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

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ARTICLE INFO

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.

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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 (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],

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.

Table 1
Catalytic performance of metal oxides for the ammoxidation of benzyl alcohol.[a]

Entry	Catalyst	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)[b]			
					2	3	4	5
1	Al_2O_3	100	4	0	0	0	0	0
2	TiO_2	100	4	2	0	2	0	0
3	V_2O_5	100	4	0	0	0	0	0
4	MnO_2	100	4	100	96	1	0	0
5	MnO_2	100	0.5	100	100	0	0	0
6[c]	MnO_2	100	0.5	86	78	0	0	0
7	MnO_2	60	1	56	48	1	0	0
8[d]	MnO_2	60	1	56	47	1	0	0
9	Fe_2O_3	100	4	0	0	0	0	0
10	Co_3O_4	100	4	96	94	0	0	0
11	NiO	100	4	67	34	8	0	14
12	CuO	100	4	23	11	0	0	0
13	MoO_3	100	4	0	0	0	0	0
14	PdO	100	4	7	4	0	0	0
15	CeO_2	100	4	19	0	2	0	0

[a] Conditions: benzyl alcohol (0.5 mmol), metal oxide (20 mg), toluene (3 mL), pNH_3 (0.85 MPa), pO_2 (0.5 MPa).
[b] Calculated based on GC analysis using anisole as an internal standard.
[c] MnO_2 (5 mg),
[d] Ammoxidation of the reaction solution (entry 7) after the removal of MnO_2 by filtration. Conditions: pNH_3 (0.85 MPa), pO_2 (0.5 MPa).

Further, lesser amount of MnO_2 (Mn 12 mol%) was enough to promote the reaction (entry 6), proving that the reaction proceeded catalytically. Furthermore, a metal-time yield ($mol_{nitrile} mol_{Mn}^{-1} h^{-1}$) was recorded to be 13.4 $mol_{nitrile} mol_{Mn}^{-1} h^{-1}$ which was much higher than that of $Ru(OH)_x/Al_2O_3$ (1.4 $mol_{nitrile} mol_{Ru}^{-1} h^{-1}$) [9]. In order to investigate whether the reaction proceeded heterogeneously or by leached Mn(IV) species, the ammoxidation was carried out after the removal of MnO_2 at a conversion of 56% (entry 7). After the filtration of MnO_2, the conversions and the yields were the same as those in entry 7, suggesting that the reaction took place heterogeneously (entry 8).

Effect on calcination temperatures of MnO_2 was investigated (Table 2). An increase in calcination temperatures led to a decrease in both specific surface area and catalytic activity of MnO_2, when the yield of benzonitrile after 10 min was compared (entries 1, 2, 6, and 10). With regard to the recycling test, the catalytic activity of MnO_2 calcined at 300 °C was slightly decreased for the third run (entry 5). Although the initial catalytic activity was better for the calcination at 300 °C than 400 °C, MnO_2 calcined at 400 °C showed better recyclability after the third run (entry 9).

Manganese dioxide was also applicable to other primary alcohols (Scheme 1). Cinnamyl alcohol was converted to cinnamonitrile without the isomerization and the hydrogenation of C=C double bonds (Scheme 1a). Heteroaromatic alcohols also reacted to form the corresponding nitriles (Scheme 1b and c). Taylor et al. [8] reported that MnO_2 only oxidized activated alcohols such as benzyl alcohol even large excess amount of MnO_2 was used. In contrast, MnO_2 prepared by the reaction of $KMnO_4$ with $Mn(NO_3)_2$ catalyzed the ammoxidation of unactivated alcohols such as 1-octanol to yield octanenitrile with high yield (Scheme 1d).

3.2. Characterization of MnO_2

Fig. 1 shows the X-ray diffraction (XRD) patterns of MnO_2 calcined at different temperatures. For MnO_2 calcined at 250 and 300 °C, weak and broad diffraction peaks at around 2θ of 12° and 38° were observed (Fig. 1a and b). Crystalline phases of Fig. 1a and

b could not be assigned due to very broad diffraction patterns. For MnO_2 calcined at 400 and 500 °C, diffraction peaks were observed at 12°, 18°, 29°, 38°, and 50° (Fig. 1e and f). These two MnO_2 samples had the same crystalline phase and were assigned to α-MnO_2 (JCPDS #44-0141) [35]. It can be said that a high calcination temperature caused an increase in crystallinity and a decrease in specific surface area without the change of crystalline phase. Thus, it can be concluded that the difference in catalytic activity of MnO_2 calcined at different temperatures was derived from the amount of active sites on MnO_2 surface. XRD patterns of MnO_2 (calcined at 300 °C) after the reaction (Fig. 1c) and the re-calcined MnO_2 at 300 °C after the reaction (Fig. 1d) were almost identical to the fresh MnO_2 (Fig. 1b), suggesting that the crystalline nature of MnO_2 catalyst did not change during the reaction.

Scheme 1. Ammoxidation of other primary alcohols: cinnamyl alcohol (a), 2-pyridine methanol (b), 2-thiophene methanol (c), 1-octanol (d). Reaction conditions: substrate (0.5 mmol), toluene (3 mL), MnO_2 (20 mg), pNH_3 (0.85 MPa), pO_2 (0.5 MPa), 100 °C. Calculated based on GC analysis using anisole as an internal standard.

Table 2
Catalytic properties of MnO_2 calcined at different temperatures for the ammoxidation of benzyl alcohol.[a]

Entry	Calcined temp.	Specific surface area	Reaction time	Conv.	Yield (%)[b]	
	(°C)	(m²/g)	(min)	(%)[b]	Nitrile	Aldehyde
1	250	107	10	100	98	0
2	300	70	10	88	82	0
3	300	–	30	100	100	0
4[c]	300	–	30	100	100	0
5[d]	300	–	30	92	90	1
6	400	51	10	87	78	1
7	400	–	30	100	95	0
8[c]	400	–	30	96	94	0
9[d]	400	–	30	98	93	0
10	500	19	10	31	19	5

[a] Conditions: benzyl alcohol (0.5 mmol), toluene (3 mL), MnO_2 (20 mg, 0.23 mmol), pNH_3 (0.85 MPa), pO_2 (0.5 MPa), 100 °C.

[b] Calculated based on GC analysis using anisole as an internal standard.

[c] Second run.

[d] Third run.

Fig. 1. XRD patterns of MnO_2 calcined at 250 °C (a), 300 °C (b), 300 °C after the reaction (c), MnO_2 treated by re-calcination in air at 300 °C for 4 h after the reaction (d), 400 °C (e), and at 500 °C (f).

3.3. One-pot benzamide formation from benzyl alcohol

One-pot, two-steps amide synthesis from alcohol by the ammxoidation of alcohols followed by the hydration of nitriles with the addition of excess amount of water at the second step has been reported over $Ru(OH)_x/Al_2O_3$ [9]. However, the removal of water after the reaction is a high-cost process and minimizing the amount of water is strongly desired. When the ammoxidation of an alcohol to a nitrile proceeded, three equimolar amount of water is produced (Scheme 2). Thus, we tried to use the water generated by the nitrile formation for the next hydration step (Table 3). A

Scheme 2. Ammoxidation of benzyl alcohol over metal oxide catalysts.

Longer reaction time (12 h) gave benzamide in 11% yield, suggesting that the sequential ammoxidation and hydration of the nitrile occurred (entry 1). Lower pressures of NH_3 and O_2 (0.4 MPa each) improved the amide yield, indicating that the hydration was suppressed under high NH_3/O_2 pressures (entry 2). Thus, the gases (NH_3 and O_2) were released after the ammoxidation step for 1 h and filled with atmospheric pressure of N_2, and then the reaction mixture was heated again to 100 °C to promote the hydration for additional hours (condition B). As a result, the yield of amide reached to 57% after 24 h (entry 4) which was higher than that for the hydration of benzonitrile over MnO_2 (entry 7). When the initial NH_3/O_2 pressure was reduced to 0.1/0.1 MPa of NH_3/O_2, the ammoxidation of alcohol completely proceeded whereas amide yield was not improved (entry 5). Increase in the amount of MnO_2 was not effective for the hydration efficiency (entry 6).

3.4. Effect of gold on ammoxidation and one-pot amide synthesis

Since it has been reported that MnO_2 supported Au NPs exhibited high catalytic activity for alcohol oxidation [36], the effect of Au NPs on the ammoxidation of alcohol was investigated (Table 4). The deposition of Au NPs onto MnO_2 did not enhance the reaction rate of the ammoxidation (entry 1) as compared to that for MnO_2 (entry 6 in Table 1). In contrast, a promotion effect of Au NPs was observed for the hydration step, i.e., the yield of amide increased to 58% (entry 2) from 34% for MnO_2 (entry 6 in Table 3). The catalytic activity of Au/MnO_2 for the hydration of benzonitrile itself was slightly higher (entry 4) than that of MnO_2 (entry 7 in Table 3). Consequently, optimized reaction conditions achieved 81% amide yield for the one-pot amide synthesis without further addition of water (entry 3).

As shown in Table 4, Au/Al_2O_3 (entry 5) and Au/CeO_2 (entry 8) catalyzed the ammoxidation although support metal oxides alone did not catalyze the reaction (entries 1 and 15 in Table 1). In contrast, neither ammoxidation nor alcohol oxidation to aldehyde underwent over Au/TiO_2 (entry 6), suggesting that Au/TiO_2 might be deactivated by NH_3. In addition, the product selectivity strongly depended on the kind of supports, i.e., Au/CeO_2 and Au/Al_2O_3 gave benzamide together with benzonitrile, N-benzylidenebenzylamine, and triphenyl triazine as by-products, whereas Au/CuO gave benzonitrile as a major product with high selectivity (90%).

4. Discussions

4.1. Reaction pathway for MnO_2 catalyzed ammoxidation

Since benzaldehyde was obtained as a by-product over MnO_2 and Co_3O_4, benzyl alcohol was firstly oxidized to benzaldehyde and

Table 3
One-pot benzamide synthesis from benzyl alcohol over MnO_2 catalysts.

Entry	Catalyst	NH_3/O_2	Time	Conditions[a]	Conv.[b]	Yield(%)[b]	
		(MPa/MPa)	(h)		(%)	Nitrile	Amide
1	MnO_2	0.85/0.5	12	A	100	85	11
2		0.4/0.4	12	A	100	73	21
3		0.4/0.4	12	B	100	57	38
4		0.4/0.4	24	B	100	41	57
5		0.1/0.1	12	B	100	61	30
6[c]		0.1/0.1	12	B	100	59	34
7		0/0	24	C	45	–	40

[a] Reaction condition A: benzyl alcohol (0.5 mmol), toluene (3 mL), MnO_2 (20 mg), 100 °C. Condition B: the reaction was performed under the pressure of NH_3/O_2 for 1 h and then for additional hours under N_2 atmospheric pressure. Condition C: benzonitrile (0.5 mmol) was used as a substrate. Catalyst (20 mg), toluene (3 mL), H_2O (1.5 mmol), atmospheric pressure of N_2, 100 °C.

[b] Calculated based on GC analysis using anisole as an internal standard.

[c] MnO_2 (50 mg).

Scheme 3. Plausible reaction pathway for the ammoxidation of alcohol over MnO_2.

then imine was formed by dehydrative condensation of aldehyde with NH_3 via the hemiaminal formation (Scheme 3). It was confirmed that Fe_2O_3 catalyzed neither benzyl alcohol oxidation nor the ammoximation of benzaldehyde with NH_3. Thus, it appeared

that Mn, Co, and Ni oxides catalyzed not only alcohol oxidation but also imine oxidation to form nitrile. For MnO_2-catalyzed aerobic oxidation of alcohols, a redox mechanism between MnO_2 and MnO_x was assumed [18]. In the case of MnO_2-catalyzed ammoxidation of alcohols, similar redox mechanism might be involved; $Mn(IV)O_2$ oxidized an alcohol to an aldehyde and an imine to a nitrile. Then, Mn(IV) was reduced to Mn(III), which was re-oxidized to Mn(IV) by molecular oxygen.

4.2. Catalytic activity of supported gold catalysts

For Au-catalyzed ammoxidation of benzyl alcohol, the selection of supports, which are not deactivated by NH_3, is a key factor. In addition, the reaction route could be controlled by the selection of

Scheme 4. Plausible reaction pathway for the ammoxidation and amidation over supported Au catalysts.

Table 4
Effect of gold deposition on metal oxides in the ammoxidation of benzyl alcohol and amide synthesis.

Entry	Catalyst	NH_3/O_2	Temp.	Time	Conditions[a]	Conv.[b]	Yield (%)[b]	
		(MPa/MPa)	(°C)	(h)		(%)	Nitrile	Amide
1	Au/MnO_2	0.85/0.5	100	0.5	A	87	77	0
2		0.1/0.1	100	12	B	100	33	58
3		0.1/0.1	100	72	B	100	9	81
4		0/0	100	24	C	56	–	51
5	Au/Al_2O_3	0.85/0.5	150	23	A[c]	100	22	45
6	Au/TiO_2	0.85/0.5	120	23	A[c]	15	0	0
7	Au/CuO	0.85/0.5	120	23	A[c]	61	55	0
8	Au/CeO_2	0.85/0.5	120	23	A[c]	61	10	28

[a] Reaction condition A: benzyl alcohol (0.5 mmol), toluene (3 mL), catalyst (50 mg). Condition B: the reaction was performed under the pressure of NH_3/O_2 for 1 h and then for additional hours under N_2 atmospheric pressure. Condition C: benzonitrile (0.5 mmol) was used as a substrate. Catalyst (20 mg), toluene (3 mL), H_2O (1.5 mmol), atmospheric pressure of N_2, 100 °C.

[b] Calculated based on GC analysis using anisole as an internal standard.

[c] Au 2 mol%, toluene (2 mL).

suitable supports for Au NPs and reaction conditions. Au/CuO (solid line in Scheme 4) did not enhance the hydration, giving benzonitrile as a major product. On the other hand, Au/Al$_2$O$_3$ and Au/CeO$_2$ would enhance the hydration of benzonitrile or the direct oxidation of hemiaminal to produce benzamide as a major product (dashed line in Scheme 4). According to the fact that benzonitrile, N-benzylidenebenzylamine, and 2,4,6-triphenyl-1,3,5-triazine were obtained as by-products over Au/Al$_2$O$_3$ and Au/CeO$_2$, the one-pot ammoxidation followed by the hydration is more likely. In our experiments, the ammoxidation was carried out under the pressurized NH$_3$ in organic solvents in contrast to the direct amidation of alcohols in aqueous solution of NH$_3$ in the presence of inorganic base [15]. These conditions facilitated preferentially the dehydration of hemiaminal to form imine which was easily oxidized to nitrile.

5. Conclusions

We have found that MnO$_2$, Co$_3$O$_4$, and NiO were catalytically active for the ammoxidation of primary alcohols including unactivated alcohols to produce nitriles. In particular, MnO$_2$ exhibited remarkably high catalytic activity and excellent selectivity to nitriles. The MnO$_2$ catalyst could be reused at least for three times. We have also found that Au NPs deposited on MnO$_2$ promoted the hydration of benzonitrile to form benzamide without further addition of water. Some other supported Au catalysts were also active for the ammoxidation of benzyl alcohol to produce benzonitrile and benzamide, presenting a new type of catalysis by Au NPs.

Acknowledgments

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