



Hydration of nitriles to amides in water by SiO₂-supported Ag catalysts promoted by adsorbed oxygen atoms

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ABSTRACT

A series of silica-supported silver catalysts with similar Ag loading (5 or 7 wt%) but with different preparation methods (calcination in air and reduction by H₂ or NaBH₄) were prepared, and their structure was characterized by microscopy (STEM), X-ray absorption fine structure (XAFS), and CO-titration of surface oxygen atom. Ag is present as metal nanoparticle with a size range of 17–30 nm. Their surface was partially covered with oxygen atoms, and the surface coverage of the oxygen depends on the preparation condition. For hydration of 2-cyanopyridine as a test reaction, turnover frequency (TOF) per surface Ag species is estimated. TOF does not show a good correlation with Ag particle size, but it linearly increases with the coverage of the surface oxygen atoms on Ag particles. The Ag/SiO₂ catalyst prepared by H₂ reduction at 700 °C shows the highest TOF and it acts as effective and recyclable heterogeneous catalyst for selective hydration of various nitriles to the corresponding amides. Kinetic and Raman spectroscopic studies suggest that the surface oxygen atom adjacent to Ag⁰ sites plays an important role in the dissociation of H₂O.

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1. Introduction

Hydration of nitriles to the corresponding amides is an important transformation from both organic chemistry and industrial points of view. Conventional methods of nitrile hydration with strong acid or base catalysts have drawbacks such as over-hydrolysis of amides into carboxylic acids and the formation of salts after neutralization of the catalysts [1]. Homogeneous catalytic systems using complexes [2–7] and colloids [8,9] of transition metals under neutral conditions have been reported. However, they have disadvantages such as difficulty in catalyst/product separation, use of organic solvent, high price of ligands and platinum group metals, and low activity for hydration of heteroaromatic nitriles because of their strong coordination to the metal centers. Use of recyclable heterogeneous catalyst in water is an ideal system from environmental and practical viewpoints [10–18]. Previously, Sugiyama et al. [11] reported that hydration of acrylonitrile by SiO₂-supported Ag catalyst gave 100% selectivity to acrylamide at 75 °C, though its activity was much lower than other metal catalysts. Mitsudome et al. [15] developed hydroxyapatite-supported Ag nanoparticles (AgHAP) which effectively catalyzed the selective

hydration of aromatic and heteroaromatic nitriles, though the catalyst was not effective for less reactive aliphatic nitriles.

Unsupported or supported large Ag particles are well established catalysts for partial oxidation reactions and are the commercial catalysts for production of ethylene oxide and formaldehyde [19]. Salts of Ag(I) are effective homogeneous Lewis acid catalysts in organic synthesis [20]. In the research area of organic synthesis, however, less attempts have been focused on catalytic properties of metallic Ag species [15,21,22] (nanoparticles and nanoclusters) compared with well known catalysts based on platinum-group-metals, Ni, Cu, and Au. Our group has paid attention to unique catalytic properties of Ag clusters for a series of organic reactions involving C–H and H–H activation as a key step, such as dehydrogenation of alcohols, one-pot C–C and C–N bonds formation reactions using alcohols, and selective hydrogenation. We have found general tendencies that Ag clusters with size below a few nanometers give higher TOF than larger Ag nanoparticles, which indicates that coordinatively unsaturated Ag atom plays an important role [22]. In contrast, Mitsudome et al. [15,21] reported that relatively large Ag nanoparticles (7.6 nm) on HAP showed significantly high activity for selective hydration reactions (silanes to silanols and nitriles to amide). These findings lead us to hypothesize that relatively large Ag metal particles may have a specific site for dissociative activation of water. However, experimental and theoretical studies of water adsorption on Ag surfaces have established that water dissociation does not occur on clean Ag surfaces [23,24] but occurs on the Ag surface precovered with oxygen

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