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Conversions of Cyclic Amines to Nylon Precursor Lactams Using Bulk Gold and Fumed Silica Catalysts[†]

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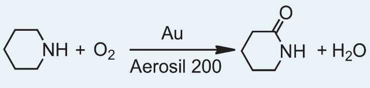
S *Supporting Information*

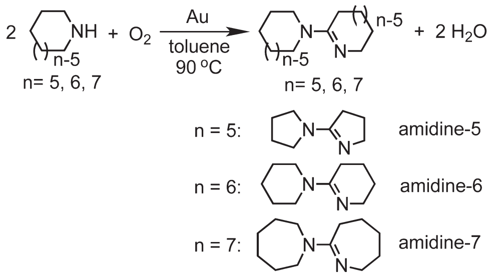
ABSTRACT: *Bulk* gold powder (~50 μm) and alumina-supported gold catalyzed the oxidative dehydrogenation of 5-, 6-, and 7-membered cyclic amines to amidines. These amidines were hydrolyzed upon treatment with Aerosil 200 (fumed silica gel) and water, producing lactams in 42−73% yields and amines in 36−63% yields. The gold and Aerosil 200 catalysts could also be combined in a one-pot reaction to catalyze the conversion of cyclic amines to lactams in yields up to 51%.



KEYWORDS: gold, oxidative-dehydrogenation, catalysis, amidine, hydrolysis, amine, caprolactam, nylon

1. INTRODUCTION

While supported nanogold particles (<5 nm) have attracted much interest because of their ability to catalyze several different types of reactions,[1−7] *bulk* Au powder (~50 μm) has a reputation as a poor catalyst.[1] However, we have shown it to be an effective catalyst in a number of different reactions, such as the reaction of isocyanides with amines and O_2 to form carbodiimides[8] or ureas,[9] the reaction of CO with amines and O_2 to give ureas,[10] the coupling of carbene precursors to olefins,[11] and the reaction of diazoalkanes with amines and O_2 to give enamines.[12] In addition, we have demonstrated that bulk Au and 5% Au/Al_2O_3 catalyze the oxidative dehydrogenation of cyclic amines with O_2 to form amidines (eq 1).[13,14]



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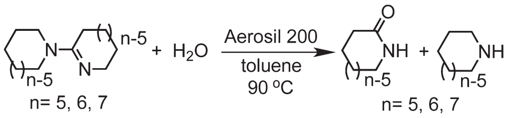
To the best of our knowledge, only two other examples have been reported in which cyclic amines are catalytically converted to amidines, and these both involved pyrrolidine. One used Pd black to catalyze the dehydrogenation of pyrrolidine under an Ar atmosphere at 80 °C to give amidine-5 in 65% yield.[15,16] The other catalyst for this conversion is carbon-supported nanogold, which catalyzed the oxidative dehydrogenation of pyrrolidine to amidine-5 in 99% yield.[17]

We have now found that cyclic amidines undergo hydrolysis to form lactams upon heating with Aerosil 200 and water (eq 2). In addition, we report that these lactams can be produced directly by treating cyclic amines with Au, Aerosil, oxygen, and water in one pot (eq 3). This represents a potentially significant improvement for the multistep production of industrially important nylon precursors such as caprolactam.[18,19] This compound is traditionally prepared from cyclohexane using harsh conditions in a process that generates substantial waste ammonium sulfate.[20] The large-scale manufacture of caprolactam and its subsequent polymerization to nylon-6 is driven by the low cost of benzene and its conversion to cyclohexane.[19,21] The analogous polymerization of butyrolactam and valerolactam to nylons-4 and -5, respectively,[22,23] has tremendous potential for use in textile fibers as these nylons are able to absorb more moisture and generate less static buildup compared to nylon-6.[24] Despite these advantages, nylons-4 and −5 are a minor component of the polyamide fiber industry. However, improved syntheses of butyro- and valerolactam may enhance the market viability of nylons-4 and -5. Details of the hydrolysis of amidines (eq 2) and the overall conversion of cyclic amines (eq 3) to lactams are described in this paper.



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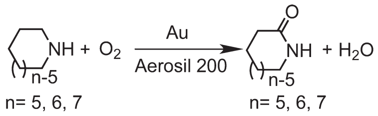

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2. EXPERIMENTAL SECTION

All amines were dried over calcium hydride, distilled under reduced pressure according to literature procedures,[25] and stored over type 4A molecular sieves, prior to use. All other solvents and compounds were used as received, unless otherwise noted. Toluene, *p*-xylene, decane, dodecane, triphenylmethane, γ-butyrolactam, δ-valerolactam, ε-caprolactam, and oxygen (99.9%) were purchased commercially. Alumina (Basic Brockman Activity I,

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150 m^2/g, particle size = 44−250 μm, pore volume = 0.25 mL/g, pore diameter = 60 Å) was purchased from Fisher, and Amberlyst-15, a porous sulfonated cross-linked polystyrene (40−50 m^2/g, particle size = 300−1150 μm, pore volume = 0.24−0.40 mL/g, pore diameter = 300 Å) was acquired from Sigma- Aldrich. Aerosil 200 (nonporous silica gel, 200 m^2/g, average primary particle size = 12 nm), hereafter referred to as Aerosil, was a gift from the Evonik Degussa Corporation, and silica gel (500−600 m^2/g, particle size = 40−63 μm, pore volume = 0.65−0.85 mL/g, pore diameter =60 Å) was purchased from Sorbent Technologies. Hydrotalcite (82 m^2/g, pore diameter = 250 Å) was prepared using a published procedure.[26]

2.1. General Procedure for the Preparation and Cleaning of Gold Powder. Gold powder was prepared from $HAuCl_4$ and cleaned as described previously.[11] The powder consists of large particles (5−50 μm), which were previously characterized by electron microscopy.[8,11] Because of gradual loss of activity with each run, comparisons of catalytic results were restricted to those with batches of gold powder that had previously undergone the same number and type of reactions. Once a batch was used for the comparative studies, it was recycled for the next cycle of experiments using the following multistep treatment: the gold was collected by filtration from a catalytic reaction mixture, rinsed with 50 mL of acetonitrile, washed with 50 mL of methanol, stirred with 40 mL of “piranha” solution[11] for 4 h, diluted with 200 mL of water, filtered on filter paper, washed 10 times with 40-mL volumes of deionized water, rinsed with five 40-mL methanol aliquots, and oven-dried overnight in air at 110 °C.

2.2. General Procedure for Separation of Aerosil and Au. Following a one-pot reaction using both gold powder and Aerosil, the solution was filtered, and the solid residues were transferred to a beaker containing 25 mL of deionized H_2O. The Aerosil was removed by agitating the mixture and removing the suspended particles with a pipet. Additional fresh deionized water was added, until all of the Aerosil was removed by pipetting. The gold was then cleaned and dried as described above.

2.3. Preparation of 5% Au/Al_2O_3. Au/Al_2O_3 was prepared by an incipient wetness impregnation method similar to that used previously[14] with the following modification: Alumina (γ-Al_2O_3) was purchased from Alfa Aesar (200 m^2/g, particle size = 40 μm). Au/Al_2O_3 was characterized by STEM, TEM, and EDX. The Au particle shapes were irregular, and the sizes were in the 20−700 nm range (see Supporting Information).

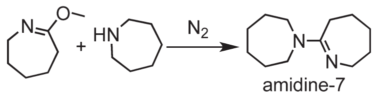
2.4. Au-Catalyzed Reaction of Amines and O_2. A glass tube (2.0 × 17 cm, ∼65 mL volume) was loaded with 1.00 g of Au powder or 100 mg of 5% Au/Al_2O_3. Stock solutions, in toluene, of the desired amine (1.0 mL, 200.0 mM) and decane or dodecane internal standard (4.0 mL, 4.5 mM) were then added to the tube to produce a 5.0 mL solution with the desired substrate concentration (40.0 mM). The vessel was capped with a rubber septum through which oxygen gas was delivered by the insertion of a syringe needle that was attached to a balloon of oxygen (∼1.0 L at ∼1 atm). The reaction was stirred with a magnetic stirbar at 90 °C in an oil bath. Aliquots (∼50 μL) were withdrawn periodically by a syringe and analyzed by GC (see below).

2.5. Aerosil-Catalyzed Hydrolysis of Amidines. A glass tube (2.0 × 17 cm, ∼65 mL volume) was charged with 5.0 mL of a solution containing the desired concentration of amidine (20.0 mM) and internal standard (decane or dodecane) in a given solvent, after which 50 mg of Aerosil and 200 μL of water were added. The tube was then capped with a septum, and the mixture was stirred at 90 °C in air in an oil bath. Aliquots were periodically extracted with a syringe and analyzed by GC (see below).

2.6. Combined Au Powder/Aerosil-Catalyzed Conversion of Amines to Lactams. A 5.0 mL solution with the desired concentrations of the amine (40.0 mM) and internal standard was prepared by the addition and subsequent dilution of stock solutions. To a Schlenk tube (2.5 × 17 cm, ∼80 mL volume) was added 1.0 mL of a 200.0 mM solution of the amine, followed by 4.0 mL of a stock solution of internal standard in the same solvent. The contents of the tube were then shaken to mix the solution together. Gold powder (1.00 g) or 5% Au/Al_2O_3 (100. mg), 50 mg of Aerosil, and 200. μL of deionized water were then added to the prepared solution. A 28-cm water-cooled condenser was fitted with a rubber septum and attached to the Schlenk tube. Oxygen was supplied to the reaction system with a balloon of O_2 (∼1.0 L @ ∼1 atm) attached to a syringe needle inserted into the septum at the top of the condenser. The reaction was then stirred at 90 °C in an oil bath. Aliquots were taken periodically and analyzed by GC (see below). Prior to GC analysis, the aliquots were filtered through a cotton plug to remove suspended Aerosil particles.

2.7. Preparation of Authentic Amidine Samples. The amidines (amidine-5 and amidine-6) that are generated from the oxidative dehydrogenation of pyrrolidine and piperidine were prepared using larger scale reaction conditions.[13] The ^1H NMR and GCMS results for these compounds matched reported values for amidine-5[15] and amidine-6.[13] Amidine-5: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.67$ (t, $^3J(H,H) = 6.9$ Hz, 2H; CH_2), 3.37 (t, $^3J(H,H) = 7.8$ Hz, 4H; CH_2), 2.19 (t, $^3J(H,H) = 7.8$ Hz, 2H; CH_2), 2.00−1.86 ppm (m, 6H; CH_2). Amidine-6: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.50$ (t, $^3J(H,H) = 5.6$ Hz, 2H; CH_2), 3.26 (t, $^3J(H,H) = 5.6$ Hz, 4H; CH_2), 2.19 (t, $^3J(H,H) = 6.4$ Hz, 2H; CH_2), 1.70 (m, 2H; CH_2), 1.54 ppm (m, 8H; CH_2).

Authentic amidine-7 was prepared through an independent synthesis using a modified procedure involving the addition of hexamethyleneimine (211 mg, 2.11 mmol) to neat caprolactim methyl ether (250 mg, 1.97 mmol) (eq 4).[27]



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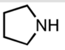
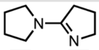
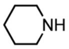
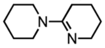
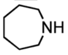
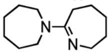
The reaction was stirred under nitrogen for 8 h at 100 °C, and then for 8 h at 70 °C. Unreacted reagents and volatile components were removed under reduced pressure to afford amidine-7 (159 mg, 42% yield). The ^1H NMR spectrum matched reported literature values.[13] Caprolactim methyl ether was prepared according to a published procedure.[28] Amidine-7: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.41$ (m, 6H; CH_2), 2.49 (m, 2H; CH_2), 1.73−1.48 ppm (m, 14H; CH_2)

2.8. GC and GC-MS Analyses. GC analyses were performed on an HP-6890 instrument equipped with an HP-5 capillary column (30 m length, 0.25 mm internal diameter, 0.25 μm film thickness, 5% phenyl, 95% methyl silicone polymer). The GC analysis conditions were as follows: He carrier gas; constant flow mode; initial column temperature, 50 °C for 2 min; heating rate, 15 °C/min; final temperature, 280 °C.

Reaction products were identified by comparison of their mass spectra and GC retention times with those of authentic samples.

Table 1. Product Yields for the Au-Catalyzed Oxidative Dehydrogenation Reaction (eq 1) of Various Cyclic Amines[a]

		Yield (%)		
Amine	Product	Au powder[b]	Au/Al_2O_3[c]	New Au/Al_2O_3[c]
		93[d]	98[d]	58
		87	95[d]	54
		20	33[d]	24

[a] Reaction conditions: 40.0 mM amine, O_2 (~1.0 L @ ~1 atm) in 5.0 mL of toluene solvent at 100 °C for 24 h. [b] 1.00 g of Au powder catalyst. [c] 100 mg of 5% Au/Al_2O_3 catalyst. [d] Ref 14.

Yields were determined by GC integrations using authentic samples of the products for response factors. GC-MS measurements were obtained from a Finnegan Magnum GC-MS or a Waters Micromass GCT instrument.

3. RESULTS AND DISCUSSION

3.1. Au-Catalyzed Reaction of Cyclic Amines and O_2. We reported previously that both bulk Au[13] and 5% Au/Al_2O_3[14] catalyzed the oxidative dehydrogenation reaction of the cyclic amines, pyrrolidine, piperidine, and hexamethyleneimine to amidines (eq 1, Table 1). In the present work, the 5% Au/Al_2O_3 catalyst was prepared using a different commercially available γ-alumina as the support. When used in the oxidative dehydrogenation of cyclic amines under the same conditions as the previous studies, the new 5% Au/Al_2O_3 showed the same trend in decreasing product yield as the size of the amine ring increased. However, this batch of catalyst was not as active as the previously reported Au/Al_2O_3[14] (Table 1).

While the previously synthesized 5% Au/Al_2O_3 consisted primarily of smaller Au particles (50–150 nm), the new supported catalyst contained Au particle sizes in the 20–700 nm range. The size and broad Au particle distribution in the new supported catalyst may explain its reduced activity, as compared with that for the previously reported 5% Au/Al_2O_3.

3.2. Aerosil-Catalyzed Hydrolysis of Amidines. Amidines generally undergo hydrolysis with water[29] under both homogeneous base[30,31] and acid[32] catalysis. However, the hydrolysis of the amidines in Table 1 had not been studied. Thus, we sought to determine the optimum conditions for the hydrolysis (eq 2) of our cyclic amidines in the presence of various heterogeneous catalysts. Both acidic and basic oxides were tested, as well as a solid acid catalyst. The materials examined included Aerosil, basic alumina, silica gel, hydrotalcite, and Amberlyst-15. Treatment of amidine-6 with all oxide catalysts led to hydrolysis and gave valerolactam and piperidine as the only observable products (eq 2). As described below, Aerosil was the most effective catalyst (Table 2).

When a solution of amidine-6 (20.0 mM) in 5.0 mL of toluene at 90 °C was treated with 50 mg of nonporous fumed silica Aerosil in the absence of added water, it underwent hydrolysis to form valerolactam in 26% yield after 36 h. When more than 50 mg of Aerosil was used as the catalyst, the mixture became a gel that was difficult to separate and analyze. An important factor in this process is the amount of water present. Although Aerosil contains adsorbed water, the addition of extra water to the reaction mixture, up to 200 μL, was observed to increase the rate and yield of hydrolysis. The addition of 400 μL of water resulted in no additional hydrolysis beyond that produced by 200 μL of water. Moreover, the addition of 1.5 mL of water drastically inhibited the reaction, reducing the yield to <5% valerolactam after 36 h (Figure 1). Optimized conditions, using 50 mg of Aerosil with water (200 μL, 2.2 M) in toluene resulted in a 60% yield of valerolactam. It should be noted that the use of *p*-xylene as the solvent gave essentially the same yield of lactam as toluene in this reaction. Other catalysts hydrolyzed amidine-6 to valerolactam in considerably lower yields when studied using the optimized conditions (Table 2).

Table 2. Catalyst Performance in the Hydrolysis Reaction of Amidine-6 (eq 2)[a]

Entry	Catalyst	% Conversion	% Yield
1	Aerosil	100 (100)[b]	60 (29)[b]
2	Alumina	85 (67)[b]	35 (16)[b]
3	Hydrotalcite	48 (27)[b]	20 (6)[b]
4	Silica Gel	100	19
5	Amberlyst-15	100	0
6	None	16	16

[a] Reaction conditions: amidine-6 (20.0 mM), catalyst (50 mg), H_2O (200 μL) in 5.0 mL of toluene at 90 °C for 48 h. [b] Numbers in parentheses were from runs in which no water was added.

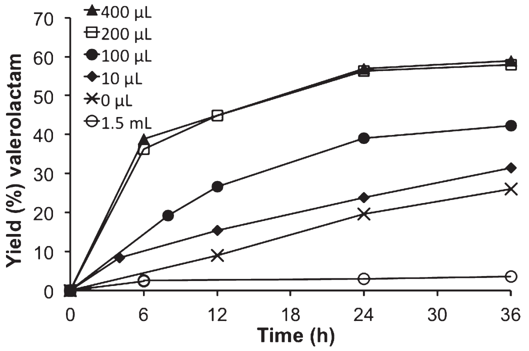


Figure 1. Effect of the addition of various amounts of water to the Aerosil-catalyzed hydrolysis (eq 2) of amidine-6 (20.0 mM) at 90 °C in 5 mL of toluene.

Using the optimized conditions, amidine-7 was hydrolyzed to caprolactam (73%) and hexamethyleneimine (63%), while amidine-5 was hydrolyzed under the same conditions to produce butyrolactam (42%) along with pyrrolidine (36%) (Figure 2). At reaction times greater than 24 h, the lactam yield increased only slightly and after 24 h, very little amidine was detected by GC (Figure 3).

In seeking to improve yields, we sought to determine if some of the valerolactam and piperidine products remained adsorbed on the Aerosil. Using quantities similar to those in our reaction conditions, 5.0 mL of a 20.0 mM toluene solution of valerolactam was stirred with 200 μL of water and 50 mg of Aerosil for 48 h at 90 °C. GC analysis of the resulting solution showed that about 30% of the lactam had adsorbed on the Aerosil. After the solution was removed by filtration, the Aerosil was stirred in 5.0 mL of methanol at ambient temperature with an internal standard for 48 h in a capped tube; GC analysis showed that approximately 33% of the adsorbed valerolactam was extracted into the methanol. The remaining 67% of the valerolactam may be strongly adsorbed to the Aerosil or may have undergone hydrolysis or polymerization under the conditions of the adsorption (90 °C and 200 μL of water) and would not have been detected by GC. In a separate experiment using *p*-xylene as the solvent so that the amount of piperidine product could be quantified by GC analysis, the Aerosil-catalyzed hydrolysis of amidine-6 was run for 48 h at 90 °C, after which GC analysis of the solution showed a 57% conversion of amidine-6 to valerolactam and a 46% yield of piperidine. The Aerosil was recovered by filtration and then stirred for 48 h at ambient temperature in 5.0 mL of methanol with triphenylmethane as an internal standard. GC analysis of the methanol solution detected additional amounts of valerolactam and piperidine which increased the overall yields of these products to 65% and 51%, respectively. Since all of the amidine-6 is consumed under the conditions of the hydrolysis reaction (90 °C, 48 h), 35% of the amidine is not converted to detectable lactam product. Some of the valerolactam could have undergone hydrolysis or polymerization, as suggested by the previous experiment in which valerolactam is converted on Aerosil at 90 °C to compounds that could not be extracted from the Aerosil and/or were not sufficiently volatile to be detected by GC.

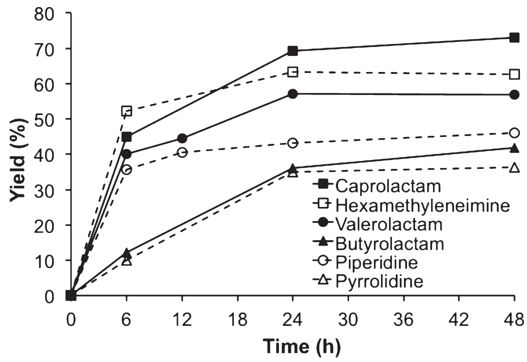


Figure 2. Aerosil-catalyzed hydrolysis (eq 2) of amidines. Conditions: 20.0 mM amidine, 50 mg of Aerosil, and 200 μL of H_2O in 5.0 mL of toluene at 90 °C. Amidine-6 hydrolysis was run in *p*-xylene.

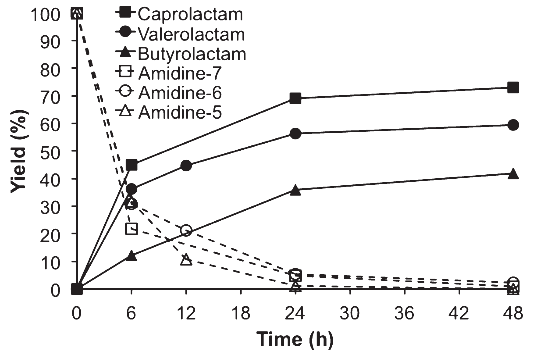


Figure 3. Aerosil-catalyzed hydrolysis (eq 2) of amidines. Conditions: 20.0 mM amidine-6, 50 mg of Aerosil, and 200 μL of H_2O in 5.0 mL of toluene at 90 °C. Dashed lines indicate disappearance of amidines and solid lines show formation of lactams.

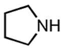
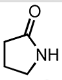
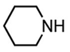
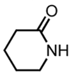
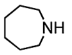
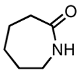
The low yield of the piperidine product (51%) from the hydrolysis (eq 3) of amidine-6 suggests that it also is either strongly adsorbed on the Aerosil and/or reacts (perhaps with the lactam) to give a nonvolatile product. Previous studies showed that piperidine is strongly adsorbed on hydrated silica because of protonation to form the piperidinium cation;[33] this may account for the low quantity of detected piperidine product.

3.3. Combined Au Powder/Aerosil-Catalyzed Conversion of Amines to Lactams (eq 3).

As an alternative to running the oxidative dehydrogenation and hydrolysis processes as separate batch reactions, we examined a one-pot, tandem catalyst system that combines both the Au and the Aerosil. We chose reaction conditions (90 °C, in toluene, 1.00 g of Au, 50 mg of Aerosil, ~1.0 L at ~1 atm of O_2) that were suitable for both steps. When no additional water was added, the yield of valerolactam from piperidine was only 21%, according to the stoichiometry in eq 3. However, under the same conditions but with 200 μL of water added, the lactam yield improved to 51%. The same conditions were used in directly converting the other cyclic amines. Piperidine is converted to the corresponding lactam in the highest yield of all of the cyclic amines that were tested (Table 3).

The amount of lactam produced is a net result of contributions from the two steps (oxidative dehydrogenation and hydrolysis, eqs 1, 2) involved in the overall transformation (eq 3). The most favorable oxidative dehydrogenation step occurs with pyrrolidine and piperidine which gave amidines in 93% and 87% yields, respectively (Table 1). On the other hand, the hydrolysis step gives the highest yield (73%) of lactam with amidine-7 (Figure 2). When the new Au/Al_2O_3 was used as the catalyst, the valerolactam yield was much lower (24% vs 51%) as compared with gold powder, presumably because of its decreased efficiency in producing amidine-6 in the oxidative dehydrogenation of the amine (Table 1). In contrast, the very low overall yield of caprolactam reflects the low yield of amidine-7 in the Au-catalyzed oxidative dehydrogenation of hexamethyleneimine.

Table 3. Lactam Yields (eq 3) for the Combined Au/Aerosil- Catalyzed Oxidative Dehydrogenation and Subsequent Hydrolysis Reactions of Various Cyclic Amines[a]

Entry	Amine	Product	Conversion (%)	Yield (%)	TON[e]
1			100[b]	35[b]	12
2			100[b]	51[b] (24)[c] (21)[bd]	16[b] (1600)[c]
3			100[b]	11[b]	4

[a] Reaction conditions: 40.0 mM amine, O_2 (~1.0 L @ ~1 atm), 50 mg of Aerosil, 200 μL of H_2O in 5.0 mL of toluene solvent at 90 °C for 96 h. [b] 1.00 g of Au powder. [c] 100 mg of Au/Al_2O_3 in place of Au powder. [d] No water added. [e] Estimated TONs were based on the number of surface atoms[34] and assuming all were active sites.

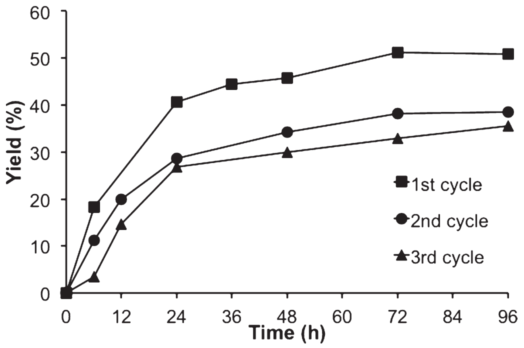


Figure 4. Product Yields for the Au/Aerosil-catalyzed conversion of piperidine to valerolactam (eq 3). Conditions: amine (0.2 mmol), O_2 (~1.0 L @ ~1 atm), Au powder (1.00 g), Aerosil (50. mg), H_2O (200 μL) in 5.0 mL of toluene at 90 °C.

3.4. Catalyst Recycling. After each combined Au/Aerosil catalyzed reaction of amines to lactams, the solid catalyst was recovered by filtration. Removal of the Aerosil catalyst from the Au powder was accomplished by utilizing density differences as described in the Experimental Section. The gold was then treated with "piranaha" solution (see Experimental Section). This recycled Au catalyst together with fresh Aerosil was used again in a reaction of piperidine with oxygen and water (Figure 4).

The first use of the Au/Aerosil catalyst produced the highest yield of valerolactam (51%). When this batch of gold was cleaned and used in a second reaction, the valerolactam yield decreased to 39%. On reuse of the Au a third time, the decrease in activity was less pronounced (36% yield). The loss of activity is most likely due to the incomplete removal of organic material on the Au surface, even after piranha treatment. A similar loss in activity was observed in self-coupling reactions of diazoalkanes catalyzed by bulk Au.[11]

4. CONCLUSIONS

Both bulk gold powder (~50 μm) and 5% gold supported on alumina catalyzed the oxidative dehydrogenation of cyclic amines to amidines (eq 1) in yields up to 98% (Table 1). Subsequent conversion of the amidines to lactams was most effectively accomplished with Aerosil 200 (fumed silica gel) as a hydrolysis catalyst (eq 2). The hydrolysis rate could be enhanced by adding an optimal amount of water to the solution. A convenient one-pot process using a tandem catalyst system of bulk gold or 5% Au/Al_2O_3 with Aerosil 200 was developed for the overall catalytic conversion of amines to lactams. In the case of piperidine, valerolactam was produced in >50% yield. In summary, we have developed a heterogeneous catalytic system that is able to perform a tandem process involving oxidative dehydrogenation of cyclic amines, followed by a subsequent hydrolysis of the resulting amidine to form lactams. This is a novel route for the synthesis of industrially important nylon precursors from readily available cyclic amines using oxygen, water, and commercially available catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. STEM, TEM, and EDX analysis data for 5% Au/Al_2O_3 catalyst (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ DEDICATION

[†] Dedicated to the memory of our dear friend, Victor S.-Y. Lin.

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