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Research Note

Origin of the superior hydrogenation selectivity of gold nanoparticles in alkyne + alkene mixtures: Triple- versus double-bond activation

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Abstract

DFT simulations have uncovered the origin of the highly selective character of gold nanoparticles in hydrogenation of triple bonds. This is ascribed to the better adsorption of C≡C at the edges of Au nanoparticles compared with C=C. Since the barriers for hydrogenation of triple and double bonds on gold are comparable, selectivity is determined by the binding energy of the reactants. The situation is less favorable over palladium (commercial hydrorefining catalyst), because both C=C and C≡C bonds are adsorbed on the Pd surface. The outcome of the simulations was demonstrated experimentally in mixtures with both propyne and propylene over a Au/CeO_2 catalyst, where C_3H_6 selectivities up to 95% were attained. Our finding opens a new path for chemoselective hydrogenation of molecules containing -yne and -ene groups on gold, with prospective application in petrochemical operations and in the fine chemical industry.

Keywords: Gold nanoparticles; Alkyne hydrogenation; Selectivity; Hydrorefining; Palladium; Steam cracking; DFT; Au/CeO_2

1. Introduction

Gold catalysis has emerged as one of the most exciting and fruitful research areas in chemistry [1,2]. Following initial low-temperature CO oxidation work [3], more sophisticated problems dealing with (chemo)selectivity have been tackled with supported gold nanoparticles. Relevant examples are the preferential oxidation of CO in H_2-containing feeds [4], the hydrogenation of C=O groups in α, β-unsaturated aldehydes and ketones to unsaturated alcohols [1,3], and the hydrogenation of aromatic nitro compounds to amines [5–7]. Yet another type of reactions where selectivity is an issue is that of hydrogenation of triple bonds in the presence of double bonds. These reactions are industrially relevant for hydrorefining of the different cuts produced in steam crackers [8]; for example, the C_2 cut typically contains 90% of ethylene and 0.5–3% of acetylene, whereas the C_3 cut contains 90% of propylene and 2–8% of propyne and propadiene. The concentrations of these highly unsaturated (alkyne and diene) compounds in the alkene stream should be brought down to <5 ppm, because they are undesirable in both chemical and polymer-grade propylene and ethylene.

Alkyne hydrogenation studies have classically focused on supported Pd catalysts [9], although other systems based on Pt, Cu, and Ni are also quite selective [9–11]. Palladium-based catalysts (e.g., 0.04 wt% Pd/Al_2O_3) are mostly used in industry for the gas- and liquid-phase hydrogenation of alkynes and dienes, gradually replacing the older nickel-based catalysts [12]. However, commercial hydrogenation catalysts are not 100% selective, suffering from problems of producing significant amounts of saturates and green oil. The saturates come from the over-hydrogenation of the alkynes and/or alkadienes and the hydrogenation of olefins to the corresponding alkanes. Green oil results from the oligomerization of alkynes, alkadienes, and/or olefins. Both saturates and green oil are undesirable owing to their adverse effect on the olefins-gain selectivity. Moreover, green oil is detrimental to the catalyst lifetime.

Supported gold catalysts (Au/Al_2O_3, Au/TiO_2, Au/Fe_2O_3) display remarkable performance in acetylene or propyne hydro-

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genation, with selectivities >90% to ethylene and propylene, respectively [13–15]. Jia et al. [13] demonstrated that the hydrogenation of acetylene and ethylene are decoupled in temperature over Au/Al_2O_3, in contrast to other monometallic systems, explaining the remarkable selectivity of gold catalysts. Those authors conducted $C_2H_4 + H_2$ and $C_2H_6 + H_2$ reactions over alumina-supported gold in a batch system, observing that the rate of selective hydrogenation of acetylene was 3 orders of magnitude greater than that of hydrogenation of ethylene at 523 K. The weak adsorption of ethylene on the surface of ultrafine gold particles was speculated as a possible reason for its poor hydrogenation activity. However, in none of these works was the olefin co-fed with the alkyne to demonstrate the catalyst's inability to prevent undesired olefin hydrogenation under more realistic conditions. This is required for establishing whether Au-based catalysts represent a competitive alternative to the commercial Pd-based system. Critically, a molecular-level understanding of the mechanism inducing the unique selectivity of gold catalysts in alkyne hydrogenations has not yet been attained.

In this work, we carried out density functional theory (DFT) simulations to elucidate the fundamental reasons behind the highly selective character of gold in the hydrogenation of triple bonds. The calculations over gold nanoparticle are compared with those over a palladium surface. The remarkable performance of gold is demonstrated experimentally in mixtures containing both -yne and -ene compounds over a reference Au/CeO_2 catalyst.

2. Methods

2.1. Computational details

DFT calculations have been performed [16] on different models (Fig. 1), including Au(111), Pd(111), Au_{rod} (1D infinite structure), and a Au_{19} cluster (ca. 1 nm diameter). The Au_{19} cluster shows the facets of nanosized particles in the catalysts, together with extremely low-coordinated atoms at the edges and corners, which have been reported to be the most active sites for CO oxidation [17]. The Au_{19} clusters have been calculated in a box of 17 × 15 × 12 Å with a single k-point, for the surfaces and the rod, k-point meshes of 5 × 5 × 1 and 3 × 3 × 1 were considered [18]. The energy profiles for the hydrogenation process have been studied within the PW91 functional [19]; the inner electrons are represented by PAW pseudopotentials [20], whereas the monoelectronic valence states have been expanded with plane waves with kinetic energies below 315 eV. The reaction paths have been sampled with the CI-NEB [21]. Previous calculations have indicated the presence of a barrier for H_2 dissociation on similar model clusters [22,23] smaller than that on the clean Au(111) surface.

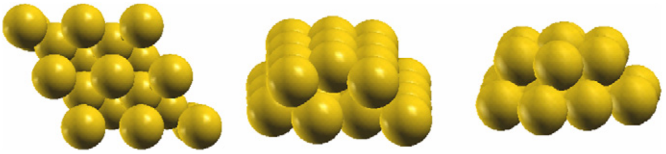

Fig. 1. Schematic representation of gold models: Au(111) (left), Au_{rod} (center), and Au_{19} (right).

2.2. Catalyst testing

The hydrogenation of propyne was carried out over a reference 2.6 wt% Au/CeO_2 catalyst (code SPC127) provided by the Instituto de Tecnología Química (Valencia, Spain). This material consists of a nanocrystalline CeO_2 support (particles of 4 nm; BET surface area of 180 $m^2\,g^{-1}$), with gold introduced by a deposition–precipitation method using $HAuCl_4$ as the gold precursor and NaOH as the precipitating agent. The average size of the Au nanoparticles is 4 nm, with a distribution in the range of 1–11 nm [4]. Catalytic activity was evaluated at ambient pressure in a MicroActivity Reference setup (PID Eng&Tech) using a quartz microreactor (12 mm i.d.). The catalyst sample (0.15 g; sieve fraction, 125–300 µm) was heated in He at 723 K for 30 min, cooled to 523 K in the same gas, and pretreated at this temperature in a mixture of 15 vol% H_2 in He for 60 min. The catalyst was tested isothermally at intervals of 50 K in the range 373–573 K starting at the highest temperature using feed mixtures of $C_3H_4/H_2/He = 2.5/7.5/90$ or $C_3H_4/C_3H_6/H_2/He = 2.5/2.5/7.5/90$, and a total gas flow rate of 42 ml STP min^{-1}. The product gases were analyzed by a gas chromatograph (Agilent GC6890N) equipped with a GS-GasPro column and a thermal conductivity detector. The C_3H_6 selectivity to propylene was determined as the amount of propylene formed divided by the amount of propyne reacted.

3. Results and discussion

The binding energies for double and triple carbon–carbon bonds on the gold models is very low (<0.24 eV, Table 1) unless Au_{19} is considered. On the latter, propyne is exothermically adsorbed by 0.42 eV and activated; the C≡C bond is elongated from 1.210 to 1.342 Å on adsorption (Fig. 2). In contrast, propylene is hardly bonded to the surface; the binding energy is close to zero, and the C=C deformation is accordingly smaller (0.06 Å). Hydrogenation of alkenes and alkynes has been classically described by the Horiuti–Polanyi mechanism [24], consisting of the successive addition of atomic hydrogen to the substrate. The calculated barrier for the first hydrogenation step is 0.49 eV for propyne and 0.63 eV for propylene. As expected, the second hydrogenation step is less demanding,

Table 1

Binding energy (in eV) of C_2 and C_3 molecules containing double or triple bonds to Au(111), Au_{rod}, Au_{19}, and Pd(111)

System	Molecule	C≡C	C=C
Au(111)	C_2	+0.13	+0.05
Au_{rod}	C_2	−0.24	−0.04
Au_{19}	C_2	−0.67	−0.01
Au_{19}	C_3	−0.42	−0.01
Pd(111)	C_2	−1.86	−0.86
Pd(111)	C_3	−1.69	−0.73

Positive values refer to endothermic adsorption while negative values refer to exothermic adsorption.

with barriers of 0.46 eV for propyne and 0.28 eV for propylene. These results are compared with the hydrogenation of propyne on Pd(111), for which only a 32% selectivity to propylene has been reported elsewhere [25,26]. The binding energies of C_3H_4 and C_3H_6 on Pd(111) are 1.69 and 0.72 eV, respectively. This is more than 0.5 eV larger than for Au nanoparticles, and both double and triple bonds are adsorbed on the Pd surface. The barriers for the first hydrogenation step are 0.64 eV for triple carbon bonds and 0.84 eV for double carbon bonds. The second hydrogenation step has a barrier of 0.66 eV for propyne and of 0.58 eV for propylene. Analogous calculations to those described for the C_3 system were performed over Au_{19} and Pd(111) for the C_2 system (acetylene–ethylene), leading to similar results.

From these data, it can be concluded that only C≡Cs are adsorbed and activated in the periphery of Au nanoparticles, whereas C=Cs are not bonded. In contrast, both triple and double bonds are adsorbed on Pd(111), in good agreement with the literature [26]. Thus, whereas on Pd, C=C and C≡Cs compete for the active sites, on Au nanoparticles, molecules containing C=C readily leave the catalyst, and only triple bonds can be hydrogenated. A priori, these results can be generalized to molecules in which both functional -yne and -ene groups are present. This finding is of relevance in the fine chemical industry, where hydrogenations of multiply unsaturated molecules should be practiced chemoselectively.

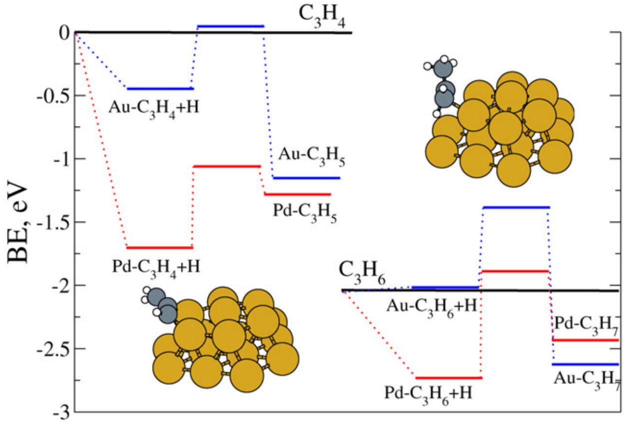

Fig. 2. Reaction scheme for the hydrogenation of propyne and propene on Au_{19} and Pd(111). The insets show the structure for adsorbed propyne and propene on the Au_{19} cluster.

DFT simulation results have been validated by catalytic hydrogenation tests in alkyne–alkene mixtures. As stressed in the Introduction, studies in the literature were conducted in alkyne–hydrogen mixtures. This situation is not realistic, because alkynes are accompanied by large amounts of olefins in the cuts from steam crackers. The performance of Au/CeO_2 for propyne hydrogenation is shown in Fig. 3. Selectivities to propene in the range of 80–95% are achieved, which remain practically constant in the temperature range of 473–573 K. These values of selectivity to the olefin are in good agreement with those reported for single-component acetylene and propyne hydrogenation over Au-based catalysts [13–15]. Remarkably, the reaction proceeds with slightly higher C_3H_6 selectivity (up to 95%) when propene is also added to the propyne–hydrogen mixture (Fig. 3, right). In contrast to the unchanged selectivity, the degree of propyne conversion depends strongly on the reaction temperature, approaching ca. 85% at 573 K and decreasing to ca. 50% at 523 K and 20% at 473 K. The presence of propene in the feed leads to a slightly decreased conversion over the range of temperatures studied. The degree of propyne conversion decreases rather rapidly with time on stream at 573 K, remaining stable at 523 and 473 K. In both mixtures, propyne conversions <10% are attained below 423 K. The reason for the dependence of activity on temperature is compatible with H_2 splitting being the rate-limiting step for the hydrogenation process.

In summary, we have demonstrated by means of experiments over Au/CeO_2 that supported gold nanoparticles are extremely selective for the hydrogenation of triple bonds in alkyne–alkene mixtures. DFT simulations prove that the observed activity and selectivity is related to the adsorption of only one of these components—that is, the one containing C≡C. This preferential adsorption also explains why selectivity is independent of the temperature, because neither ethene nor propene are adsorbed on the Au nanoparticles under these conditions. On this basis, gold catalysts can be considered a promising alternative

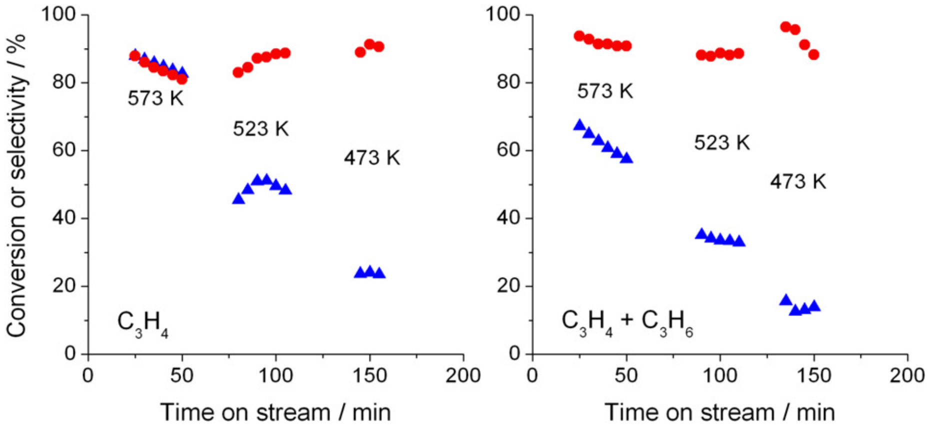

Fig. 3. Conversion of propyne (triangles) and selectivity to propylene (circles) at different temperatures during hydrogenation of propyne in the absence (left) or presence (right) of propylene. Conditions as described in Section 2.2.

to promoted Pd-based catalysts used industrially in the gas-phase deacetylenization of C_2 and C_3 cuts from steam crackers. The different optimal temperature windows of the catalysts (473–573 K for Au/CeO_2 and 293–393 K for Pd/Al_2O_3 [8]), which is likely related to the easier dissociation of hydrogen on palladium, does not enable a straightforward drop-in solution in current hydrorefining reactors. Accordingly, tuning gold-based catalysts for selective alkyne hydrogenation at lower temperatures with stable performance is a decisive aspect for successful implementation in industry.

Acknowledgments

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