Platinum-Based Heterogeneous Catalysts for Nitrile Synthesis via Aerobic Oxidative Coupling of Alcohols and Ammonia

Yuliya Preger,† Thatcher W. Root,*†,‡ and Shannon S. Stahl*†,‡

†Department of Chemical and Biological Engineering, University of Wisconsin—Madison, 1415 Engineering Drive, Madison, Wisconsin 53706, United States
‡Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

Supporting Information

ABSTRACT: Transition-metal-catalyzed aerobic oxidative coupling of alcohols and ammonia represents an attractive atom-economical synthetic route to prepare nitriles. Heterogeneous platinum catalysts have been widely used for aerobic alcohol oxidation to aldehydes and carboxylic acids but have not been applied to nitrile synthesis. In this work, we show that carbon-supported Pt catalysts are effective for this transformation. Unpromoted Pt is competent with benzylic substrates bearing either electron-donating or electron-withdrawing substituents. Use of both K2CO3 and Bi additives accelerates the rate of alcohol oxidation and affords high yields with challenging heterocyclic alcohols.

INTRODUCTION

Tandem oxidative coupling reactions between an alcohol and a nucleophilic partner have emerged as efficient routes to value-added molecules.1 Many reactions of this type emerged in the 1990s and various functional groups, such as esters, imines, and amides, are accessible by such methods. Whereas heterogeneous platinum catalysts have been widely used in the oxidation of alcohols to aldehydes and carboxylic acids, they have not been used significantly in tandem oxidation reactions (Scheme 1A,B).2,3 Here, we report the demonstration and development of Pt-based catalysts for the four-electron oxidative coupling of benzylic alcohols and ammonia to afford (hetero)aromatic nitriles (Scheme 1C).

Aromatic nitriles are a prominent functional group featured in the synthesis and/or chemical structures of pharmaceuticals, agrochemicals, herbicides, dyes, and polymers.4 Their importance underlies recent efforts toward catalytic methods for nitrile synthesis via alcohol/ammonia coupling with homogeneous5 and heterogeneous6 catalysts. Observation of trace amounts of aldehydes in some of these methods implicates the sequential reaction path shown in Scheme 2, wherein the alcohol is oxidized to an aldehyde, which then reacts with ammonia to form a hemiaminal intermediate A. The hemiaminal could undergo dehydration to the imine B, followed by further dehydrogenation to the nitrile, or it could undergo direct dehydrogenation to the amide.7

RESULTS AND DISCUSSION

We initiated the present study with benzyl alcohol 1a using supported Pt and other commercially available catalysts known...
for alcohol oxidation. Many catalysts exhibited <1% alcohol conversion, likely due to catalyst poisoning by ammonia, but various Pt catalysts supported on carbon, silica, and alumina exhibited both alcohol conversion and nitrile formation (Figure 1A). In an effort to explore Pt-catalyst formulations beyond those available commercially and to probe factors that contribute to catalyst activity and selectivity, we synthesized a series of other Pt and mixed-metal catalysts on various supports and tested their utility in the oxidative coupling of benzyl alcohol and ammonia (Figure 1B).

We selected synthetic protocols for catalysts that had previously been reported for the oxidation of alcohols to aldehydes or carboxylic acids under comparable reaction conditions (liquid phase, mild temperatures). Variables that were evaluated in these syntheses included the reducing agent, support, and metal co-catalyst. The details concerning the syntheses of these catalysts and characterization of the best performing catalyst are provided in section 2 of the Supporting Information.

The best catalyst that emerged from these initial efforts was Pt supported on graphite oxide (GO) prepared by the polyol method. Reduction of chloroplatinic acid by ethylene glycol consistently led to more active catalysts than reduction with NaBH₄, as has been observed in other studies and attributed to the reduced particle size associated with this method. Different yields with Pt/Al₂O₃ in parts (A) and (B) reflect the difference between the commercial and synthesized catalysts, respectively. Carbon supports proved to be more effective than metal oxide supports, and among carbon supports, GO led to the highest activity. Incorporation of other metals, such as Ru, Au, and Co, generally reduced the activity. Quantitative conversion to 3a was achieved in 7 h under the conditions with a catalyst loading of 2.5 mol%. Experiments using aqueous or anhydrous ammonia showed similar catalytic trends. Addition of water (up to 5 equiv) to reactions with anhydrous ammonia showed no inhibition from the water, establishing that either ammonia source could be used.

The new Pt/GO catalyst was tested with diverse substrates to assess the reaction scope and limitations (Table 1). Primary benzylic alcohols with a variety of substituents reacted to afford the corresponding nitriles in good to excellent yields. Electron-donating and electron-withdrawing groups, ranging from −OMe to −CF₃, were all well-tolerated in the reactions, and the method was compatible with aryl chlorides and bromides. The catalyst was not effective with aliphatic alcohols, such as cyclohexylmethanol and 1-octanol, and exhibited only moderate activity with several heteroaromatic alcohols, as shown in Figure 1.

![Figure 1. Aerobic alcohol oxidation of benzyl alcohol to benzonitrile using (A) commercially available catalysts and (B) synthesized Pt catalysts. Conditions: 1a (0.25 mmol) and catalyst in CH₃CN with aqueous NH₃ at 90 °C for 7 h. Reactions carried out in a CAT24 pressure reactor using diluted oxygen (9% in N₂). Yields determined by gas chromatography (GC) analysis with mesitylene as an internal standard.](image)

Table 1. Substrate Scope of Pt-Catalyzed Aerobic Oxidation of Alcohols to Nitriles

| R     | 2a Yield | 3a Yield |
|-------|----------|----------|
| Me    | 96%      | 94% (88%)|
| MeO   | 97%      | 99% (95%)|
| Cl    | 79% (80%)| 72%      |
| Br    | 84%      | 84%      |
| F     | 76%      | 90%      |

*Conditions: 1 (0.3 mmol) and Pt on GO in CH₃CN (1.5 mL) at 90 °C for 20 h. Reactions carried out in a Parr pressure reactor with NH₃ and diluted oxygen (9% in N₂). Yield determined by GC analysis or by ¹H NMR spectroscopy with mesitylene as an internal standard. Isolated yields in parentheses.
Table 2. The low activity with heterocycles, which represent an important motif in industrial nitrile-containing molecules, prompted us to probe the mechanism of the reaction.

Table 2. Problematic Substrates for Pt-Catalyzed Aerobic Oxidation of Alcohols to Nitriles

| Substrate | Conversion (%) |
|-----------|----------------|
| 1m | 53% |
| 2m | 39% |
| 3o | 18% |
| 3p | 59% |

Figure 2. Time course of Pt-catalyzed nitrile formation. Fit reflects a first-order reaction model with concomitant catalyst deactivation (see section 3 of the Supporting Information). Conditions: \(1a = 0.2\) M, Pt/GO = 2 mol%, 5 atm NH\(_3\), 3 atm O\(_2\) (9% in N\(_2\)), 90 °C, MeCN. Reactions carried out in a Parr pressure reactor. Yields determined by GC analysis with mesitylene as an internal standard.

When the reaction progress was monitored, relatively little build-up of aldehyde was observed (Figure 2), suggesting that the aldehyde is relatively rapidly converted to the nitrile. A time course for the reaction of benzyl alcohol \(1a\) was modeled as a first-order series reaction in which the oxidation of the alcohol to the aldehyde is the first step and the oxidation of the aldehyde to the nitrile the second step. A discrepancy between a pure first-order series model and the experimental data indicates modest deactivation, which is fit well by a model (provided in section 3 of the Supporting Information) relating the slow decay in catalyst activity to aldehyde exposure. The fit yielded a \(k_1\) of 0.46 h\(^{-1}\) and a \(k_2\) of 5.7 h\(^{-1}\).

We then examined whether the excess ammonia could be inhibiting the alcohol oxidation. Ammonia has been shown to poison Pt catalysts in other contexts, for example, as a trace contaminant in fuel cells. A time profile complementary to the one in Figure 2 was completed in the absence of ammonia, with the aldehyde as the final product (Figure 3). Alcohol oxidation was nearly 6 times slower in the absence of ammonia, exhibiting a \(k_1\) of 0.08 h\(^{-1}\), thus indicating that ammonia instead promotes the alcohol oxidation reaction.

Higher alcohol conversion in the presence of other nitrogen-containing bases suggested that ammonia could function as a base as well as a coupling partner (Table 3). Pt-catalyzed oxidation of benzyl alcohol to aldehyde in the absence of any additives afforded only 21% alcohol conversion after 2 h (entry 1). NH\(_3\) addition doubled the alcohol conversion, with the product consisting of both aldehyde and nitrite (entry 2). Other amine bases, such as quinuclidine (entry 3) and DABCO (entry 5), also significantly increased the alcohol conversion beyond that of the base-free conditions. Though the addition of triethylamine (entry 4) lowered alcohol conversion, the results in Table 3 show that amine additives do not necessarily inhibit activity by coordinating to the Pt. The positive effect of the basic additive is attributed to promotion of alcohol deprotonation.

K\(_2\)CO\(_3\) was also tested as a basic additive and found to enable near-quantitative conversion of the alcohol to the aldehyde (entry 6). This result motivated the inclusion of K\(_2\)CO\(_3\) in the nitride reaction, and addition of 2 mol% K\(_2\)CO\(_3\) to the Pt catalyst increased benzyl alcohol conversion after 2 h from 34

Table 3. Impact of Nitrogen Bases on Pt-Catalyzed Aerobic Oxidation of Alcohols

| Entry | Base | \(pK_a\) | Alcohol Conversion (%) |
|-------|------|---------|-----------------------|
| 1     | none | --      | 21%                   |
| 2     | NH\(_3\) | 10.5   | 45%\(^d\)             |
|       |       |         | 49%\(^e\)             |
| 3     | Et\(_3\)N | 9.8    | 60%                   |
| 4     | 8.8   | 12%     |
| 5     | 9      | 64%     |
| 6     | K\(_2\)CO\(_3\) | -- | 99%                   |

\(^d\)Conditions: \(1a\) (0.3 mmol), base, and Pt/GO in CH\(_3\)CN at 90 °C for 2 h. Reactions carried out in a Parr pressure reactor with diluted oxygen (9% in N\(_2\)). \(^e\)Yields determined by GC analysis with mesitylene as an internal standard. Alcohol conversion encompasses aldehyde (and nitrite, for NH\(_3\)) formation. \(^f\)5 atm NH\(_3\), 0.3 atm N\(_2\).
to 65% (see Table S1 in the Supporting Information for optimization of the K₂CO₃ loading for nitrile formation). K₂CO₃ was then tested as an additive in the reaction of more challenging alcohols, such as heterocycle 1o, and the yield of the nitrile improved to 44% (Table 4, entries 1 and 2; cf. Table 2).

### Table 4. Improved Heterocycle Yields with K₂CO₃ and Bi₄

| entry | additive (%) | K₂CO₃ (%) | yield (%) |
|-------|--------------|-----------|-----------|
| 1     | –            | –         | 18        |
| 2     | –            | 2         | 44        |
| 3     | Bi(NO₃)₃ (0.5) | 2         | 71        |
| 4     | Bi(NO₃)₃ (1) | 2         | 71        |
| 5     | Bi(NO₃)₃ (2.5)| 2         | 68        |
| 6     | Bi (1)       | 2         | 41        |
| 7     | BiCl (1)     | 2         | 43        |
| 8     | PtBi (1)     | 2         | 25        |
| 9     | PtBi (JM)    | 2         | 51        |
| 10    | Bi(NO₃)₃ (3.5)| 2.8      | 91        |
| 11    | Fe(NO₃)₃ (1) | 2         | 42        |
| 12    | Pb(NO₃)₂ (1) | 2         | 59        |
| 13    | PtBi₄        | 2         | 37        |

*aConditions: 1o (0.3 mmol), K₂CO₃, additive, and Pt in CH₂CN at 90 °C for 20 h. Reactions carried out in a Parr pressure reactor with NH₃ and diluted oxygen (9% in N₂). Yields determined by ¹H NMR spectroscopy with mesitylene as an internal standard. *Research sample of 5 wt% Pt–1.5 wt% Bi/C (PtBi₄) from Johnson Matthey. *Bi(NO₃)₃ (3.5)% from Johnson Matthey (entry 9). Increasing the Pt to 3.5 mol% (a 40% change in loading) with a concomitant increase in the Bi and K₂CO₃ to maintain the relative ratios in entry 5, enabled an excellent yield of product (91%, entry 10). A nitrate salt with Fe exhibited a low yield (entry 11). However, a nitrate salt containing Pb, another known Pt promoter, did increase the yield (entry 12). Similar to the well-defined PtBi₄ case, a PtPb₄ case (entry 13) exhibited inferior results to the admixture catalyst (entry 12).

The promotional effect of the Bi and base was probed with other molecules that afforded low yields with the unpromoted Pt catalyst. The incorporation of base and Bi increased the yield of 3m from 53 to 93% (Table 5). Significantly improved yields were also observed with 3n (81%) and 3p (86%). The new catalyst system also afforded improved yields with halogen-containing benzyl alcohols, and the utility of this method was demonstrated in a 1 g-scale oxidative coupling with 1h, which afforded 4-fluorobenzonitrile 3h in 96% yield (eq 1).

### Table 5. Nitrile Yields under Original (A) and Improved (B) Conditions

| Condition A: 2.5 mol% Pt | Condition B: 1 mol% Bi(NO₃)₃, 2 mol% K₂CO₃ |
|--------------------------|---------------------------------------------|
| A: 72%                   | B: 97%                                      |
| 3h                       | 3i                                          |
| F                      | CN                                          |
| N                      | S                                           |
| N                      | O                                           |
| 3n                       | 3o                                          |
| A: 39%                   | B: 81%                                      |
| 3p                       | 3p                                          |

*Conditions: [substrate] = 0.2 M, 1 atm NH₃, 3 atm O₂ (9% in N₂), MeCN, 90 °C, 20 h. Yields determined by GC analysis or ¹H NMR spectroscopy with mesitylene as an internal standard. °70 °C (to avoid side reactions).

In conclusion, we have demonstrated that carbon-supported Pt nanoparticles can mediate the one-pot aerobic oxidation of alcohols to nitriles. The Pt catalyst itself enables effective conversion of many benzyl alcohols to the corresponding benzonitriles, but addition of K₂CO₃ and Bi significantly improves the catalytic performance with heterocycle-containing substrates. This work illustrates the broad utility of Pt in four-electron coupling reactions, as well as the ease with which its activity may be modified via the use of promoter metals.

## EXPERIMENTAL SECTION

### General Information

All commercially available compounds and solvents were purchased and used as received, unless otherwise noted. No precautions were taken to exclude air or water from the solvent or reaction mixtures. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III 400 or Bruker AVANCE III 500 spectrometer. Chemical shift values are given in parts per million relative to internal tetramethylsilane (0.00 ppm for ¹H) or CDCl₃ (77.16 ppm for ¹³C). The following abbreviations were used to describe peak splitting...
patterns when appropriate: s = singlet, d = doublet, m = multiplet, dd = doublet of doublets. Coupling constants, J, were reported in hertz (Hz). Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). Flash chromatography was performed on an Isco Combiflash system using SiliaFlash P60 (Silicycle, particle size 40–63 μm, 230–400 mesh).

Procedure for Batch Oxidation of Alcohols in a CAT24 Pressure Reactor. Solutions of alcohol (0.25 mmol), mesitylene (25 mol%) as an internal standard, and aqueous NH₃ (3 equiv) in acetonitrile (0.5 mL) were added to thick-walled glass tubes containing the platinum catalyst (1 mol% or 2 mg based on Bi(NO₃)₃·5H₂O), and 2.8 mol% K₂CO₃ (31 mg) relative to the alcohol. Given the greater quantity of alcohol, the Parr vessel was agitated using a custom vortexer at 90 °C for 7 h. Afterward, the reactor was allowed to cool down to <40 °C for 2 h. Upon completion, the reactor was opened and washed with ethyl acetate. The acetate mixture was transferred to an NMR tube, and the tube was centrifuged to settle the solid catalyst prior to analysis.

Isolation. For collection of the isolated product, the catalyst was filtered off and washed with ethyl acetate. The filtrate was concentrated in vacuo and the corresponding nitrile was purified by column chromatography (silica; hexanes–ethyl acetate mixture). The appropriate solvent ratio was identified by TLC. The chromatography solvents were removed in vacuo to afford the isolated nitrile. Spectral properties of all products are consistent with the literature values.

Isolated yields are shown below. To facilitate isolation, the reactions were performed on a 4 mL scale (instead of the 1.5 mL scale noted in Table 1). The NH₃ pressure was increased to 3 atm given the larger scale.

4-Methylbenzonitrile (3b, 88%); ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 143.73, 132.01, 129.84, 119.16, 109.25, 21.82.

4-Methoxybenzonitrile (3c, 95%); ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.91, 134.05, 119.32, 114.83, 103.99, 55.63.

4-Bromobenzonitrile (3j, 80%); ¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 133.51, 132.74, 128.12, 118.16, 111.32.

4-Fluorobenzonitrile scale-up (3k, 96%); ¹H NMR (400 MHz, CDCl₃): δ 7.68 (dd, J = 8.8, 5.1 Hz, 2H), 7.26–7.06 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 165.14, 134.79, 118.15, 116.97, 108.63.

ASSOCIATED CONTENT

Supporting Information
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AUTHOR INFORMATION

Corresponding Authors
*E-mail: twroot@wisc.edu (T.W.R.).
*E-mail: stahl@chem.wisc.edu (S.S.S.).

ORCID

Thatcher W. Root: 0000-0002-8182-9835
Shannon S. Stahl: 0000-0002-9000-7665

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Notes
The authors declare no competing financial interest.

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