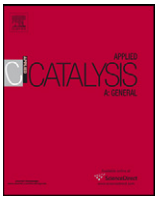
Applied Catalysis A: General 425–426 (2012) 85–90

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



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

Tamao Ishida[a,c,*], Hiroto Watanabe[b], Takashi Takei[b,c], Akiyuki Hamasaki[a,c], Makoto Tokunaga[a,c], Masatake Haruta[b,c,**]

[a] *Department of Chemistry, Graduate School of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*
[b] *Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan*
[c] *Japan Science and Technology Agency (JST), CREST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

ARTICLE INFO

Article history:
Received 29 December 2011
Received in revised form 26 February 2012
Accepted 2 March 2012
Available online 10 March 2012

Keywords:
Metal oxides
Gold nanoparticles
Ammoxidation
Nitrile hydration
Alcohol

ABSTRACT

Transition metal oxides (MnO_2, Co_3O_4, and NiO) are catalytically active for the ammoxidation of alcohols to nitriles. In particular, MnO_2 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 MnO_2 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 MnO_2 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 Al_2O_3, CuO, and CeO_2 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.

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 (NH_3) 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 Ag_2O and $Pb(OAc)_2$. One of the other methods is the ammoxidation of aldehyde in the presence of stoichiometric oxidants such as MnO_2 with $MgSO_4$ [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 $NiSO_4/K_2S_2O_8$–NaOH [5], I_2 with 1,3-diiodo-5,5-dimethylhydantoin [6], nickel–copper formate with $(Bu_4N)_2S_2O_8$ [7], and MnO_2 with $MgSO_4$ [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 Al_2O_3. 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 NH_3 to produce nitrile and amide. During the course of our investigation, we found that MnO_2, Co_3O_4, 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 NH_3. However, a large excess (more than 15 equimolar amount of substrates) of MnO_2 has to be used [8]. In addition, the substrates were limited to benzylic alcohols and unsaturated alcohols. Whereas metal oxides such as MnO_2 [16–20], Co_3O_4 [21,22],

---

* Corresponding author at: Department of Chemistry, Graduate School of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan. Tel.: +81 92 642 7528; fax: +81 92 642 7528.

** Corresponding author at: Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan. Tel: +81 42 677 2852; fax: +81 92 677 2852.

E-mail addresses: tishida@chem.kyushu-univ.jp (T. Ishida), haruta-masatake@center.tmu.ac.jp (M. Haruta).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.03.006

and NiO [23] have been revealed to be catalytically active for the aerobic oxidation of alcohols, catalytic ammoxidation of alcohol over these metal oxides is very limited. Very recently, Mizuno and his co-workers demonstrated that the amide synthesis from primary alcohol was catalyzed over manganese oxide based molecular sieves via the ammoxidation of alochols to nitriles [24]. However, excess amount of Mn (ca. 2 equiv.) was still required.

In this paper, we report the catalytic performance of MnO_2, Co_3O_4, and NiO for the ammoxidation of alcohols including unactivated alcohols. Since MnO_2 can be used for hydration of nitriles [25–30], the one-pot synthesis of an amide from an alcohol over MnO_2 was also investigated. We also found that metal oxide-supported Au catalysts promoted the ammoxidation of an alcohol to produce a nitrile and an amide.

2. Experimental

2.1. Materials

Reagent grades, $Mn(NO_3)_2{\cdot}6H_2O$, $KMnO_4$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, Na_2CO_3, NaOH, urea, were used as received. Molybdenum oxide (MoO_3) was supplied by Kojundo Chemical Laboratory Co., Ltd. High purity nanoparticulate CeO_2, TiO_2 (P-25), and Al_2O_3, were supplied by Daiichi Kigenso Kagaku Kogyo, Nippon Aerosil Co., Ltd., and JGC Catalysts and Chemicals Ltd., respectively. Vanadium oxide (V_2O_5) was purchased from Kanto Chemical Co. Tetrachloroauric acid tetrahydrate ($HAuCl_4{\cdot}4H_2O$) was purchased from Tanaka Kikinzoku KKK and used as received. Benzyl alcohol, cinnamyl alcohol, 2-pyridine methanol, 2-thiophene methanol, 1-octanol, and toluene (dehydrated grade) were purchased and used without further purifications.

2.2. Instruments

Specific surface area was obtained from nitrogen adsorption measurements. The samples were pretreated under vacuum at 200 °C for 2 h. Then, N_2 adsorption isotherms were measured at 77 K with a SHIMADZU Tristar. X-ray powder diffraction (XRD) patterns were obtained by Rigaku RINT-TTR III at a scanning rate of 2°/min and a sampling angle interval of 0.02° in 2θ ranging from 10° to 80° with high-intensity Cu Kα radiation ($\lambda = 0.151478$ nm). The operating voltage and current were 50 kV and 300 mA. The phase of components was identified by matching diffraction patterns to the JCPDS powder diffraction file. The conversions and product yields were measured by gas chromatography by using Agilent GC-7890A with HP-5 capillary column (0.32 mm i.d., 30 m, 0.25 μm thickness) using anisole as an internal standard. Qualitative analysis was performed with a GC–MS (SHIMADZU PARVUM2 and GC-2010 with Shinwa Chemical ULBON HR-1 capillary column, 0.25 mm i.d., 30 m).

2.3. Catalyst preparation

2.3.1. Metal oxides

Ferric oxide (Fe_2O_3), Co_3O_4, CuO, and NiO were prepared by the neutralization method. Briefly, an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (0.1 M, 200 mL) was rapidly added into an aqueous solution of Na_2CO_3 (0.1 M, 240 mL) at 70 °C and the mixture was stirred at 70 °C for 1 h. The precipitate was washed with distilled water, filtered, dried at 100 °C overnight, and then calcined in air at 300 °C for 4 h. Cobalt oxide (Co_3O_4) was prepared in a similar manner except for aging at room temperature.

For the preparation of MnO_2, an aqueous solution (500 mL) of $KMnO_4$ (0.2 mol) and NaOH (0.6 mol) was added to an aqueous solution (500 mL) of $Mn(NO_3)_2{\cdot}6H_2O$ (0.3 mol) at room temperature [31]. The mixture was stirred at room temperature for 1 h. The precipitate was collected by filtration, dried at 65 °C overnight, and then calcined in air at 300 °C for 4 h.

2.3.2. Deposition of gold onto metal oxides

Gold on NiO and Au/CuO were prepared by the co-precipitation (CP) [32]. Gold on Co_3O_4 was prepared by a similar manner to Au/NiO except for precipitaion and aging at room temperature for aging. Gold on CeO_2 and Au/Al_2O_3 were prepared by the deposition–precipitation (DP) method [33].

Gold on MnO_2 was prepared by the homogeneous deposition–precipitation (HDP) with urea [34]. To an aqueous solution (200 mL) of $HAuCl_4$ (0.3 mmol) and urea (60 mmol) was added MnO_2 (1.1 g, Au 5 wt%) at room temperature. The suspension was gradually warmed to 90 °C and stirred for 16 h. The solid was washed with water, dried at 65 °C overnight, and then calcined in air for 4 h.

2.4. Catalytic test

2.4.1. Ammoxidation of alcohol to nitrile

To an autoclave was charged benzyl alcohol (50 μL, 0.5 mmol), toluene (3 mL), metal oxide catalysts (20 mg), and a magnetic stirring bar. The autoclave was purged and filled with NH_3 until the pressure reached 0.85 MPa. Then O_2 was introduced until the total pressure reached to 1.35 MPa (pO_2 0.5 MPa). The reaction mixture was stirred at a controlled temperature. After the reaction, the mixture was extracted with Et_2O and filtered. The filtrate was analyzed by GC–MS and GC by using anisole as an internal standard. For recycling tests, the catalyst was filtered after the reaction, washed with acetone for three times, dried under vacuum, calcined in air at 300 or 400 °C for 4 h, and then used for the next run.

2.4.2. One-pot synthesis of benzamide from benzyl alcohol

After the nitrile formation at 100 °C for 1 h, the reactant gases were released. Then the autoclave was purged and filled with N_2. The reaction mixture was stirred again at 100 °C. The mixture was extracted with Et_2O and toluene, and then filtered. The filtrate was measured by GC–MS and GC using anisole as an internal standard.

3. Results

3.1. Ammoxidation of benzyl alcohol to benzonitrile over metal oxides

Various kinds of metal oxides have been screened for the ammoxidation of benzyl alcohol (**1**) (Table 1). Although V_2O_5 (entry 3), Fe_2O_3 (entry 9) and MoO_3 (entry 13) are active for the gas phase ammoxidation of alkanes and alkenes, they can not catalyze the ammoxidation of an alcohol in liquid phase. Among the metal oxides, MnO_2 (entry 4) and Co_3O_4 (entry 10) promoted the reaction to yield benzonitrile (**2**) with remarkably high selectivity. The reaction also proceeded in the presence of NiO. However, benzaldehyde (**3**) and *N*-benzylidenebenzylamine (imine, **5**) were also formed as by-products (entry 11). In particular, MnO_2 exhibited superior catalytic activity and selectivity to the nitrile. Namely, the ammoxidation reaction completed within 30 min over MnO_2 (entry 5) while it completed after 4 h in the presence of Co_3O_4 (entry 10). The catalytic activity order was as the same as that for alcohol oxidation in the absence of NH_3 (data are not shown). Toluene, which was used as a solvent, was not converted to benzonitrile under our conditions.