

Influence of the Support during Homocoupling of Phenylboronic Acid Catalyzed by Supported Gold and Palladium

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Introduction

Coupling reactions are largely dominated by the use of palladium catalysts and are a powerful and versatile tool in synthetic organic chemistry for the formation of carbon-carbon bonds [1]. Among the different coupling reactions, the Suzuki reaction plays important roles because of the formation of biaryls which are relevant for active pharmaceuticals, herbicides, conducting polymers, and liquid crystals [2]. Biaryls can be prepared by two different types of reactions: homocoupling or cross-coupling. Some of us recently reported that supported gold catalyzes the homocoupling of phenylboronic acids with high conversion and selectivity [3]. Two possible reaction mechanisms were postulated for the homocoupling of phenylboronic acid on Au/CeO₂ catalysts, for both mechanisms, Au³⁺ was suggested to be present in the active site. Although the support was shown to influence the stabilization of the active sites and therefore the catalytic activity, it was not clear whether the support facilitates the water that is required to hydrolyze the boronic acid through surface hydroxyl groups.

In the present work, we report the influence of the crystallite size, degree of hydroxylation, and crystallinity of TiO₂, ZrO₂, CeO₂, and SiO₂ on the conversion and selectivity during the homocoupling of phenylboronic acid catalyzed by supported gold and palladium. Moreover, we compare the results for equivalent supported catalysts containing either gold or palladium and investigate the influence, if any, that the support has for the catalytic activity.

Materials and Methods

Colloidal dispersions of CeO₂, TiO₂, and ZrO₂ (10 wt% of metal oxide) were used to obtain nanocrystalline metal oxides with average crystallite size of 5–10 nm [3]. Gold or palladium were deposited (1 wt% of metal) on the different metal oxide supports by deposition-precipitation using a solution of HAuCl₄ or Pd(NO₃)₂ at constant pH of 9. The supports and catalysts were characterized by N₂ adsorption, XRD, TEM, XPS, and UV-vis and FTIR spectroscopy. The reaction was carried out at 333 K and atmospheric pressure. Toluene, the catalyst, phenylboronic acid, K₂CO₃, and *p*-iodobenzophenone were mixed in a reaction flask. The products were determined by gas chromatography-mass spectroscopy (GC-MS) analysis using decane as internal standard.

Results and Discussion

Nanoparticles of gold with an average diameter of 20 nm were supported on nanocrystalline (crystallite sizes of about 10 nm) TiO₂, CeO₂, ZrO₂, and SiO₂ as determined by TEM and XRD. Similarly, nanoparticles of palladium (average diameter of 25 nm) were supported on nanocrystalline TiO₂, CeO₂, ZrO₂, and SiO₂. As a reference, supported gold and supported palladium catalysts were prepared using conventional metal oxide supports

(crystallite size of about 30–50 nm). XPS, UV-vis spectroscopy, and FTIR during CO adsorption indicate the presence of cationic gold (Au³⁺) in the fresh gold catalyst [4]. The samples were tested for the Suzuki homocoupling reaction and the conversion and selectivity of the supported gold and palladium catalysts are shown in Figure 1. Under the same reaction condition, the supported palladium catalysts are less active than the supported gold catalysts. Furthermore, the palladium catalysts show a selectivity of about 75 % with formation of benzene and phenol as byproducts. However, when supported gold is used for the reaction, a selectivity of 100 % towards biphenyl is obtained in all cases except when SiO₂ is used as support. We will present a mechanistic explanation for our observations and the role of the support during catalysis.

Significance

This work is relevant for the design of new supported metal catalysts for the synthesis of complex organic molecules that are significant for the fine-chemistry industry.

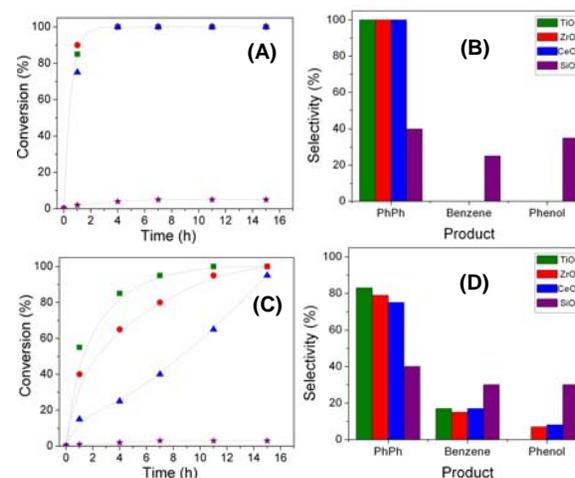


Figure 1. Influence of the support on the homocoupling of phenylboronic acid catalyzed by gold and palladium. (A) Reaction catalyzed by supported gold and (C) supported palladium [TiO₂ (green squares); ZrO₂ (red circles); CeO₂ (blue triangles); and SiO₂ (purple stars)]. Selectivity during the homocoupling reaction catalyzed by (B) supported gold and (D) supported palladium. Temperature of 333 K and 1 atm.

References

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