PAPER • OPEN ACCESS

Hydration of Aromatic Nitrile Catalyzed by a Polyoxopalladate

View the article online for updates and enhancements.

Hydration of Aromatic Nitrile Catalyzed by a Polyoxopalladate

Tao Wang, Dan Liu, Jing Dong*

Key laboratory of cluster science, Ministry of Education, School of chemistry and chemical engineering, Beijing Institute of technology, Beijing 102488, PR China

*Corresponding author's e-mail: djbjlg@sina.com

Abstract. An open-shell polyoxopalladate(II), TBA-Na-SrPd$_{12}$(pent)$_3$ (TBA = [(n-C$_4$H$_9$)$_4$N]$^+$, pent = [C$_5$H$_9$O$_2$]$^-$), was used as catalyst in the hydration of aromatic nitrile for the first time, because such structure exhibits ligand exchange ability. TBA-Na-SrPd$_{12}$(pent)$_3$ has been proven to be active for a series of substrates and interestingly the yield (22% ~ 98%) is significantly influenced by the steric hindrance of aromatic nitriles. Furthermore, this polyoxopalladate can promote the hydration of benzonitrile under solvent-free conditions giving the yield of 99%.

1. Introduction

The synthesis of amides has attracted much attention due to its extensive use in the manufacture of pharmaceuticals and fine chemicals. For example, benzamide, the simplest aromatic amide, is widely used in biochemical research as a characteristic inhibitor of poly ADP ribosyl polymerase and nicotinamide is a whitening agent in the cosmetics industry. Nitrile hydration is promising route for the synthesis of amides because it is atom efficient, environmentally friendly and high selective. Therefore, several kinds of catalysts for nitrile hydration have been explored including the commonly used strong acids and bases [1]. Although traditional acids and bases are inexpensive and easy to obtain, it is difficult to control the reaction process, the selectivity is unsatisfactory, and these catalysts are corrosive to equipment. For example, when strong base is used as catalyst, the corresponding carboxylic acid is obtained, which subsequently reacts with alkali catalyst to form a salt causing serious trouble during the purification.

In order to overcome these disadvantages, many new catalysts have been developed in nitrile hydration, such as nitrile hydratase [2-4], transition metal oxides [5-10], metal-nanoparticles [11-15], and organometallic complexes [16, 17]. However, most of the catalysts exhibit low catalytic activity and/or need harsh reaction conditions. Polyoxometalates are a kind of green catalysts with atomically-precise structures, interesting redox and acidity properties. Mizuno and coworkers reported that a Pd-containing γ-Keggin silicodecatungstate, [γ-H$_2$SiW$_{10}$O$_{36}$Pd$_2$(OAc)$_2$]$^{4-}$, is highly effective catalyst for the hydration of nitriles and during the reaction, acetate ligands of Pd can be replaced by substrate molecules and the dipalladium site plays a crucial role in the catalytic process [18]. From then on, no further investigation was performed on Pd-containing compounds. Polyoxopalladates are new family member of polyoxometalates, which is composed of palladium centers and O-donor ligands. TBA$_3$Na[SrPd$_{12}$O$_6$(OH)$_3$(C$_6$H$_5$AsO$_3$)$_6$(C$_5$H$_9$O$_2$)$_3$]·0.5C$_5$H$_9$O$_2$Na·22H$_2$O (TBA-Na-SrPd$_{12}$(pent)$_3$) was first synthesized in Kortz's group and they found that the carboxylic ligand, C$_5$H$_9$O$_2$, can be exchanged by other carboxylic ligands. This fact indicates the Pd centers in such polyoxopalladate might be active for nitrile hydration [19]. In this work, we systematically investigate the catalytic performance of TBA-Na-SrPd$_{12}$(pent)$_3$ in the hydration of aromatic nitriles.

2. Results and discussion
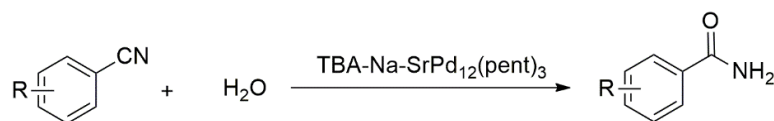
Scheme 1. Nitrile hydration by TBA-Na-SrPd$_{12}$(pent)$_3$
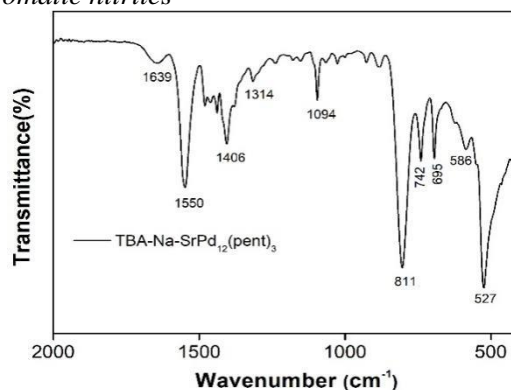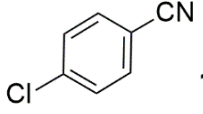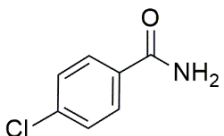
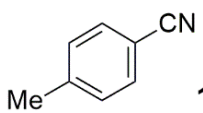*2.1. Hydration of different aromatic nitriles*
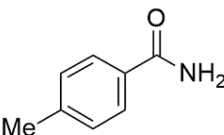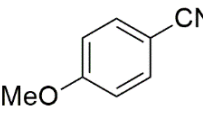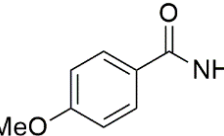
Figure 1. FT-IR spectrum of TBA-Na-SrPd$_{12}$(pent)$_3$.

The catalyst, TBA-Na-SrPd$_{12}$(pent)$_3$, was prepared according to the literature [19] and characterized by FT-IR spectrum. As shown in figure 1, the characteristic peaks of the synthesized sample are consistent with the reported ones (figure 1) [19]. In a typical reaction, TBA-Na-SrPd$_{12}$(pent)$_3$ was dissolved in 1 mL DMF and to this aromatic nitrile (0.5 mmol) and deionized water (10 mmol) were added with naphthalene (4 mg) as internal standard. The reaction was heated in the range of 90 to 120°C with stirring and monitored by gas chromatography. As shown in table 1 and scheme 1, TBA-Na-SrPd$_{12}$(pent)$_3$ can catalyse the hydration of different arom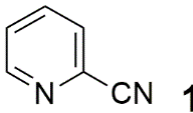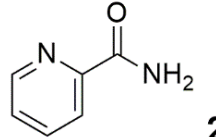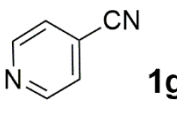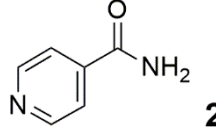atic nitriles. When benzonitrile was used as substrate, the hydration reaction goes smoothly at 90°C and the yield of the target amide is up to 88% (entry 1), which is higher than other substrates. When 2-chlorobenzonitrile was used instead of benzonitrile, the yield of product is dramatically decreased (entry 2, 28%). At beginning, we think the low yield is caused by the electron-withdrawing substituent group on benzonitrile. However, we found that 4-chlorobenzonitrile give a yield of 74%, which is much higher than that of 2-chlorobenzonitrile. The comparison displays that electronic effect is not the main reason to influence the yield. Similar phenomenon was observed in 2-cyanopyridine (entry 6) and 4-cyanopyridine (entry 7). The yield of 4-cyanopyridine is 62% but 2-cyanopyridine only gives the yield of 18%. Based on above results, we propose that the steric hindrance is the main factor to affect the yield. To confirm that, 4-methyl benzonitrie (entry 4) and 4-methoxybenzonitrile (entry 5) with the substituent group on the para position were used and their yield (84% and 59%, respectively) are basically comparable to those of 4-cyanopyridine (62%) and 4-chlorobenzonitrile (74%).

Table 1. Hydration of different aromatic nitriles [a]

Entry	Substrate	Conditions	Product	Yield (%) [b]
1	**1a**	90°C 10 h	**2a**	88
2	**1b**	100°C 8 h	**2b**	28

3	1c (4-Cl-benzonitrile)	100°C 8 h	2c (4-Cl-benzamide)	74
4	1d (4-Me-benzonitrile)	100°C 12 h	2d (4-Me-benzamide)	84
5	1e (4-MeO-benzonitrile)	100°C 12 h	2e (4-MeO-benzamide)	59
6	1f (2-pyridinecarbonitrile)	120°C 8 h	2f (2-pyridinecarboxamide)	18
7	1g (4-pyridinecarbonitrile)	100°C 8 h	2g (4-pyridinecarboxamide)	62

[a.] Reaction conditions: nitrile (0.5 mmol), H_2O (10 mmol), catalyst (15 mg), DMF (1 mL), temperature (90-120°C), time (8-12 h). [b.] All yields were detected by GC with naphthalene (4 mg) as internal standard.

As mentioned above, the carboxylic ligand, $C_5H_9O_2$, of TBA-Na-SrPd$_{12}$(pent)$_3$ can be replaced by other ligands [19] in solution. Therefore, we speculate during the catalytic reaction the carboxylic ligand is possibly substituted with aromatic nitrile molecule and the cyano group coordinates with Pd center. When a substituent group presents on the ortho position, it could prohibit the coordination of cyano group to Pd center and as a result the yield is quite low. In this reaction, electronic effect is not obvious, that is, the electron-withdrawing substituent group and the electron-donating substituent group have no obvious influence on the yield. Notably, for all the substrates, the selectivity for aromatic amides reaches 100%.

2.2. Benzonitrile hydration under solvent-free conditions
In the organic synthesis, solvent-free conditions can simplify the process and reduce pollution. Generally, the liquid substrate can be used solvent instead of additional solvent (such as DMF in above reaction system) [20]. As the catalyst, TBA-Na-SrPd$_{12}$(pent)$_3$, can be dissolved in benzonitrile, we attempt to study the hydration reaction under solvent-free conditions.
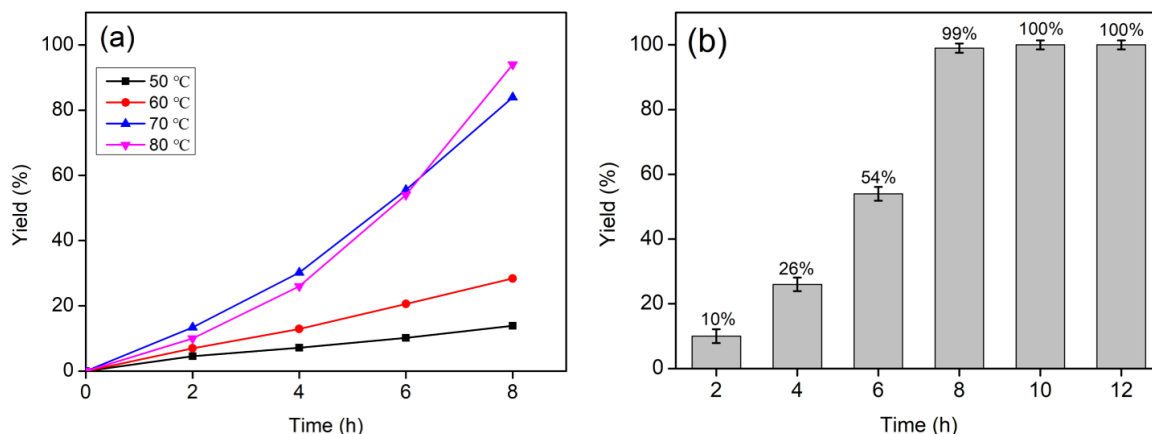
Figure 2. (a) Yield-time-curve plots for benzonitrile hydration at different temperature; (b) the yield of benzonitrile hydration at different reaction time. Reaction conditions: water (0.5 mmol), benzonitrile (1 mL), catalyst (5 mg) at 80°C.

The figure 2a shows that the yield of benzamide increase with the temperature and as the good performance 80°C is used in the following reactions. In addition, the yield of benzamide increases with reaction time from the 10% in 2 h to 99% in 8 h (figure 2b). As a result, 8 h is the best reaction time for the hydration of benzonitrile. Interestingly, the reaction time can be dramatically shortened from 8 h to 2 h by adding a few drops of acetic acid. The performance of solvent-free reaction system is much better than that in DMF (table 1, entry 1). Moreover, when the reaction is cooled to 0°C, the product can precipitate as pure crystals from reaction system. Almost 80% of product could be simply collected by filtration. Accordingly, the solvent-free reaction system is beneficial to industrial production of benzamide. TBA-Na-SrPd$_{12}$(pent)$_3$ can be reused for 5 cycles and its activity basically maintains for three cycles but obviously decreases at the fifth one (figure 3).
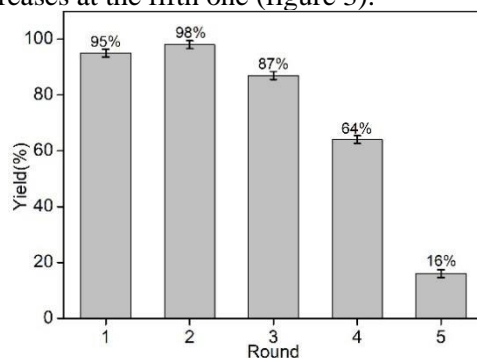

Figure 3. Recycling test of benzonitrile hydration under solvent-free conditions.

3. Conclusions

In summary, TBA-Na-SrPd$_{12}$(pent)$_3$ is first used to catalyze the hydration of aromatic nitriles and the steric hindrance effect was observed. In addition, under solvent-free conditions, benzonitrile can be converted to benzamide with the yield of 99% and the product is simply separated from the reaction system by cooling and filtration. The catalyst can be reused and its activity is maintained for four cycles. The present work not only enriches the catalytic chemistry of polyoxopalladates but also provides a feasible route for the synthesis of benzamide.

Reference

[1] Zhao X. F., Zhang Y. C., Zhang H. Y., Zhao J. Q. (2016) Progress on hydration of nitriles to amides catalyzed by transition metal oxides. Chem. Ind. Eng. Prog., 35(7): 2071-2080.
[2] Mascharak P. K. (2002) Structural and functional models of nitrile hydratase. Coord. Chem. Rev., 225(7-8): 949-974.

[3] Huang W., Jia J., Cummings J., Nelson M., Schneider G., Lindqvist Y. (1997) Crystal structure of nitrile hydratase reveals a novel iron centre in a novel fold. Structure (London), *5*(5): 691-699.

[4] Yamanaka Y., Kato Y., Hashimoto K., Iida K., Nagasawa K., Nakayama H., Dohmae N., Noguchi K., Noguchi T., Yohda M., Odaka M. (2015) Time-resolved crystallography of the reaction intermediate of nitrile hydratase: revealing a role for the cysteinesulfenic acid ligand as a catalytic nucleophile. Angew. Chem. Int. Ed., 54(37): 10763-10767.

[5] Battilocchio C., Hawkins J. M., Ley S. V. (2014) Mild and selective heterogeneous catalytic hydration of nitriles to amides by flowing through manganese dioxide. Org. Lett., 16(4): 1060-1063.

[6] Gangarajula Y., Gopal B. (2014) Investigation of nano NiO, supported and metal ion substituted NiO for selective hydration of aromatic nitriles to amides. Appl. Catal. A: Gen., 475: 211-217.

[7] Yamaguchi K., Matsushita M., Mizuno N. (2004) Efficient hydration of nitriles to amides in water, catalyzed by ruthenium hydroxide supported on alumina. Angew. Chem. Int. Ed., 43(12): 1576-1580.

[8] Mari M., Muller B., Landfester K. (2015) Ceria/polymer hybrid nanoparticles as efficient catalysts for the hydration of nitriles to amides. ACS. Appl. Mater. Inter., 7(20): 10727-10733.

[9] Amura M., Sawabe K., Tomishige K., Satsuma A., Shimizu K. I. (2014) Substrate-specific heterogeneous catalysis of CeO_2 by entropic effects via multiple interactions. ACS Catal., 5(1): 20-26.

[10] Li J., Zhang Z., Gao W. (2016) Pressure regulations on the surface properties of CeO_2 nanorods and their catalytic activity for co-oxidation and nitrile hydrolysis reactions. ACS. Appl. Mater. Inter., 8(35): 22988-22996.

[11] Ishizuka A., Nakazaki Y., Oshiki T. (2009) The hydration of nitriles catalyzed by the combination of palladium nanoparticles and copper compounds. Chem. Lett., 38(4): 360-361.

[12] Baig R. B. N., Varma R. S. (2012) A facile one-pot synthesis of ruthenium hydroxide nanoparticles on magnetic silica: aqueous hydration of nitriles to amides. Chem. Commun., 48(50): 6220-6222.

[13] Kumar s., Das p. (2013) Solid-supported ruthenium(0): an efficient heterogeneous catalyst for hydration of nitriles to amides under microwave irradiation. New. J. Chem., 37(10): 2987-2990.

[14] Subramanian T., Pitchumani K. (2012) An efficient hydration of nitriles to amides in aqueous media by hydrotalcite-clay supported nickel nanoparticles. Catal. Commun., 29(48): 109-113.

[15] Kumar S., Sharma S., Das P. (2016) Supported gold nanoparticles-catalyzed microwave-assisted hydration of nitriles to amides under base-free conditions. Adv. Synth. Catal., 358(18): 2889-2894.

[16] Ramon R. S, Marion N., Nolan S. P. (2009) Gold activation of nitriles: catalytic hydration to amides. Chem., 15(35): 8695-8697.

[17] Ahmed T. J., Knapp S. M. M., Tyler D. R. (2010) Frontiers in catalytic nitrile hydration: Nitrile and cyanohydrin hydration catalyzed by homogeneous organometallic complexes. Coord. Chem. Rev., 255(7): 949-974.

[18] Hirano T., Uehara K., Kamata K., Mizuno N. (2012) Palladium(II) containing gamma-keggin silicodecatungstate that efficiently catalyzes hydration of nitriles. J. Am. Chem. Soc., 134(14): 6425-6433.

[19] Yang P., Li H., Ma T., Haso F., Liu T. B., Fan L. Y., Lin Z. G., Hu C. W., Kortz U. (2018) Rational design of organically functionalized polyoxopalladates and their supramolecular properties. Chem. Eur. J., 24(10): 2466-2478.

[20] Kesavan L., Tiruvalam R., Rahim M. H. A., Saiman M. I. B., Enache D. I., Jenkins R. L., Dimitratos N., Lopez-Sanchez J. A., Taylor S. H., Knight D. W., Kiely C. J., Hutchings G. J. (2011) Solvent-Free Oxidation of Primary Carbon-Hydrogen Bonds in Toluene Using Au-Pd Alloy Nanoparticles. Science, 311: 195-199.