



Metal oxide-catalyzed ammoxidation of alcohols to nitriles and promotion effect of gold nanoparticles for one-pot amide synthesis

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ABSTRACT

Transition metal oxides (MnO₂, Co₃O₄, and NiO) are catalytically active for the ammoxidation of alcohols to nitriles. In particular, MnO₂ exhibited remarkably high catalytic activity and selectivity for the ammoxidation of alcohols to produce nitriles. Benzyl alcohol could also be directly converted to benzonitrile by MnO₂ catalyst by the one-pot ammoxidation and the hydration with water which was formed by the first ammoxidation step. The deposition of gold nanoparticles (Au NPs) onto MnO₂ did not enhance the ammoxidation of benzyl alcohol but promoted the hydration of benzonitrile to produce benzamide with high selectivity. In contrast, Au NPs supported on Al₂O₃, CuO, and CeO₂ catalyzed the ammoxidation of benzyl alcohol, whereas these metal oxides themselves were inactive for the ammoxidation or showed low catalytic activity. These results have demonstrated that gold is intrinsically active as a catalyst for the ammoxidation of alcohols.

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1. Introduction

Nitriles and amides are important class of organic compounds for chemical industries. Nitriles are generally produced by the ammoxidation of alkenes or alkanes over Bi–Mo mixed oxides in gas phase [1]. Some aromatic nitriles such as *m*-tolunitrile and cyanopyridines (nicotinonitrile) are synthesized by the ammoxidation of methyl groups connected to the aromatic rings over vanadium-based oxide catalysts in gas phase [2]. However, these ammoxidation methods are hardly applied to the production of aliphatic nitriles. They are generally produced by the condensation of carboxylic acids or esters with ammonia (NH₃) to form amides followed by the dehydration of amides over metal oxides at temperatures above 300 °C [3].

In laboratory, on the other hand, there are many synthetic routes for nitriles such as the substitution of alkyl halides with metal cyanides. Oxidative conversion of primary amines to the

corresponding nitriles has also been known by using stoichiometric oxidants such as Ag₂O and Pb(OAc)₂. One of the other methods is the ammoxidation of aldehyde in the presence of stoichiometric oxidants such as MnO₂ with MgSO₄ [4]. Since aldehydes are produced by the oxidation of alcohols, the direct conversion of alcohols to produce nitriles is preferred and has been studied by using NiSO₄/K₂S₂O₈–NaOH [5], I₂ with 1,3-diiodo-5,5-dimethylhydantoin [6], nickel–copper formate with (Bu₄N)₂S₂O₈ [7], and MnO₂ with MgSO₄ [8]. However, these methods have drawbacks that they need stoichiometric amount of oxidants.

Recently, Mizuno et al. [9,10] reported the catalytic ammoxidation of alcohols into nitriles followed by the hydration of nitriles with an excess amount of water to yield amides over ruthenium hydroxide supported on Al₂O₃. Since Au catalysts have been reported to be active for alcohol oxidations in the presence of amine to yield imine [11,12] and for direct amide synthesis from alcohol with amine [12–15], we have attempted to apply Au catalysts to alcohol oxidation in the presence of NH₃ to produce nitrile and amide. During the course of our investigation, we found that MnO₂, Co₃O₄, NiO, CuO catalyzed the ammoxidation of alcohols without the deposition of Au. Manganese dioxide is well known as a stoichiometric oxidant that can be used for nitrile synthesis from alcohols with NH₃. However, a large excess (more than 15 equimolar amount of substrates) of MnO₂ has to be used [8]. In addition, the substrates were limited to benzylic alcohols and unsaturated alcohols. Whereas metal oxides such as MnO₂ [16–20], Co₃O₄ [21,22],

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