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Silver Nanoparticle Catalyzed Selective Hydration of Nitriles to Amides in Water Under Neutral Conditions

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Abstract Ag NPs can efficiently catalyze hydration of nitriles to amide in water. This hydration method used water as solvent and Ag catalyst that can be recycled under neutral conditions, so it can make a great contribution settling the process that is environmentally better and industrially more satisfactory.

Keywords Silver · Nanoparticles · Hydration · Nitriles · Water · Catalyst

1 Introduction

Metal nanoparticles have attracted a great deal of attention due to their chemical and physical characteristics that distinguish themselves from bulk metal. For the last several years, nearly all metals listed on the periodic table have opened applications for various fields ranging from photo and DNA assays to quantum dots (QDT). Among those applications, transition metal nanoparticles have become a very important class of catalysts, particularly those applied towards hydrogenation, oxidation, coupling reactions, and select photocatalytic reactions [1–4]. Furthermore, an increasing number of contributions reporting the preparation of Ag NPs have recently been published [5–7] with successful examples of application of Ag NPs in catalytic reactions such as oxidation of styrene, oxidation of alcohols, oxidation of phenylsilanes, C–C cross-coupling, and epoxidation of alkenes [7–9].

Hydration of nitriles into their corresponding amides are very important organic syntheses given their role as key synthetic intermediates in the production of pharmacological products, drug stabilizers, raw materials for engineering plastics, detergents, polymers, and lubricants [10–12]. The traditional catalyst system requires an organic solvent in the presence of homogeneous strong acid and base catalysis [13–18]. Upon the mentioned fact, it was demanded to develop a heterogeneous catalytic system that utilizes water solvent instead of organic solvent. We have found only a few reports, which introduce efficient heterogeneous catalyst for hydration of diverse nitriles into amides using only water. Recently, Kaneda's group used supported silver nanoparticle catalyst for hydration of nitriles to amides [12]. Key weaknesses of this classical method are: (1) harsh conditions are generally required that interfere with the existence of sensitive functional groups;(2) difficulty in stopping the reaction at the amide, and further, hydrolysis to the carboxylic acid. In addition, in regard of industry, the last neutralization step causes unnecessary product contamination and generates large amounts of salt (pollution effect). Therefore, chemists have strived to develop an effective metal catalyst for the hydration of nitriles. In order to increase the options of amide synthesis, cobalt, palladium, rhodium, sodium percarbonate, hydrogen peroxide, sodium perborate, chloromethylsilane, potassium trimethylsilanolate, and other chemicals are used as catalysts or reagents.

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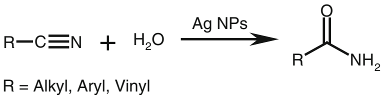


(1)

This paper reveals that Ag NPs can efficiently catalyze the hydration of nitriles to amide in water. (Eq. 1) This hydration method employs water solvent and an Ag catalyst that can be recycled under neutral conditions, thus decreasing the environmental impact of the process and increasing its overall industrial applicability.

2 Experimental

2.1 General Remarks

Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and used as received. Reaction products were analyzed by ^{1}H-NMR, on a Varian Mercury Plus (300 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard, unless otherwise indicated, and coupling constants in Hertz. Reaction products were assigned by comparison with the literature value of known compounds. The samples were characterized by TEM (Philips F20 Tecnai operated at 200 kV, KAIST), placing a few drops of the corresponding colloidal solution on carbon-coated copper grids (Ted Pellar, Inc). The X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE (3 kW) diffractometer. The copper loading amounts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.2 A Typical Synthesis for Catalyst

Silver nanoparticles were synthesized by a modified solvent-based polyol reduction using PVP [5, 6, 19]. In a typical synthesis, 30 mL of ethylene glycol solution (0.1 M) with silver nitrate (Aldrich, St. Louis, MO, USA)

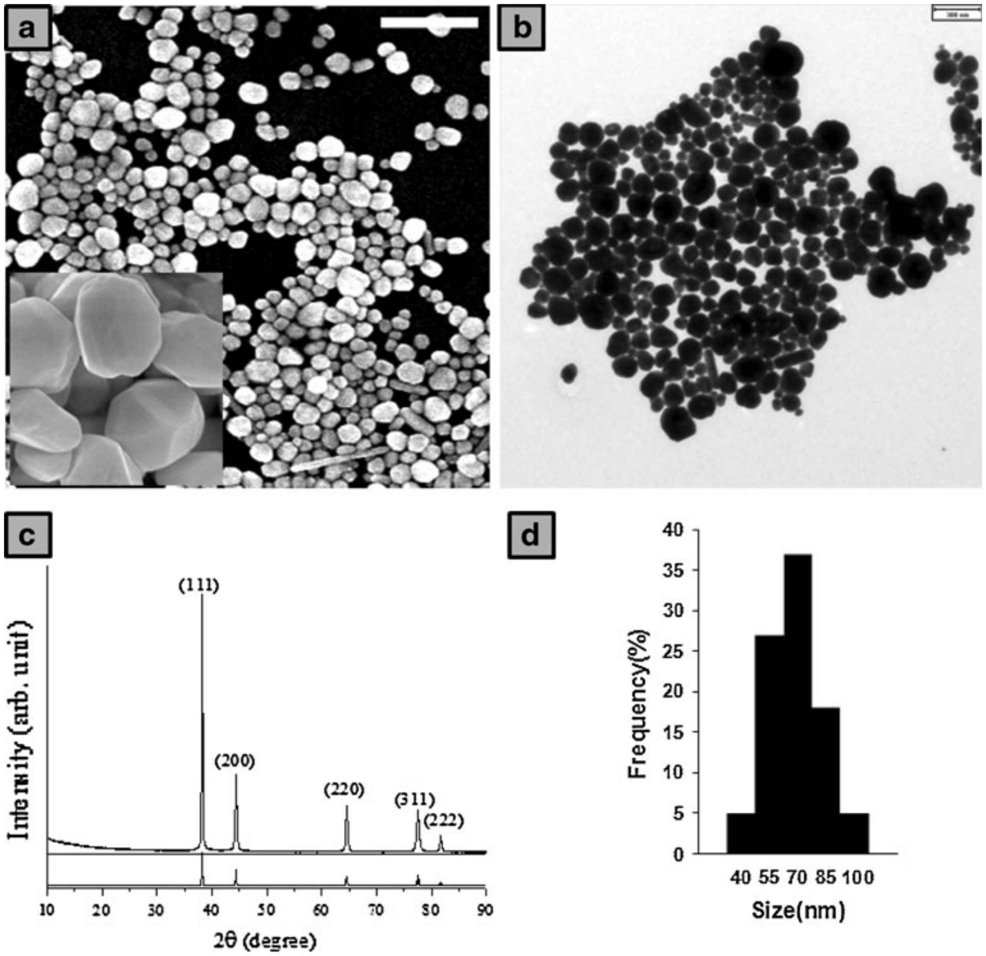


Fig. 1 **a** SEM image and high magnification SEM images (*inset*), **b** TEM image, **c** XRD pattern, and **d** size distribution diagrams of the Ag NPs. The *scale bars* represent **a** 250 nm and **b** 300 nm, respectively

and 30 mL of ethylene glycol solution (1.5 M) with poly(vinyl pyrrolidone) (PVP, Aldrich, Mw = 55,000) were injected into 15 mL of ethylene glycol (anhydrous, 99.8%, Aldrich) at a rate of ~0.3 mL/min using a syringe pump (KDS-100, Kd Scientific Co., Wood Dale, IL, USA). After injection, the reaction mixture was refluxed at 433 K for 60 min. The ochre colloidal dispersion was cooled to room temperature and precipitated with acetone, followed by centrifugation at 8,000 rpm for 10 min. The precipitated Ag NPs were washed with ethanol several times.

2.3 A Typical Procedure for the Hydration of Nitriles

Ag NPs catalyst (16.0 mg, 0.3 mol%), water (7.0 mL), and the corresponding nitrile (0.3 mL, 3.0 mmol) were introduced into a stainless steel reactor and the reaction mixture stirred at 423 K for 1 h. After the reaction, the nanoparticles were separated from the solution by centrifugation. The reaction products were analyzed by ^{1}H-NMR using Varian Mercury Plus (300 MHz). The identity of the resulting amides was assessed by comparison of their ^{1}H-NMR spectroscopic data with those reported in the literature. Afterwards, we conducted a ^{1}H-NMR experiment to gain information of the resultant product. The mixture of benzonitrile and Ag NPs was separately heated for 0.5 and 1 h in water. ^{1}H-NMR spectrum of the resultant product (Fig. 2c) revealed the disappearance of proton peak in benzene ring (7.85, 7.73, 7.58 ppm.)

3 Results and Discussion

3.1 Catalyst Characterization

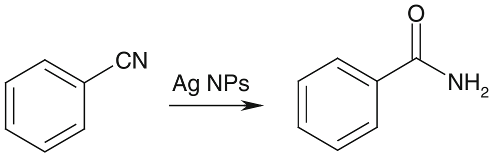
The scanning electron microscope (SEM) image in Fig. 1a and transmission electron microscopy (TEM) image in Fig. 1b show the regular polyhedral shape of the silver nanoparticles. The Ag NPs were well dispersed and isolated with an approximate 100 nm average diameter. The crystalline features of the polyhedral spheres are represented in the XRD data (Fig. 1c). The main peaks at 38.2°, 44.4°, 64.5°, 77.4 °, and 81.6° are assigned to the reflections of the (111), (200), (220), (311), and (222) planes in the Ag phase (JCPDS No. 04-07831). The powder X-ray diffraction pattern of these precipitates show the presence of metallic silver. It is also useful to calculate the average grain size (D) of the NPs from X-ray diffraction data using Scherrer formula, $D = 0.9\lambda/(B\cos\theta_B)$, where λ is the X-ray wavelength used for the diffraction experiments (Cu-Kα = 1.54 Å), B is the full width of the half maximum of a particular peak in the radian unit, and θ_B is the peak position. For the (111) peak, we obtained the grain size normal to the scattering plane is about 55 nm, which is smaller than what we obtained from TEM topography for the most of NPs that is about 66 nm.

3.2 Reaction Test

Research studies testing catalyst effectiveness have employed benzonitrile as a benchmark substrate. As shown in Table 1, the best results were obtained when water was used as the solvent. Foremost, no reaction occurred without a catalyst. When the Ag NPs (0.5 mol%) were used, benzamide was obtained in 100% conversion at reflux (373 K) within 3 h (Table 1, entry 2).

In general, it was found that increasing the reaction temperature and time were effective means of increasing conversion (Table 1, entries 3, 4). Furthermore, when 0.3 mol% of the catalyst was used, 25% yield was achieved under the same reaction times (Table 1, entry 6). When the catalyst amount was decreased to 0.1 mol%, 25% conversion was found. In entry 5,100% conversion was achieved by employing only 0.3 mol% of Ag NPs. Finally, the optimum reaction conditions were established: the nitrile (0.3 mL, 3.0 mmol) with Ag NPs (16.0 mg, 0.3 mol%) in H_2O (7.0 mL) contained in a 25 mL stainless steel reactor (Table 1. entry 5). The catalytic activity of other Ag particles was compared. The use of Ag/HAP (average particle size = 7.6 nm) showed a relatively high conversion of benzonitrile [12]. The hydration reaction did not proceed when Ag^0 powder (average particle size = 106 nm) was used. The mixture was stirred at 423 K for 1 h.

Table 1 The catalytic hydration of benzonitrile using the Ag NPs



Entry	Cat	Temp (K)	Time(h)	Conv(%)[a]
1	Blank	Reflux	3	N.R.
2	0.5 mol%	Reflux	3	100
3	0.5 mol%	423	0.5	100
4	0.5 mol%	373	0.5	69
5	0.3 mol%	423	1	100
6	0.3 mol%	423	0.5	25
7	0.1 mol%	423	0.5	25
8	Recovered form #5	423	1	100
9	Recovered form #8	423	1	100
10	Recovered form #9	423	1	100
11	Recovered form #10	423	1	100
12	0.3 mol%	423	1	8[b]

[a] Determined by ^{1}H-NMR. Yields are based on the amount of benzonitrile used

[b] Mixture solvent was used (water/toluene: 7/0.25 ml)

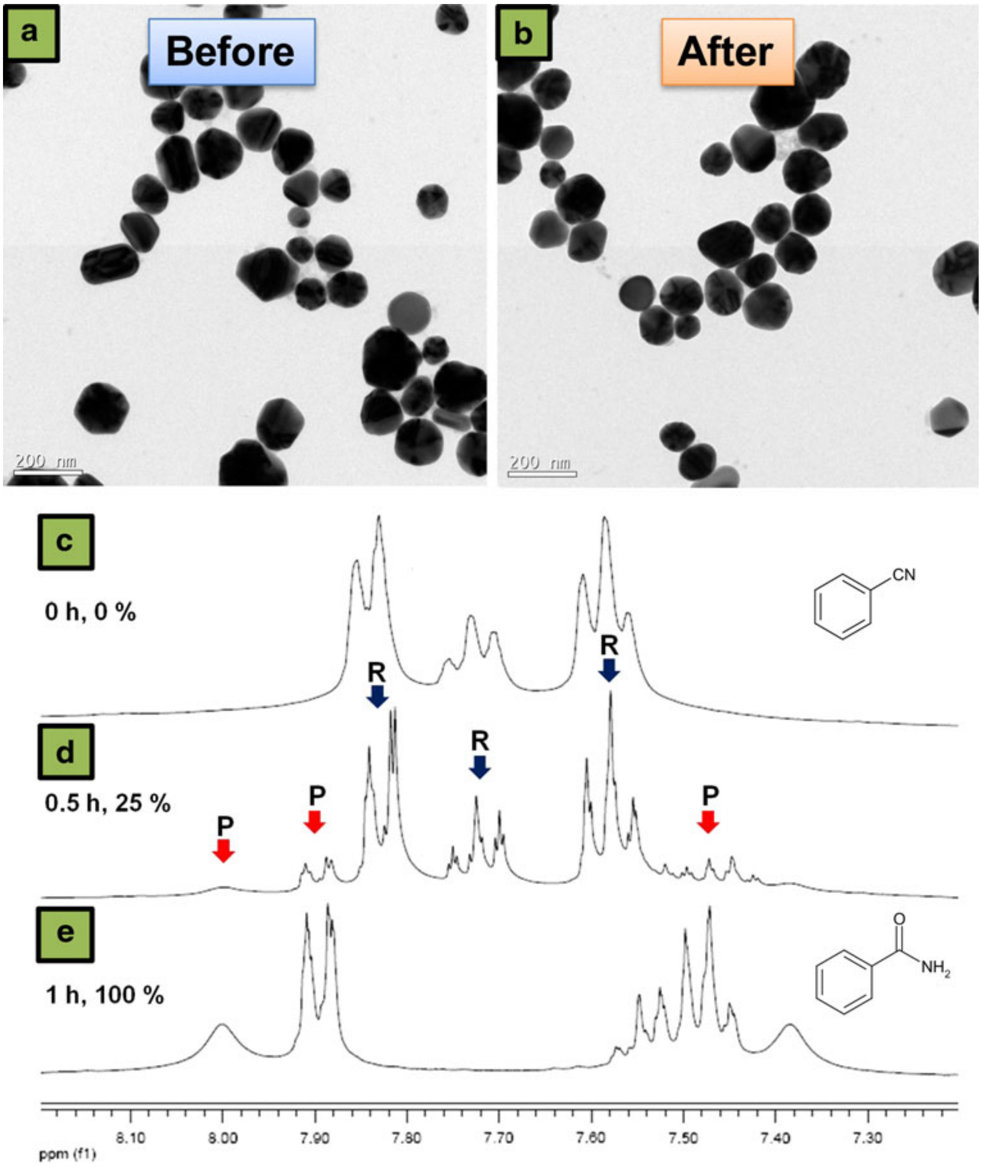
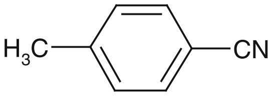
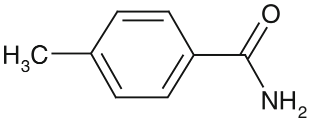
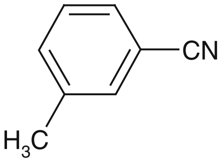
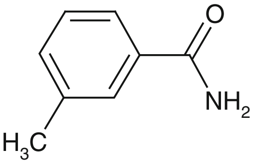
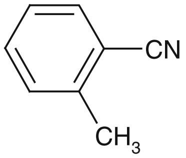
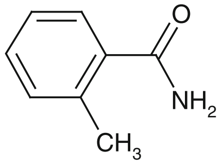
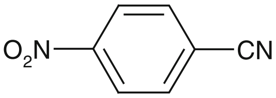
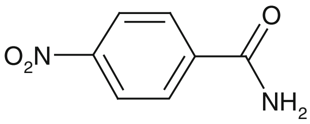
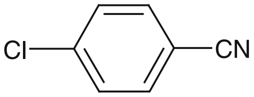
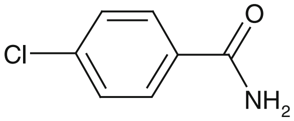
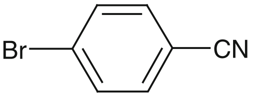
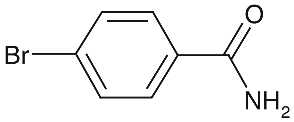
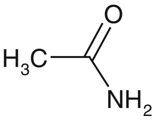
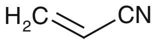
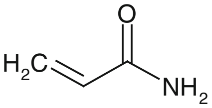


Fig. 2 TEM images of Ag NPs, before **(a)** and after use **(b)**. The *scale bars* represent 200 nm. Typical ^{1}H-NMR spectrum at the beginning **(c)** 0.5 h later **(d)** and the end of the experiment **(e)**

Remarkably, after the reaction, the Ag NPs were separated by centrifugation and reused five times under the same reaction conditions without any catalytic activity loss (Table 1, entry 8–11). After the reaction cycles, the silver ions were detected in the products with ICP-AES. These results confirm that the catalytic system presented herein satisfies the heterogeneous catalyst conditions of easy separation, recyclability, and persistence. From the TEM study shown, the structure of the Ag NPs remains unchanged after the reaction, demonstrating catalyst recyclability (Fig. 2b). In entry 12, hydration yield was significantly decreased when the hydration of benzonitrile was carried out in mixture of organic solvent (water/toluene: 7/0.25 ml).

A selection of substrates was made for further investigation (Table 2). The reactions were carried out with various nitriles at 423–453 K. Ag NPs has high catalytic activity for hydration of various nitriles in water. Generally, the enhancement of reaction yield of hydration was achieved through the use of high temperature. The rates were not much influenced by the electronic effects of the substituents on the aromatic ring of benzonitriles. When the hydration of *o*-, *m*-, and *p*-toluonitriles were catalyzed by Ag NPs, steric effect of ortho-substituted nitriles on the reaction rates was observed (Table 2, entries 2, 5, and 7). Hydration of aliphatic nitriles, such as acetonitrile and acrylonitrile, was also processed yet was less reactive) (Table 2, entries 15, 16, and 17). The substituents on

Table 2 The catalytic hydration of various nitriles by the Ag NPs

Entry	substrate	Product	Reaction conditions		Conv (%)
			Temp (K)	Time (h)	
1			423	1	12
2			423	6	86
3			453	1	100[b]
4			423	1	48
5			423	6	92
6			423	1	28
7			423	6	79
8			453	1	88
9			453	1	100
10			423	1	9
11			423	6	82
12			453	1	40
13			423	1	12
14			423	6	37
15	$H_3C—CN$		453	1	25
16			453	6	46
17			453	1	100

Reaction conditions: nitriles (3.0 mmol) with Ag NPs (16.0 mg, 0.3 mol%) in H_2O (7.0 mL) were placed in a 25 mL stainless steel reactor

[a] Used in hydration with 4-methylbenzonitrile at least three times without loss of catalytic activity

aromatic nitrile bearing electron-withdrawing groups, e.g., 4-chlorobenzonitrile and 4-bromobenzonitrile, were less reactive than that bearing electron donating groups. (Table 2, entries 10–14).

4 Conclusions

In summary, Ag NPs can serve as heterogeneous catalysts for the hydration of nitriles in water. The hydration of both activated and inactivated nitriles can be performed with high conversion and selectivity to give the corresponding amides. Furthermore, the Ag NPs were readily separated by centrifugation and could be reused five times at least with benzonitrile under the present reaction conditions without any loss of catalytic activity. This transformation has been applied to the synthesis of several amides with good yields in the environmentally sound solvent, water. This lab is currently examining the scope of this catalytic system using variously shaped Ag NPs. Attempts to improve the catalytic activities and to study the hydration mechanism are in progress.

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