistry.⁶² Then, the hydride from the surface **D** eventually transfers to the alkyne (**TS-D**) with a barrier of 0.36 eV and forms the alkenyl intermediate **E**. Final proton transfer from nitrogen to carbon has a barrier of 1.09 eV (**TS-E**) and

produces intermediate **F**, from which the product **2a** quickly desorbs (0.62 eV) and regenerates the initial species **A**. Overall, the present mechanism is in line with experiments and ilustrates the major role of nitrogen atoms during the H_2 activation process.



Figure 4. Computed reaction energy profile for the hydrogenation of **1a** on L1-functionalized Au(111) surface (Au = yellow, N = blue, C = grey, H = white).

CONCLUSIONS

We have prepared, for the first time, a N-doped carbon supported gold-based catalyst that exhibited excellent activity and selectivity for the hydrogenation of alkynes to alkenes, in a broad scope of substrates, at mild reaction condition. The intriguing structure of the novel gold heterogeneous catalyst, which could be understood as frustrated Lewis pairs (FLP) interfaces according to computational studies, enables the heterolytic activation of molecular hydrogen,

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boosting gold catalytic activity while avoiding addition of external ligands to improve activity and selectivity. The graphenization of the ligand ensures that it is present on the surface and not removed by the solvent or the reactants, which explains the robustness of the material under reaction conditions. We demonstrated that the heterolytic dissociation of H₂ can occur in a fullyheterogeneous catalyst, which will be economically and environmentally attractive. The Au@Ndoped carbon catalyst tolerates other reducible functional groups, including C–C double bonds, nitro, aldehydes, epoxides, ketones, nitriles, esters, heteroaromatic *N*-oxides and amides, and can be recycled without loss of activity. The surface-FLP concept is in its infancy when compared to main group-FLP^{32,63} and transition metal-based FLP,⁶⁴ but has shown many interesting features. The expansion of this concept for a broad range of applications in the field of heterogeneous catalysis is encouraged. New reactivity patterns, not limited to activation of H₂, will be soon explored.

EXPERIMENTAL SECTION

Procedure to preparation of Au-L/Support

Typically, Au(OAc)₃ (19 mg, 0.05 mmol) and amine ligand (18 mg, 0.1 mmol) (molar ratio Au:L = 1:2) were stirred in 20 mL of ethanol for approximately 5 minutes at 60 °C. The support was then added and the mixture was stirred for more 20 min. After, the solvent was dried by rotary evaporation. The as obtained solid was ground to a fine powder and then pyrolyzed under nitrogen atmosphere in the desired temperature in an oven at a rate of 10 °C per minute and held at temperature for 2 hours.

General procedure for alkynes hydrogenation

Unless otherwise stated a typical procedure for the semihydrogenation of alkynes is as follows: alkyne (0.14 mmol), Au catalyst (2 mol % Au), and 2 mL of solvent were placed in a modified Fischer–Porter 100 mL glass reactor. The reactor was purged five times with H₂, leaving the vessel at 6 bar. The resulting mixture was vigorously stirred and the temperature was maintained with an oil bath. After the desired time, the catalyst was removed by centrifugation and the products were analyzed by GC with an internal standard to determine the conversion of alkyne and the selectivity for alkene. To determine the isolated yield of the obtained products, after the reaction was complete, the solvent was evaporated and the crude reaction mixture was purified by column chromatography on silica gel to afford corresponding alkenes. ¹H confirmed the purity of the isolated products.

Computational details

All calculations were performed at Density Functional Theory (DFT) level using the Vienna Ab-initio Simulation Package (VASP).^{65,66} We use the PBE functional⁶⁷ supplemented with Grimme's D2 dispersion scheme⁶⁸ and refined parameters for transition metals.⁶¹ Core electrons were described by projector augmented wave (PAW) pseudopotentials⁶⁹ and valence electrons by a kinetic energy cutoff of 450 eV. The Au(111) surface was modeled by a (4×4) supercell with four-layer thick slabs, where the two upper layers were relaxed and the two bottom ones were fixed to mimic the bulk. The Brillouin zone was sampled by a $3\times3\times1$ k-points mesh, generated through the Monkhorst–Pack method.⁷⁰ To avoid spurious interactions between the periodic images, a vacuum region between the slabs of 15 Å and dipole correction along z were included.⁷¹ Transition states were located with the climbing image nudged elastic band (CI-NEB) method.⁷² The assessment of the minima and transition states was performed by diagonalizing the numerical Hessian matrix obtained by ± 0.015 Å displacements. Metal and ligand atoms were

fixed during frequency calculations. All inputs and final structures can be found in the ioChem-BD repository.^{73,74}

ASSOCIATED CONTENT

Supporting Information. These materials are available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website. Experimental details, additional experimental results, characterization of the catalyst (XRD, TEM, UV-vis), and L1/Au adsorption energies.

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