doi:10.1246/cl.2012.101

Spinel Cobalt Oxide Catalyzed Controlled Hydration of Aromatic Nitriles

Yuvaraj Gangarajula and Buvaneswari Gopal*
Materials Division, School of Advanced Sciences, VIT University, Vellore-632014, Tamil Nadu, India

(Received September 5, 2011; CL-110735; E-mail: gbhuvaneswari@vit.ac.in)

Selective hydration of aromatic nitriles to their respective amides has been achieved in the presence of spinel cobalt oxide, Co_3O_4 as a heterogeneous catalyst. Higher yields of the products in shorter duration have been accomplished under hydrothermal condition compared to thermal refluxing.

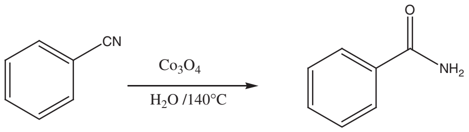
Spinel cobalt oxide, Co_3O_4 is an important functional material which has been studied for various applications such as solid sensors, electrode material, and magnetic material.[1,2] In the field of catalysis, the utility of the oxide has been reported for diverse reactions such as oxidation of CO,[3] combustion of CH_4,[4] photocatalytic degradation of dyes,[5] oxidation of hydrocarbons,[6] ammonia oxidation,[7] oxidation of benzyl alcohols,[8] and nitrogen oxide decomposition.[9]

Amides are versatile building blocks in synthetic organic chemistry. Developing an efficient method for the formation of amide linkage is of great importance because of the high synthetic utility of amides such as acrylamide, nicotinamide, etc., with respect to their industrial applications and pharmacological interest.[10] Hydration of nitriles using water is an environmentally friendly synthetic route to obtain amide directly. Conventionally hydration of nitrile is achieved in the presence of strong acids or bases. The method is associated with disadvantages such as harsh conditions, over hydrolysis to acid, salt formation, and polymerization.[11–13] This results in lesser yield of amides and also the procedure involves tedious separation of the product. To overcome these problems several homogeneous and heterogeneous catalysts have been tested. Catalysts such as hydrogen peroxide, sodium perborate, palladium, and sodium percarbonate[14] have been reported. A rapid method for the transformation of nitriles to amides on treating the nitriles with basic hydrogen peroxide in dimethyl sulfoxide has been reported by Katritzky et al.[15]

Alternatively, due to efficient work up in addition to the high-performance hydration of nitriles has been carried out under heterogeneous conditions also. Heterogeneous catalysts such as KF/Al_2O_3,[16] KF/natural phosphate,[17] Na/HAP,[14] Na/FAP,[18] and MnO_2/SiO_2[19] have been reported. However, most of these catalysts cannot be reused. Mitsudome et al.[20] studied Ag-supported systems such as Ag/HAP, Ag/TiO_2, Ag/SiO_2, Ag/MgO, and Ag/C as catalysts for hydration of aliphatic and aromatic nitriles. Among these Ag/TiO_2 showed higher conversion of benzonitrile but benzoic acid formed as a side product. Zeolite-based heterogeneous catalyst has been studied for hydration of aromatic nitriles. But only low yield of the products is achieved.[21] Though the hydrolysis involving metal centers is an attractive route to amide, only few reports are available on metal oxides as heterogeneous catalysts. Recently application of rare earth oxide, CeO_2 for the hydration of specific nitriles in the temperature range 30–100 °C is reported.[22] In the category of transition-metal oxides, Miura et al. reported on the selective hydration of acrylonitrile to acrylamide on oxides of Mn, Fe, Co, Ni, Cu, and Ag.[23] Oxides such as MnO_2, CuO, and Co_3O_4 are found to be active. However, lower yields are reported. Various metal oxides such as MnO_2, ZnO, CuO, Fe_2O_3, Co_2O_3, Ni_2O_3, etc. have been used as catalysts for hydration of aromatic nitriles.[24] In the presence of CuO the reaction products interact with the catalyst, while in the presence of ZnO the hydration is accompanied to a large extent by the hydrolysis of the benzamide, and CdO forms salt with benzoic acid. Among lead(II), zirconium, and germanium(IV) oxides, only lead(II) oxide gives moderate yield of benzamide (59%) and the other two oxides exhibit weak catalytic activity. Titanium(IV) and silicon oxides are almost inactive.[24] Nickel oxide, NiO has been used as a catalyst for the hydration of 3-cyanopyridine to nicotinamide.[25] The drawbacks are lower catalytic activity with low yield. From the literature we understood that generally metal oxides required high temperature in nitrile hydration. But such procedures are associated with problems such as over hydrolysis and reusability of the catalyst. For example, in the case of Fe_2O_3, benzamide has been obtained in moderate yield at 225 °C and also benzoic acid formed as by-product. The oxides such as Co_2O_3 (225 °C), Ni_2O_3 (175 °C), and CuO (225 °C) ruled out their reuse.[24] Therefore, from an industrial point of view the development of selective, efficient, reusable, low cost, and eco-friendly catalyst in addition to simplicity in the process and in handling is of great importance. There are apparently fewer reports on the hydration of nitriles to amides at relatively low temperature in a shorter duration in the presence of metal oxides. Herein we report on the catalytic activity of the spinel oxide, Co_3O_4 for the selective hydration of diverse aromatic nitriles to their respective amides. The scheme of the reaction is as below (Scheme 1).

The hydration reaction was performed under two experimental conditions: (i) under reflux conditions and (ii) using an autoclave. The ratio of the reactants to catalyst was maintained the same in both the cases. Under reflux condition maximum yield (89%) of benzamide was obtained during 24 h reaction. To achieve higher yield in a shorter period, the reaction was switched over to an autoclave. The catalytic test that was performed as using autoclave is described below.

Cobalt oxide and benzonitrile were obtained from Sd-fine chemicals, India. Other derivatives used were from Sigma-Aldrich chemical Co. Benzonitrile (5 mmol), Co_3O_4 (0.2 g), and water (15 mL) were placed in a Teflon vessel with a magnetic stir



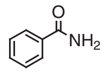
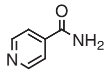
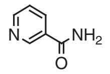
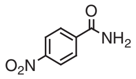
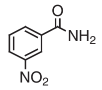
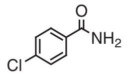
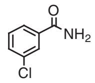
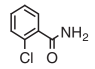
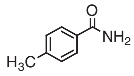
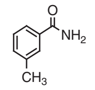
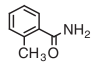
Scheme 1.

Table 1. Optimization of experimental conditions for hydration of benzonitrile[a]

Entry	Temperature /°C	Stirring status	Time /h	Yield /%
1	100	No stirring	24	84
2	125	No stirring	12	84
3	125	No stirring	16	95
4	125	No stirring	24	99.2
5	140	No stirring	6	70
6	140	No stirring	8	82
7	140	No stirring	10	99.7
8	150	No stirring	8	95
9	160	No stirring	6	99.8
10	140	Stirring	7	99.2

[a]Reactants: nitrile (5 mmol), catalyst (0.2 g), and water (15 mL).

Table 2. Hydration of various nitriles catalyzed by Co_3O_4[a]

Entry	Product	Time/h	Yield/%
1 2[b] 3[b]		7 7 7	99.1 99 96
4		9	99.8
5		9	99.9
6		12	99
7		24	99
8		17.5	94
9		24	80
10		24	75
11		24	99
12		24	94
13		24	38

[a]Reaction conditions: nitrile (5 mmol), catalyst (0.2 g), and water (15 mL) were placed in a 200 mL stainless steel reactor at 140 °C. Note: Mp, ^{1}H NMR, ^{13}C NMR, and IR data are given in Supporting Information.[32] [b]Experiments carried out with recycled catalyst: 1st reuse (Entry 2), 2nd reuse (Entry 3).

bar. The Teflon vessel was inserted into a stainless steel vessel (autoclave, 125 mL, model 4748 from Parr Instrument company) and heated at 140 °C (bath temperature) in an oil bath with stirring. Stirring rate was kept around 550–600 rpm. Work up included the addition of ethanol, and filtration to separate the catalyst. For comparison, a similar experiment was carried out under thermal reflux conditions using a round bottom flask. The solvent was removed by evaporation.

Products were identified by their melting points, ^{1}H NMR, ^{13}C NMR (Bruker AVANCE III 400 and 500 MHz (AV 500) and IR (JASCO FT-IR-4100) spectra. The metal oxide was analyzed by powder X-ray diffraction (Cu Kα, D8 Advance, Bruker) before and after the reaction.

The optimization of experimental conditions such as temperature, stirring, and reaction duration in the case of conversion of benzonitrile to benzamide was carried out and the details are given in Table 1. The experimental conditions shown in Entry 10 are followed in the hydration of other derivatives. As observed in the current work, such a high yield of benzamide is reported in the presence of sodium nitrate modified hydroxy- and fluoroapatites such as Na/HAP and Na/FAP[14,18] at 100 °C in a shorter duration. However, such a protocol involves separate catalyst preparation and the catalysts may not be reusable. Greater than 99% yield of benzamide was achieved under similar experimental conditions at 140 °C by Yamaguchi et al.[26] using expensive ruthenium hydroxide supported alumina.

Various benzonitrile derivatives such as chloro-, methyl-, nitro-, and cyanopyridines have been hydrated. Derivatives of benzonitrile and 3- and 4-cyanopyridines are selectively hydrated to corresponding amides with high yields. The results are compiled in Table 2. Comparison of the substrates with electron-withdrawing groups and the substrates with electron-donating groups indicates lesser influence of the substituents on the reactivity. A similar trend has been shown by other bulk heterogeneous catalytic systems such as Na/HAP[14] and $Ru(OH)_x/Al_2O_3$[26] though there is a difference in the rate of reactions. Among the *ortho*-reactants, the *o*-tolunitrile shows poor conversion due to strong steric effect of the bulkier methyl group which inhibits the formation of coordination bond between nitrogen atom of the nitrile group and the metal. In the case of *p*-nitrobenzonitrile, compared to Na/HAP, relatively higher yield in shorter duration is achieved. Among the chloro derivatives, *para*-form gets converted faster and results in better yield compared to the other two forms. In the case of heteroaromatic nitriles, 3- and 4-cyanopyridines are hydrated to their corresponding amides in higher yields. It is noted that the hydration is faster than the substituted benzonitriles. However, 2-cyanopyridine exhibits different reaction leading to the formation of red color product. Preliminary analyses by FT-IR and UV–vis spectroscopy indicate a possible formation of chelate along with the corresponding amide. Similar observation of formation of chelate is made in the case of NiO and CuO.[27] Complete characterization of the chelate is underway and the results will be published later.

The observations strongly suggest that the spinel cobalt oxide activates RCN and leads to controlled nucleophilic attack of OH^-. As reported in the literature[20,26] nitrile group coordinates to the metallic center on the surface of cobalt oxide. The hydroxide ion from the adsorbed water attacks the carbonium ion and the successive step is H^+ attack on the proximal nitrogen. This is followed by rearrangement and desorption of the amide from the catalyst surface. In the normal spinel

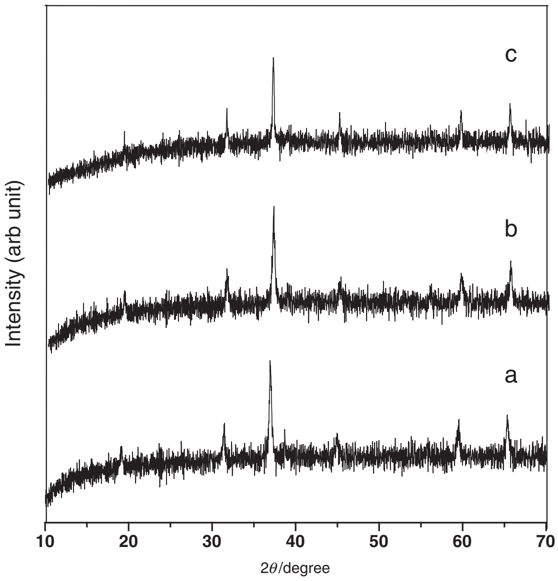


Figure 1. XRD spectrum of Co_3O_4 before nitrile hydration (a), after benzonitrile hydration (b), and after 2nd reused for benzonitrile hydration (c).

structure of Co_3O_4 made up of cubic close-packed arrangement of O^{2-} ions, trivalent cobalt exists in octahedral sites and the divalent cobalt ion locates itself in tetrahedral sites. The surface composition of the oxide plays an important role in its catalytic performance.

Kukushkin and Pombeiro in their review[12] have analyzed theoretical studies on the possible mechanism for the metal-catalyzed hydration of nitrile carried out by Barbosa and van Santen.[28] The proposed approach stresses the formation of metal–N bond though two routes of nitrile and water molecule interaction with the surface of metal oxide mentioned. Among Co^{tet} and Co^{oct} sites which are available in Co_3O_4 normal spinel, it is envisaged that the "N" of nitrile group may preferentially coordinate with Co^{oct} (Co^{3+}) which is a stronger Lewis acid site.[29–31]

The hydration of benzonitrile is noted to be faster than their substituted derivatives (electron releasing and electron withdrawing). It is clear that the speed of the reaction is influenced by the combination of nature and the position of the substituents present in the benzene ring. We established a set of experiments for the hydration of benzonitrile to check the reusability of the oxide. After the completion of the first reaction, the oxide catalyst is recovered by filtration, washed with hexane and calcined at 500 °C for 2 h. Using the activated catalyst, a new reaction is performed with fresh benzonitrile under similar reaction conditions. It is noted that the oxide could be reused without appreciable loss of catalytic performance and the results obtained are given in Table 2 (Entries 1–3). After the completion of catalytic hydration of benzonitrile, the reaction mixture is filtered to remove Co_3O_4 and then the filtrate is analyzed by atomic absortption spectroscopy (AAS) to find out the possible leachability of cobalt during the reaction. The results confirmed the absence of cobalt in the filtrate. Powder X-ray diffraction analysis of the reused oxides shows that the formed amide was expelled with the regeneration of cobalt oxide (Figure 1).

In summary, this study brings out spinel cobalt oxide as an efficient, reusable heterogeneous catalyst for the hydrolysis of benzonitrile and its derivatives. Diverse aromatic nitriles including heteroaromatic ones have been converted to respective amides in high yield and excellent selectivity in aqueous medium.

The authors thank VIT University for providing all required facilities to carry out the experiments.

References and Notes

1 M. Ando, T. Kobayashi, S. Iijima, M. Haruta, *J. Mater. Chem.* **1997**, *7*, 1779.
2 F. Huang, Z. Yuan, H. Zhan, Y. Zhou, J. Sun, *Mater. Lett.* **2003**, *57*, 3341.
3 X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, *Nature* **2009**, *458*, 746.
4 N. Bahlawane, *Appl. Catal., B* **2006**, *67*, 168.
5 X. Lou, J. Han, W. Chu, X. Wang, Q. Cheng, *Mater. Sci. Eng., B* **2007**, *137*, 268.
6 Z. Tian, N. Bahlawane, F. Qi, K. Kohse-Höinghaus, *Catal. Commun.* **2009**, *11*, 118.
7 K. Schmidt-Szałowski, K. Krawczyk, J. Petryk, *Appl. Catal., A* **1998**, *175*, 147.
8 I. Mohammad, S. Muhammad, *Int. J. Chem. React. Eng.* **2010**, *8*, A77.
9 E. Wilczkowska, K. Krawczyk, J. Petryk, J. W. Sobczak, Z. Kaszkur, *Appl. Catal., A* **2010**, *389*, 165.
10 M. N. Kopylovich, V. Yu. Kukushkin, M. Haukka, J. J. R. F. da Silva, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 4798.
11 K. L. Breno, M. D. Pluth, D. R. Tyler, *Organometallics* **2003**, *22*, 1203.
12 V. Yu. Kukushkin, A. J. L. Pombeiro, *Inorg. Chim. Acta* **2005**, *358*, 1.
13 V. Cadierno, J. Francos, J. Gimeno, *Chem.—Eur. J.* **2008**, *14*, 6601.
14 F. Bazi, H. El Badaoui, S. Tamani, S. Sokori, A. Solhy, D. J. Macquarrie, S. Sebti, *Appl. Catal., A* **2006**, *301*, 211.
15 A. R. Katritzky, B. Pilarski, L. Urogdi, *Synthesis* **1989**, 949.
16 C. G. Rao, *Synth. Commun.* **1982**, *12*, 177.
17 S. Sebti, A. Rhihil, A. Saber, N. Hanafi, *Tetrahedron Lett.* **1996**, *37*, 6555.
18 A. Solhy, A. Smahi, H. El Badaoui, B. Elaabar, A. Amoukal, A. Tikad, S. Sebti, D. J. Macquarrie, *Tetrahedron Lett.* **2003**, *44*, 4031.
19 P. Breuilles, R. Leclerc, D. Uguen, *Tetrahedron Lett.* **1994**, *35*, 1401.
20 T. Mitsudome, Y. Mikami, H. Mori, S. Arita, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 3258.
21 D. R. Milić, D. M. Opsenica, B. Adnađević, B. A. Šolaja, *Molecules* **2000**, *5*, 118.
22 M. Tamura, H. Wakasugi, K.-i. Shimizu, A. Satsuma, *Chem.—Eur. J.* **2011**, *17*, 11428.
23 H. Miura, K. Sugiyama, S. Kawakami, T. Aoyama, T. Matsuda, *Chem. Lett.* **1982**, 183.
24 E. N. Zil'berman, *Russ. Chem. Rev.* **1984**, *53*, 900.
25 S. C. Roy, P. Dutta, L. N. Nandy, S. K. Roy, P. Samuel, S. M. Pillai, V. K. Kaushik, M. Ravindranathan, *Appl. Catal., A* **2005**, *290*, 175.
26 K. Yamaguchi, M. Matsushita, N. Mizuno, *Angew. Chem., Int. Ed.* **2004**, *43*, 1576.
27 K. Sakai, T. Ito, K.-i. Watanabe, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1660.
28 L. A. M. M. Barbosa, R. A. van Santen, *J. Mol. Catal. A: Chem.* **2001**, *166*, 101.
29 K. Omata, T. Takada, S. Kasahara, M. Yamada, *Appl. Catal., A* **1996**, *146*, 255.
30 X. L. Xu, J. Q. Li, *Surf. Sci.* **2011**, *605*, 1962.
31 M. Merkx, B. A. Averill, *J. Am. Chem. Soc.* **1999**, *121*, 6683.
32 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.