

Hydroxyapatite-Supported Silver Nanoparticle Catalyst for Selective Hydration of Nitriles to Amides in Water

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Introduction

Metal nanoparticles (NPs), which reside in the size range between bulk and monomeric metal species, are applied in a wide range of technologies, from electronic, optic and magnetic devices, to advanced catalytic materials. Currently, metal NP catalysts are receiving much attention for use in organic syntheses under liquid-phase conditions. For example, gold NPs have been shown to facilitate catalysis in many organic reactions. On the other hand, there have been few studies on the prominent catalytic activity of Ag NPs for other organic reactions, except for the gas-phase epoxidation of ethylene. Our group has focused on the catalytic potential of Ag NPs, and found that supported Ag NPs show high catalytic activity for the dehydrogenation of alcohols[1], and the selective oxidation of silanes to silanols using water[2] under liquid-phase conditions. The present report demonstrates that hydroxyapatite (HAP)-supported Ag NPs (AgHAP) can catalyze hydration of nitriles to amides in water with high efficiency. Hydration of nitriles into the corresponding amides is of great importance in organic syntheses, because amides are versatile synthetic intermediates used in the production of pharmacological products, polymers, detergents, lubricants, and drug stabilizers. However, traditional catalyst systems have required organic solvents in the presence of homogeneous strong acid and base catalysts, which causes over-hydrolysis of amides into undesirable carboxylic acids, and the formation of a large amount of salts after neutralization of the catalysts. Therefore, much effort has been expended on the development of effective metal-catalysts for the hydration of nitriles. This hydration method, using a reusable Ag catalyst under neutral conditions with water as the solvent, can make a significant contribution to establish a more environmentally-benign and industrially-acceptable process.

Materials and Methods

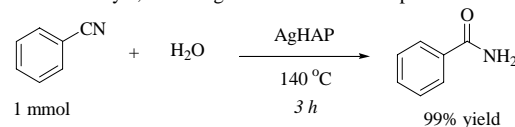
AgHAP was synthesized as follows: 2.0 g of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (HAP) was added to a 150 mL of aqueous solution of AgNO_3 (6.7×10^{-3} M) and stirred at room temperature for 6 h. The obtained slurry was filtered, washed, and dried at room temperature in vacuo. Reduction with an aqueous solution of KBH_4 yielded HAP-supported Ag (Ag 3.3 wt%).

A typical procedure for the hydration of benzonitrile using the AgHAP catalyst was as follows: AgHAP (0.10 g, 0.03 mmol Ag) was placed in a reaction vessel, followed by the addition of water (3 mL) and benzonitrile (1 mmol), and the reaction mixture was vigorously stirred at 140 °C for 3 h under Ar.

Results and Discussion

The catalytic activity of Ag^0 NPs formed on different supports was examined in the hydration of benzonitrile under aqueous conditions without organic solvents. AgHAP was

found an effective catalyst, affording benzamide as a sole product in a 99% yield (Scheme 1).

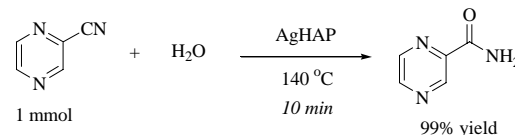


Scheme 1.

The use of Ag/TiO_2 in place of AgHAP showed a relatively high conversion of benzonitrile (93% conversion); however, benzoic acid was formed as a side product via over-hydrolysis of benzamide. Ag/MgO (59%), Ag/SiO_2 (37%) and Ag/C (30%) were significantly less active. The hydration reaction did not proceed using HAP and Ag^+HAP without a reduction treatment.

After filtration of the reaction mixture containing AgHAP at a 40% conversion of benzonitrile, further stirring of the filtrate at 140 °C for 3 h did not yield any additional products, and no Ag species was detected in the filtrate by inductively coupled plasma spectroscopy (ICP) analysis. These results show that the combination of Ag^0 NPs with HAP is essential for efficient hydration, and the hydration proceeds at the Ag NPs on the surface of HAP.

The hydration of heteroaromatic nitrile was carried out using the AgHAP catalyst. It is notable that pyrazinecarbonitrile was effectively converted into the corresponding amides within only 10 min, and no accompanying carboxylic acids were detected (Scheme 2).



Scheme 2.

The AgHAP catalyst system was also applicable for scaled-up conditions; pyrazinecarbonitrile (100 mmol; 10.5 g) was successfully converted to the amide (97% isolated yield; 12.0 g) and the turnover number (TON) reached over 10000. Furthermore, AgHAP was easily separated by centrifugation after hydration of pyrazinecarbonitrile, and could be reused four times without loss of catalytic activity and selectivity.

Significance

AgHAP acted as a highly efficient heterogeneous catalyst for hydration of diverse nitriles into amides in water.

References

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2. Mitsudome, T., Arita, S., Mori, H., Mizugaki, T., Jitsukawa, K., Kaneda, K. *Angew. Chem. Int. Ed.* 47, 7938 (2008)