Origin of the superior selectivity of gold nanoparticles for hydrogenation of triple bonds in alkyne-alkene mixtures

Yolanda Segura[1] , Núria López[1]* and Javier Pérez-Ramírez[1,2]*
[1] *Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain*
[2] *Catalan Institution for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain*
*jperez@iciq.es

Introduction

Catalysis by gold exemplifies the *nano* effect: the virtually inactive bulk gold metal radically changes when gold nanoparticles below 10 nm are stabilized [1]. Following the low-temperature CO oxidation, 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 and the hydrogenation of aromatic nitro compounds to amines. Yet another type of the reactions where selectivity is an issue is the hydrogenation of triple bonds in the presence of double bonds. The latter are industrially relevant for hydrorefining of C_2, C_3, C_4, and gasoline cuts produced by steam cracking. Gas and liquid-phase processes using promoted Pd catalysts are routinely performed in industry. However, these are not 100% selective, since part of the alkene is over-hydrogenated to the alkane.

Supported gold catalysts (Au/Al_2O_3, Au/TiO_2, Au/Fe_2O_3) display remarkable performance in acetylene or propyne hydrogenation, with selectivities >90% to the corresponding alkene [1,2]. However, in these experiments the olefin was not co-fed with the alkyne in order to demonstrate the inability of the catalyst for undesired olefin hydrogenation. Moreover insights into the mechanism inducing the unique selectivity of gold for triple-bond hydrogenations has not been attained. In this work we have carried out Density Functional Theory simulations in order to elucidate the reasons behind the selective character of gold nanoparticles in hydrogenation of triple bonds. This is confirmed experimentally in mixtures with both -yne and -ene compounds over a variety of supported gold catalysts.

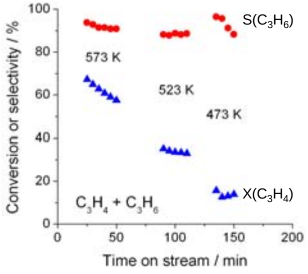
Materials and Methods

Gold-containing catalysts were prepared by coprecipitation, deposition-precipitation, and impregnation. Supports include nanocrystalline ceria and mixed oxides derived from the thermal activation of hydrotalcites. The samples were characterized by ICP, XRD, TEM, XPS, and N_2 adsorption. The hydrogenation of propyne was carried out in a quartz fixed-bed micro-reactor at ambient pressure, using different amount of catalyst and total gas flow. The sample was pretreated in 15 vol.% H_2 in He at 473 K for 1 h. Feed mixtures of $C_3H_4/H_2/He = 2.5/7.5/90$ and $C_3H_4/C_3H_6/H_2/He = 2.5/2.5/7.5/90$ were used. The product gases were analyzed by gas chromatography.

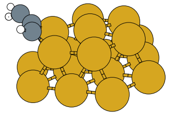
DFT calculations were performed on Au(111), Pd(111), Au_{rod}, and Au_{19} cluster. The latter contains facets of nanosized particles in the catalysts, together with extremely low-coordinated sites at the edges and corners [3]. The energy profiles have been studied within the PW91 functional and the reaction paths have been sampled with the CI-NEB.

Results and Discussion

The highly selective character of gold catalysts for hydrogenation of propyne in propyne-propylene mixtures is demonstrated over a Au/CeO_2 catalyst (see figure). Selectivities to propylene in the range of 85-95% were achieved, which remained practically constant with temperature. The degree of propyne conversion strongly depends on the reaction temperature, approaching ca. 85% at 573 K and decreasing to ca. 50% and 20% at 523 K and 473 K, respectively.



The origin of the unique selectivity of gold nanoparticles was uncovered by DFT simulations. The binding energy for double and triple C-C bonds on the various gold models was extremely low except for Au_{19}. On the latter, propyne is exothermically adsorbed by 0.42 eV (see figure). In contrast, the binding energy of propylene is practically zero. Hydrogenation of alkenes and alkynes consists on a sequential addition of hydrogen atoms, following the classical Horiuti-Polanyi mechanism. For example, the barrier for the first hydrogenation is higher for propylene (0.63 eV) than for propyne (0.49 eV). To compare these results with the commercial palladium catalyst, we have studied the hydrogenation of C_3 on Pd(111). Bond double and triple bonds are adsorbed on the Pd surface, with binding energies of 1.69 eV (C_3H_4) and 0.72 eV (C_3H_6). This is more than 0.5 eV larger than for Au_{19}. The barriers for the first hydrogenation are 0.64 and 0.84 eV for triple and double C-C bonds. Analogous calculations were performed over Au_{19} and Pd(111) for the C_2 system (ethyne-ethylene) and led to similar results. Accordingly, only C≡Cs are adsorbed and activated in the periphery of Au nanoparticles, while C=Cs are not bonded. In contrast, both are adsorbed on Pd(111). Thus while on Pd C=C and C≡Cs compete for the sites, on Au nanoparticles molecules containing C=C readily leave the catalyst surface and only triple bonds can be hydrogenated. Our results can be generalized to molecules where both functional groups are present. This finding opens a new path for chemoselective hydrogenation of molecules containing -yne and -ene groups.



An in-depth understanding of the reaction mechanism enables to design efficient Au-based catalysts for hydrorefining. We will show than an appropriate selection of the method for gold incorporation, support, and operating conditions enable to obtain a catalytic process with stable C_3H_6 selectivities of 90% at 100% C_3H_4 conversion.

Significance

Gold catalysts are an attractive alternative to the commercial palladium catalysts for the gas-phase deacetylenization of C_2 and C_3 cuts from steam crackers.

References

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