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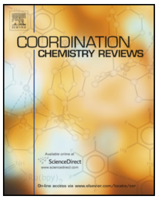

Review

Nanoparticle catalysts for nitrile hydration

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Contents

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ABSTRACT

The transition metal-catalyzed hydration of nitriles is an efficient route to amides, which are important synthetic building blocks. Many heterogeneous and homogeneous catalysts have been explored for this reaction, but there are drawbacks to each type of catalyst. Nanoparticle (NP) catalysis is a potential bridge between heterogeneous and homogeneous catalysis, frequently combining the easy separation of heterogeneous catalysts with the tunability of homogeneous catalysts. Although the field of NP catalysts is relatively new, NP catalysts have been explored for a variety of reactions, including a number of nitrile hydration reactions. This review makes a thorough assessment of these nitrile hydration reactions.

1. Introduction

Organic amides are important synthetic building blocks with a variety of applications, including many uses in pharmaceutical syntheses and in the production of acrylate monomers [1,2]. Amides are typically prepared by the hydration of nitriles (Eq. (1)) [1–5], but as we discussed in a prior review [2], there are numerous problems associated with the classical methods used to prepare amides. Consequently, the search for robust and effective nitrile hydration catalysts is an active area of research in both industrial and academic laboratories. A variety of nitrile hydration catalysts have been tested [3,6,7], including numerous metal oxides [8–15], bimetallic colloidal dispersions [16–18], and homogeneous catalysts [1,2]. In our prior review, we examined the numerous homogeneous catalysts that have been investigated for nitrile hydration [2]. Since the publication of that review, nanoparticle (NP) catalysis has blossomed as a field, including a number of papers investigating the use of nanoparticles as catalysts for nitrile hydration. In this review, we update our previous survey of nitrile hydration catalysts by covering new developments in nanoparticle-catalyzed nitrile hydration reactions. A discussion of the various NP

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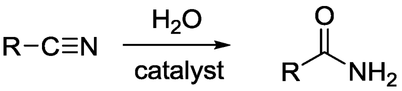
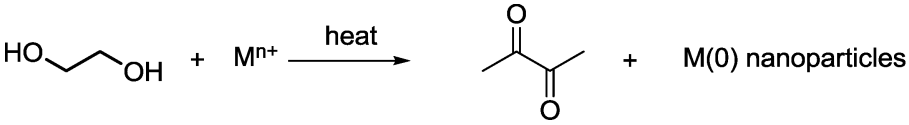
catalysts is presented, along with mechanistic interpretations of the reactions.



(1)

One of the reasons the field of nanoparticle catalysis so exciting is that it offers the prospect of new catalysts with improved properties [19]. For example, nanoparticles are often insoluble (or can be made insoluble) and thus easily separated from the reaction products, solving one of the biggest problems associated with homogeneous catalysts. The large surface area of nanoparticles mimics the high availability of active sites in solutions of homogeneous catalysts, often mitigating the low TOFs suffered by heterogeneous catalysts [20]. Furthermore, by changing the size, shape, and stabilizing agent of NP catalysts, the catalytic properties can be tuned [21].



(2)

One final introductory comment is to note that, in several systems, transition metal complexes thought to be homogeneous catalysts degrade to form NPs, which are the true catalysts [22–25]. We are unaware, however, of any supposed homogeneous nitrile hydration catalysts that are actually NPs, and therefore only intentionally designed NP catalysts are reviewed here.

2. Nanoparticle nitrile hydration catalysts

The published examples of NP nitrile hydration catalysts are shown in Table 1. Because the hydration of benzonitrile to benzamide is often used as a model reaction for nitrile hydration catalysts, the TOF (turnover frequency) for this reaction was used for comparing the activity of the various catalysts. In many cases, TOF values were not specifically reported in the papers; in those instances, the TOF values listed in Table 1 were calculated from the yield and time data in the papers. As such, they are average TOF values. Determining TOF values is often complicated for NP catalysts because the number of surface atoms (and hence the number of potentially active catalytic sites) depends on the size of the NP. In general, the TOF is calculated by taking into account the total amount of metal used. The TOF thus represents a lower limit. Finally, it is noted that, when yields of two or more catalysts are compared in this review, it should be understood that the reaction times were identical.

2.1. *Group 10*

2.1.1. *Palladium and platinum*

The first reported example of nitrile hydration by a nanoparticle catalyst was in a short letter published by Oshiki and co-workers [26]. They prepared water soluble palladium and platinum nanoparticles stabilized by a water-soluble polymer, poly(N-vinyl-2-pyrrolidone) (PVP; Fig. 1).

The “polyol method [38–41],” in which heated ethylene glycol is used to reduce a metal complex, Eq. (2), was used to prepare the catalysts from palladium acetate and platinic acid. The Pd and Pt NP particles had diameters of 1.8 and 1.5 nm, respectively. The particles themselves had little or no catalytic properties; however, in the presence of copper compounds containing an oxygen atom (e.g., Cu(acac)$_2$, CuO, and Cu(SO$_4$)$_2$), reasonable rates and yields of benzonitrile hydration were achieved. The palladium particles had a maximum turnover number (TON) of 19.6 and a turnover frequency (TOF) of 1.2 h^{-1} when the reaction was carried out at 180 °C with $CuSO_4$ as a promoter. Other copper sources (Cu(acac)$_2$, CuO, $CuCO_3 \cdot Cu(OH)_2$) gave reduced yields and rates.

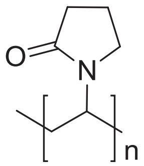


Fig. 1. Poly(N-vinyl-2-pyrrolidone) (PVP), a water-soluble polymer commonly used as a nanoparticle stabilizer.

The Pt NPs with Cu(acac)$_2$ as a promoter were far less active than their Pd counterparts, with a TON of 7.4 and a TOF of 0.46 h^{-1} [26]. No explanation was offered as to why $CuSO_4$, which was the most active promoter for the Pd NPs, was not tried as a promoter with the Pt NPs. It is suggested that the reduced activity of the Pt catalysts may be due to substrate- or product-inhibition caused by stronger binding of these molecules to the Pt surface. Alternatively, the Pt catalyst could be more sensitive to oxidative decomposition than its Pd counterpart; our research group has observed that Pt nanoparticles are susceptible to oxidative degradation under catalytic conditions [42].

It is usually of interest to determine if a catalyst decomposes during the course of a reaction, particularly with NP catalysts where aggregation and Ostwald ripening can severely decrease catalytic function. One common method to check for decomposition is to re-use the catalyst with a fresh batch of substrate and determine if there is a loss of activity. However, no recycling studies were conducted on either the Pd or Pt nanoparticle catalysts so it is not possible to say if the catalyst decomposed during the reaction.

It is interesting to note that copper sources containing a chloride (e.g., CuCl, $CuCl_2$) did not result in activation of the Pt or Pd nanoparticle catalysts. (In fact, these compounds inhibited the hydration reactions.) This result indicates that copper ion may not be the activator in these systems, but rather that the anion is. It is suggested that the oxygen-containing anion activates the nitrile hydration reaction by a bifunctional activation mechanism [43]. In bifunctional activation (Scheme 1), the nitrile is activated as usual by bonding to the metal surface but a second site is also present that activates the water molecule by deprotonating it and forming hydroxide. The generation of hydroxide (which is more nucleophilic than water) will result in a significant rate acceleration if nucleophilic attack on the nitrile carbon is the slow step in the overall reaction pathway. Note that nucleophilic attack of water or hydroxide usually is the rate-determining step in homogeneously catalyzed nitrile hydration reactions. Also note that the mechanism in Scheme 1 is analogous to the bifunctional activation reactions observed with homogeneous catalysts that have ligands capable of hydrogen bonding to water, Fig. 2 [43].

The bifunctional activation mechanism in Scheme 1 is based on a mechanism proposed by Shimizu et al. These researchers knew that Ag with oxides on the surface shows higher reactivity for water dissociation than clean Ag surfaces, and they hypothesized that a similar increase in reactivity would occur with oxidized Pd nanoparticles [27]. To test this hypothesis, an oxidized Pd NP catalyst was prepared by the reduction of Pd/C with H_2 at 500 °C. This material was then exposed to air to form sites with adsorbed oxygen (O_{ad}). (This catalyst was called Pd/C-500$_{ox}$. Catalysts prepared