Hydrogenation on gold catalysts made easy: activation of H$_2$
via frustrated Lewis pairs

L. M. Rossi$^1$, N. López$^2$, R. J. M. Silva$^1$, J. L. Fiorio$^1$

$^1$Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, São Paulo, Brazil
$^2$Institute of Chemical Research of Catalonia – ICIQ, Tarragona, Spain

The dissociation of molecular hydrogen, a crucial step in hydrogenation reactions, is not favorable on gold surfaces; though nanostructuring can improve it, high temperature is still required. The concept of ‘frustrated Lewis pairs’ (FLPs) was introduced a decade ago [1] to explain the activation of small molecules, such as H$_2$, through an ‘encounter complex’ where a Lewis acid (LA) and Lewis base (LB) are in close proximity, but prevented from forming a strong classical adduct. Stephan and co-workers [1] reported the heterolytic cleavage of H$_2$ at room temperature with FLPs of phosphorus and boron compounds. The concept has expanded rapidly from main group-FLP to metal-based FLP [2], in which the metal complex promotes the heterolytic cleavage of H$_2$ producing a hydride (delivered to a metal center) and the proton is incorporated into the ligand (e.g., amine protonation). FLP are also present in biological reactions, e.g. hydrogenases, where the heterolytic H$_2$ cleavage occurs under mild conditions.

We recently proposed that heterolytic dissociation of H$_2$ is promoted by ligands adsorbed on gold surfaces, which expands the FLP concept to gold catalysis [3]. The heterolytic cleavage of H$_2$ contrasts with the homolytic cleavage of H$_2$ commonly observed on metal surfaces of traditional heterogenous catalysts (platinum group metals), but opens up the possibility to explore less active metals that are not prone to dissociate H$_2$. We first found that the addition of nitrogen-containing bases to silica supported Au NPs made hydrogenation reactions possible to occur under mild conditions. This activity was not seen in blank experiments with gold catalyst only. We proposed that H$_2$ is heterolytically activated on the gold-ligand interface and the so-formed tight-ion pair could be selectively transferred to an alkyne in a cis configuration controlled by electrostatic interactions leading to the corresponding Z-alkene. Using DFT calculations, we were able to show that the catalytic activity correlates with H$_2$ dissociation energy, which depends on the basicity of the ligand and on the reorganization energy of the ligand on the surface required to activate hydrogen. We were able to disclose a remarkable promotional effect of nitrogen-containing bases with two heteroatoms as a new ligand-based strategy to boost gold activity. After that, the versatile FLP concept applied to gold catalysis made easy the hydrogenation of many functional groups such as alkyne-to-alkene, epoxide-to-alkene, aldehyde-to-alcohol, N-oxide-to-amine, etc. under mild conditions (Figure 1). Different ligands were explored and selected examples of successful hydrogenations catalyzed by gold will be discussed.

![Figure 1. Activation of gold catalysts for hydrogenations via FLP.](image)

References

This work was supported by FAPESP, CNPq and CAPES.
Corresponding author email: lrossi@iq.usp.br