

Rational Design of Bimetallic Gold-Platinum Catalysts for the Chemoselective Hydrogenation of Substituted Nitroaromatics

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Introduction

The discovery of gold catalysts for carrying out the chemoselective hydrogenation of nitroaromatic compounds has opened new possibilities for the production of substituted anilines and related derivatives [1]. Unfortunately, the activity of gold catalysts to perform this reaction was claimed to be too low for practical applications [2], and further efforts have been focused on providing more active, while still chemoselective, alternatives [3].

Recently, we studied at atomic scale the way that nitroaromatic compounds and H₂ interact on the surface of Au/TiO₂ catalysts, showing that while the nitro group is activated through the support at Au/Ti boundaries [4, 5], H₂ molecules are dissociated on low-coordinated Au atoms on the surface of gold nanoparticles [6]. Thus, in order to design a more active gold catalyst, one should know if the controlling step of the reaction is the rate for selectively adsorbing the substituted nitroaromatic, the rate of H₂ dissociation, or the rate of the surface reaction between both reactants.

In the present work we have carried out a detailed kinetic and isotopic study to understand the macrokinetic behaviour of the Au/TiO₂ system, which has allowed redesigning the catalyst and increasing its intrinsic activity one order of magnitude without loss of chemoselectivity.

Materials and Methods

Main kinetic study of the present work was done using the Au/TiO₂ sample provided by the World Gold Council. Additionally, other gold catalysts were prepared using a deposition-precipitation technique [7], while some bimetallic Au-Pt/TiO₂ materials were obtained after impregnating Au/TiO₂ with small amounts of H₂PtCl₆.

Kinetic measurements on the hydrogenation of nitrobenzene were performed in liquid phase using a batch reactor, and the evolution of composition with reaction time was determined by taking samples at different times on stream, which were analyzed by gas chromatography. The influence of reaction conditions (initial concentration of nitrobenzene in the feed, H₂ pressure, and reaction temperature) on the reaction rate was studied to elucidate a proper kinetic model, based on the Langmuir/Hinshelwood-Hougen/Watson approach.

H/D exchange experiments were carried out to estimate the capacity of different Au/TiO₂ catalysts for dissociating H₂, according to the procedure depicted in [8].

Results and Discussion

Taking into account previous knowledge on the Au/TiO₂ mode of action during the hydrogenation of nitroaromatic compounds [4, 5, 6], a plausible initial set of kinetic models was proposed. According to the observed influence of the nitrobenzene concentration and the H₂ pressure on the reaction rate, it was inferred that the activation of H₂ onto the catalyst surface could be the controlling step of the whole process. Confirming this scenario, H/D

exchange experiments on a series of different Au/TiO₂ catalysts showed a direct correlation between their capacity to dissociate H₂ and their activity to hydrogenate nitroaromatic compounds. According to the proposed model, kinetic parameters (kinetic and adsorption constants) were finally determined at several reaction temperatures, allowing to estimate the corresponding activation energies.

Thanks to this exhaustive kinetic study, we considered the possibility to improve the behavior of gold catalysts by designing a bifunctional Au-Pt/TiO₂ system, where the nitro group was selectively activated at Au/Ti boundaries, and the H₂ dissociation took place on very active Pt sites. After optimizing the loading of Pt, we found that when very small amounts of this metal are used, the activity of the Au/TiO₂ catalyst is raised one order of magnitude, keeping excellent levels of chemoselectivity. Moreover, it can be demonstrated that main properties of the hybrid material for activating the nitro group are still related to Au/Ti interphases, while Pt exclusively behave as an efficient supplier for pre-activated hydrogen species, which allows overcoming the rate-controlling step of Au/TiO₂ catalysts.

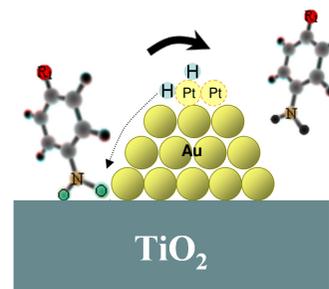


Figure 1. Representation of the Au-Pt/TiO₂ catalysts mode of action during the hydrogenation of substituted nitroaromatics. A cooperative behavior between Au/Ti boundaries (selective activation of the nitro group) and Pt sites (rapid dissociation of H₂) seems to be responsible of the high levels of activity and chemoselectivity achieved.

Significance

The present advance has a direct impact in the industrial production of substituted anilines. The proposed Au-Pt/TiO₂ system represents the most active solution, up to now, for carrying out the chemoselective hydrogenation of nitroaromatic compounds, offering the opportunity to perform this challenging reaction through environmentally friendly technology, and under industrially profitable reaction conditions (85 °C, 4 H₂ bar, and solvent-free media).

References

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