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Simple Preparation and Application of TEMPO-Coated Fe_3O_4 Superparamagnetic Nanoparticles for Selective Oxidation of Alcohols

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Abstract: The organic oxidant TEMPO (2,2,4,4-tetramethylpiperdine-1-oxyl) was immobilized on iron oxide (Fe_3O_4) superparamagnetic nanoparticles by employing strong metal-oxide chelating phosphonates and azide/alkyne "click" chemistry. This simple preparation yields recyclable TEMPO-coated nanoparticles with good TEMPO loadings. They have excellent magnetic response and efficiently catalyze the oxidation of a wide range of primary and secondary alcohols to aldehydes, ketones, and lactones under either aerobic acidic Mn^{II}/Cu^{II} oxidizing Minisci conditions, or basic NaOCl Anelli conditions. The nanoparticles could be recycled more than 20 times under the Minisci conditions and up to eight times under the Anelli conditions with good to excellent substrate conversions and product selectivities. Immobilization of the catalyst through a phosphonate linkage allows the particles to withstand acidic oxidizing environments with minimal catalyst leaching. Clicking TEMPO to the phosphonate prior to phosphonate immobilization, rather than after, ensures the clicked catalyst is the only species on the particle surface. This facilitates quantification of the catalyst loading. The stability of the phosphonate linker and simplicity of this catalyst immobilization method make this an attractive approach for tethering catalysts to oxide supports, creating magnetically separable catalysts that can be used under neutral or acidic conditions.

Keywords: alcohols · heterogeneous catalysis · nanoparticles · oxidation · supported catalysts

Introduction

Selective oxidation of alcohols to their carbonyl analogs is one of the most important chemical transformations in organic synthesis.[1] Many of the most common oxidation methods are performed by using stochiometric amounts of inorganic oxidants such as Ru-, Se-, Cr-, and Mn-based oxides.[2] These oxidants tend to be expensive and generate large amounts of toxic, heavy metal waste.[3] This has prompted researchers to develop more economical oxidants that are highly active, chemo-/regioselective, recyclable, and have a low environmental impact.[4] We report here two new simple methods for preparing 2,2,4,4-tetramethylpiperdine-1-oxyl (TEMPO) coated superparamagnetic nanoparticles (SPNs). The catalysts produced by both methods are highly active for the selective oxidation of alcohols to their carbonyl analogues and can be recycled many times.

TEMPO has been widely used over the past 20 years as an alternative oxidizing agent because of its reversible redox behavior, high catalytic efficiency, and chemo- and regioselectivity.[5] When used catalytically, TEMPO may be combined with stochiometric amounts of a co-oxidant that regenerates the active TEMPO species during the reaction. Common stochiometric co-oxidants include trichloroisocyanuric acid,[6] bis(acetoxy)iodobenzene,[7] and sodium hypochlorite.[2a,5a,8] TEMPO may also be used catalytically in the presence of excess molecular oxygen and small amounts of catalytic co-oxidants. Under these conditions, the co-oxidants utilize molecular oxygen to regenerate TEMPO during the reaction. Molecular oxygen as a terminal oxidant for TEMPO-driven oxidations is attractive from both an economic and environmental standpoint. Some examples of catalytic co-oxidants used in conjunction with molecular oxygen include *tert*-butyl nitrite/HBr, $NaNO_2$/HCl, $NaNO_2$/nBu_4NBr, $NaNO_2$/Br_2, and transition metals (Ru^{II}, $Cu^{I/II}$, Mn^{II}/Cu^{II}, $Fe^{II/III}$).[9,10]

Because TEMPO is expensive, it is desirable to isolate, purify, and recycle it for further use. TEMPO can be immobilized on organic or inorganic carriers, including task-spe-

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cific ionic liquids,[11] soluble polyethylene glycol, ROMP polymers and perfluoroalkyl chains,[12] mobile crystalline materials, mesoporous silica and silica sol–gels,[13] poly(styrene) and poly(urethane) resins,[14] and carbon-coated Co ferromagnetic nanoparticles (FNPs).[15] SPNs are proving to be excellent catalytic supports because of their high surface area ($600\,m^2cm^{-3}$) and surface curvature, which allow large catalyst loadings and maximum substrate accessibility to catalytic sites.[16] SPNs are highly dispersible and can be magnetically separated by using hand-held magnets and redispersed after removing the magnetic field. This eliminates the need for tedious and often messy catalyst filtration. The facile separation method also makes catalysts easy to handle and minimizes catalyst loss. To make TEMPO-coated SPNs, or any catalyst-coated SPNs, available for general laboratory use and attractive to industry: a) the core SPN support should be inexpensive, easily synthesized, and stable; b) the chemistry used to make and modify the catalyst should ideally be simple and high yielding; and c) the catalyst should be recyclable many times. In fact, the use of magnetic nanoparticles as supports for synthetic catalysts has already ready made the transfer to industry, with the creation of TurboBead in 2007.

To date, there is one example of TEMPO being immobilized on magnetic nanoparticles.[15] TEMPO was covalently bonded to carbon-coated/Co FNPs, which have excellent magnetic properties. The FNPs were shown to be highly active for the oxidation of alcohols using stochiometric amounts of NaOCl, and were cycled 14 times with no apparent loss of catalytic activity. We report here the immobilization of TEMPO on iron oxide SPNs, which yields a highly active catalyst for oxidizing alcohols under acidic, aerobic conditions with Mn^{II}/Cu^{II} co-catalysts (Minisci conditions) and basic conditions using NaOCl/KBr (Anelli conditions).

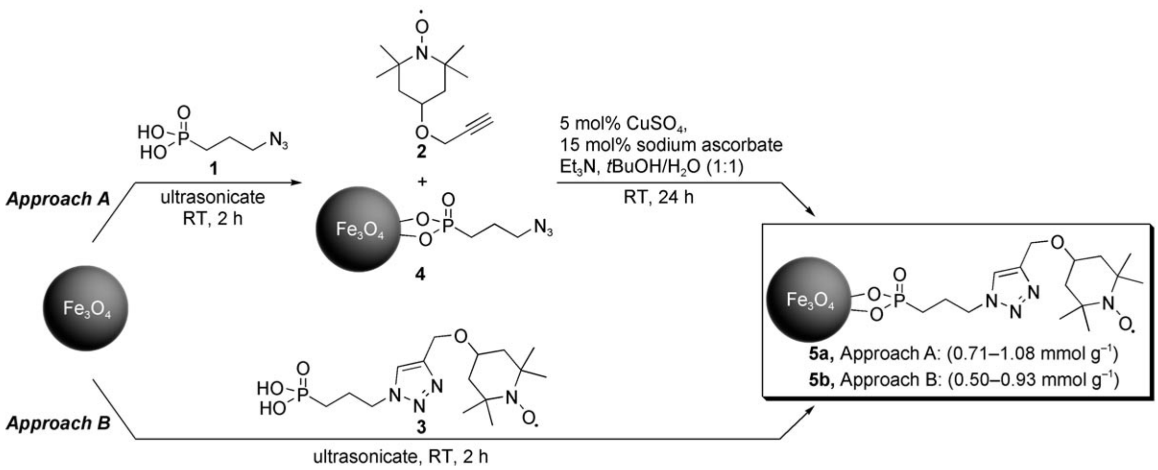
Results and Discussion

Magnetite (Fe_3O_4) SPNs were chosen as the core magnetic support because of their simple synthesis, low cost, and relatively large magnetic susceptibility. Fe_3O_4 SPNs, with 11.7 nm average diameter, were prepared by co-precipitation from $FeCl_3/FeCl_2$ solution with NH_4OH, as previously reported by Berger et al.[17] (see the Supporting Information.) Commonly, researchers modify oxide SPN surfaces by using functional silanes (e.g., aminopropyl or isocyanopropyl silanes) or catechols to create points of attachment for catalysts or other molecules. Silane-coating processes are very sensitive to factors such as moisture, which can make it challenging to control the coating amount and uniformity.[18] In particular, silane coatings may result in a substantial decrease in the magnetic susceptibility of particles unless agglomerates of SPNs are coated.[19] Functionalization of SPNs using catechols is advantageous because they can be immobilized simply by sonication. However, it has been shown that catechols, such as dopamine, can oxidize to the semiquinone and quinone forms at the surface of iron oxide SPNs. This oxidation ultimately results in degradation of the SPNs and release of the semiquinone and quinone species from the particles surface. Therefore, catechol linkers would likely not withstand the oxidizing environments under which the TEMPO is used.

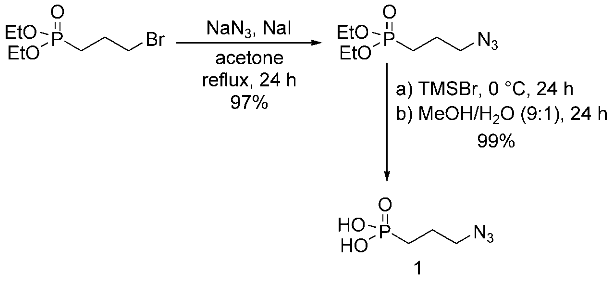
To avoid these obstacles, we decided to utilize the strong binding interactions between phosphonic acids and oxide surfaces to immobilize TEMPO to the particle surfaces. Phosphonic acids, derived from phosphonates and phosphates, bind strongly and quickly to oxide surfaces, and can be attached merely by dip coating, stirring and heating, or by short ultrasonication.[21] Simple phosphonates are easy to prepare in large quantities, and the P^V oxidation state makes this linker stable under oxidizing environments. Because of these properties, phosphonates have found applications as anticorrosion coatings on oxide surfaces.[22] We hypothesized that a phosphonate could act as an excellent anchor between our SPN surface and TEMPO, due to its ability to strongly bind oxide surfaces and withstand oxidizing environments. Additionally, the phosphonate coating could help prevent degradation of the core Fe_3O_4 SPN under oxidizing reaction conditions. Surprisingly, we could only find two literature examples in which phosphonates have been used to anchor a synthetic catalyst to oxide SPNs.[16,23]

The two approaches, A and B, that we used to immobilize TEMPO to Fe_3O_4 SPNs are shown in Scheme 1. Both approaches utilize a combination of 3-azidopropylphosphonic acid (**1**), which acts as the linker to SPN surfaces, and the copper-catalyzed azide/alkyne cycloaddition reaction (“click” reaction), which is used to connect an alkyne-functionalized TEMPO (**2**) to the phosphonate linker. In approach A we follow the protocol developed by Chouhan et al.,[23] while in approach B we separate the click reaction from the catalyst immobilization step. The synthesis of **1** was accomplished by reacting diethyl 3-bromopropylphosphonate with NaN_3 to form diethyl 3-azidopropylphosphonate, and then the phosphonate was quantitatively deprotected (Scheme 2). Alkyne functionalized TEMPO **2** was synthesized by propargylation of commercially available 4-hydroxy TEMPO. Combining **1** and **2** via the “click” reaction, a phosphonic acid functionalized TEMPO (**3**) was synthesized (Scheme 3). This click reaction was performed by using a reactive, recyclable copper-in-charcoal (Cu/C) catalyst originally developed by Lipshutz and Taft (see the Supporting Information). The Cu/C was used rather than conventional $CuSO_4$/L-ascorbic acid conditions because of its easier workup and higher activity. Furthermore, under the conditions provided by Lipshutz and Taft, the isolated product yields are typically near quantitative.[24]

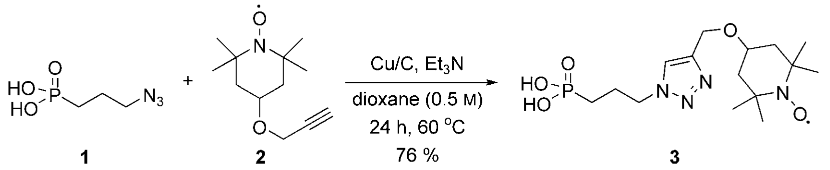
Approach A for preparing TEMPO-coated SPNs mirrors the method developed by Chouhan et al. for immobilizing proline.[23] Fe_3O_4 SPNs were sonicated with **1** to form azide-coated particles **4**. The average loading was 2.65 ± 0.27 mmol azide g^{-1}, while batch-to-batch loadings ranged from 2.40 to 2.93 mmol azide g^{-1}, as determined by elemental analysis. Azide-coated particles were then clicked with **2**, by using standard $CuSO_4$/ascorbic acid click conditions, to yield



Scheme 1. Synthesis of TEMPO-coated SPN catalyst **5a** by using Approach A and **5b** by using Approach B.



Scheme 2. Synthesis of 3-azidopropylphosphonic acid (**1**) from diethyl 3-bromopropylphosphonate.



Scheme 3. Synthesis of phosphonic acid functionalized TEMPO, **3**, by using a copper-in-carbon catalyzed "click" reaction. Note, **3** exists as a mixture of pure **3**, Et_3NH^+, and Na^+ salts due to the acidic nature of the phosphonic acid.

TEMPO-coated particles **5a** (Scheme 1). The Cu/C catalyst could not be used for this particular click reaction because the nanoparticles were irreversibly absorbed by the charcoal. In approach B, particles are constructed by simply sonicating **3** with bare Fe_3O_4 SPNs to yield TEMPO-coated particles **5b**. This process separates the click reaction from the catalyst immobilization step and greatly simplifies characterization and quantification of the catalyst. Additionally, this ensures that only the catalyst is coating the particle surface and removes the need to cap unreacted surface functionalities. A notable characteristic of approach B is that catalyst immobilization proceeds smoothly in only 2 h under ambient conditions, and any of **3** not bound to the particle surface could be recovered and reused without purification to coat addition batches of Fe_3O_4 SPNs.

FT-IR spectroscopy was used to confirm the surface coatings on particles (see the Supporting Information). In approach A, the appearance of azide (2111 cm^{-1}) and P–O (1066 cm^{-1}) stretching vibrations after sonication of **1** with Fe_3O_4 SPNs, confirmed immobilization of the phosphonic acid. Immobilization of alkyne-functionalized TEMPO to azide-coated SPNs **4** by the click reaction was monitored by the disappearance of the azide peak and growth of new C–H stretching modes. Analysis of FT-IR spectra before and after the click reaction indicated that an average of 95–96 % of azide *remaining on the particle surfaces* reacted with the alkyne-functionalized TEMPO. The final TEMPO loadings on **5a** particles were quantitatively determined using a combination of elemental analysis and FT-IR analysis (see the Supporting Information). On average, TEMPO loadings on **5a** were $0.91 \pm 0.14\ mmol\,g^{-1}$ with batch-to-batch loadings ranging from 0.71 to 1.08 $mmol\,g^{-1}$. The TEMPO loadings on **5b** could be calculated solely by elemental analysis and were found to be $0.48 \pm 0.14\ mmol\,g^{-1}$ with the batch-to-batch loading ranging from 0.30 to 0.73 $mmol\,g^{-1}$.

In approach A, analysis of azide-coated particles before and after the click reaction with TEMPO revealed that about 66 % of **1** was lost from the particle surface during the reaction. Despite this, 95 % of the azide remaining on the particles clicked with TEMPO. The azide loss is believed to have resulted from disruption of hydrogen-bonded bilayers of **1** at the particle surface by water in the click reaction mixture. It has been shown that phosphonates/phosphates on iron oxide SPNs form a bilayer architecture, with one layer bonded to the particle surface and the other hydrogen bonded to the first layer.[21d] Methanol, which is used to wash the azide-coated particles during their synthesis, does not appear to be a strong enough hydrogen bond disrupter to result in the loss of **1** from the particle surfaces; however, water is a much stronger hydrogen bond disrupter and could release **1** from the particle surface.

All synthesized particles have small coercivities (6–14 Oe), which indicate they are superparamagnetic in nature, and large saturation magnetizations (>32 emu g^{-1}), which mean they attract strongly to the magnetic fields produced from hand-held rare-earth magnets (Figure 1). The trend of decreasing saturation magnetization, Fe_3O_4 > **5b** > **5a** > **4**, is due to the increasing amount of nonmagnetic material (organic ligands) on a particle surface, which makes a larger percentage of the particle mass nonmagnetic. A direct result of this effect is that it takes longer to separate **4** and **5a** than **5b** from particle suspensions.

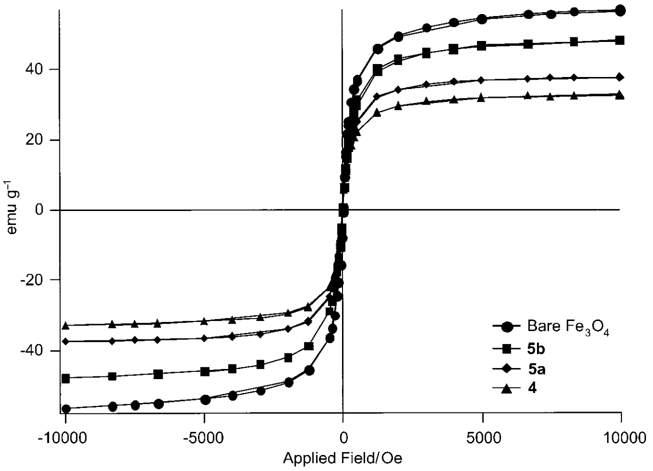


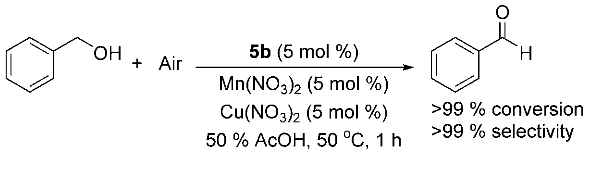
Figure 1. Magnetization curves for bare iron oxide, azide-coated nanoparticles (**4**), TEMPO-coated SPNs made in two steps by using Approach A (**5a**), and TEMPO-coated SPNs made in one step by using Approach B (**5b**).

Catalysts **5a** and **5b** were first evaluated for the aerobic oxidation of benzyl alcohol to benzaldehyde using a slightly modified version of the TEMPO and Mn^{II}/Cu^{II} co-catalyst conditions developed by Minisci et al. (Scheme 4).[10c] With mild heating and vigorous stirring, 99% benzyl alcohol was converted to benzaldehyde with 99% selectivity in only 1 h using 5 mol% of **5a** or **5b**, along with 5 mol% Mn^{II} and Cu^{II} salts. Decreasing the catalyst loading to 2.5 mol% also resulted in quantitative conversion of benzyl alcohol, but required 2 h. After each reaction, the catalyst could be magnetically separated using a hand-held rare-earth magnet, washed, and immediately reused with or without drying. Initial studies on **5a** and **5b** recyclability in the aerobic oxidation of benzyl alcohol under the Minisci condition showed that **5a** could be recycled five times and **5b** six times, with conversions > 95% and selectivities > 99%. With further cycles, the catalyst activity diminished, resulting in conversions < 90%. Minisci et al. noted a similar decrease in catalytic activity with their homogeneous macrocyclic TEMPO catalyst. They proposed that the drop in activity was caused by methylene groups alpha to amines being oxidized by Mn^{III} salt intermediates, resulting in catalyst cleavage/degradation.[10c] To overcome this problem, Minisci et al. added *p*-toluenesulfonic acid (TsOH) in the first reaction cycle to fully protonate the amines and minimize their oxidation. Because our catalyst utilizes a 1,2,3-triazole linker, we thought a similar degradation process might be occurring at the methylene units alpha to the triazole. Addition of TsOH in the first reaction cycle improved catalyst recyclability: **5a** was recyclable eight times and **5b** 12 times with conversions > 90% (Table 1). Moreover, **5b** particles could be recycled 20 times with conversions remaining ≥ 80%. That said, we found that adding TsOH did not completely prevent the gradual loss of catalytic activity of over time.

Table 1. Recyclability of **5b** in the aerobic oxidation of benzyl alcohol using Mn^{II}/Cu^{II} co-catalysts.[a]

Cycle	Conversion [%]	Selectivity [%]
1[b,c]	98	99
2[d]	99	99
3[d]	95	99
7[d]	95	99
8	94	99
12	93	99
13	84	99
14	88	99
15	85	99
19	82	99
20[d]	80	99
21	73	99
22	72	99
23[e]	56	98

[a] Benzyl alcohol (1.0 mmol), **5b** (0.05 mmol, 5 mol%, 0.30 mmol TEMPO g^{-1}), $Mn(NO_3)_2 \cdot 6H_2O$ (0.05 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.05 mmol), 50% AcOH in α,α,α-trifluorotoluene (2 mL), heat to 50 °C and stir for 1 h open to air; conversions and selectivities determined by gas chromatography/mass spectrometry (GC/MS). [b] 4-Methylbenzyl alcohol used as substrate. [c] TsOH (0.1 mmol) added. [d] Benzyl alcohol in this reaction and subsequent reactions adjusted to account for 3-4 mg of particles taken for elemental analysis. [e] Cycle run with 0.870 mmol benzyl alcohol to account for particles taken for elemental analysis.



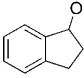
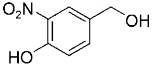
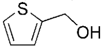
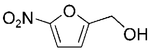
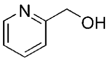
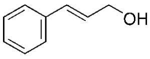
Scheme 4. Aerobic oxidation of benzyl alcohol using **5a** or **5b** with Mn^{II}/Cu^{II} co-catalysts (modified Minisci condition).

We initially hypothesized that catalyst leaching was the primary reason for the decrease in the catalytic activity of the particles over time. The catalytic activity of the supernatant from cycles 1, 2, and 23 (Table 1) was analyzed and indicated that a small amount of TEMPO was present, as evidenced by 6–9% conversion of the alcohol. To determine the mode of leaching, we investigated whether TEMPO was oxidatively cleaved from the particle surface in a manner similar to what Minisci et al. proposed for their system.[10c] For our catalyst, this would require initial oxidation of the triazole linkage in **3**, followed by hydrogen atom abstraction from the adjacent methylene unit, and finally oxidative cleavage of TEMPO into solution. To determine whether TEMPO could be released by this mechanism, we tested the stability of a model triazole, 4-butyl-1-phenethyl-1*H*-1,2,3-triazole, under typical Minisci reaction conditions. The triazole was not oxidized, and remained stable under even harsher oxidizing conditions with 20 equiv $Mn(OAc)_3{\cdot}2H_2O$ (see the Supporting Information). Because oxidation of the triazole was apparently not the reason for the loss of particle activity, we decided to analyze the particle nitrogen content to determine whether the TEMPO loading decreased over time. A large decrease in the nitrogen content would be indicative of **3** leaching as a whole from the particle surface. Elemental analysis of particles after the 23rd cycle showed that the nitrogen content had decreased by 21 % to 0.944 mmol g^{-1}, which corresponds to a 4 mol % TEMPO loading (0.263 mmol g^{-1}), assuming that all nitrogen relates to purely intact **3** on the particle surface. If this assumption is true, then at worst, the 23rd cycling reaction was run with 4 mol % TEMPO. This catalyst loading seems too high to have resulted in the relatively low (56 %) conversion we observed in the 23rd cycle. For comparison, a separate reaction was run with fresh **5b** particles at 4 mol %. This reaction resulted in 95 % conversion of benzyl alcohol in 1 h (see the Supporting Information). Therefore, it appears that TEMPO is both leached and deactivated.[5b] While it is not possible to determine how much of the loss of activity is attributable to each of these two mechanisms, it appears that deactivation is the dominant factor. That said, both leaching and deactivation appear to be extremely slow processes.

Analysis of the particles after 15 cycling experiments showed no apparent decrease in their magnetic susceptibility. Even after 23 cycles, the particles showed excellent response to an applied magnetic field (see the Supporting Information). This demonstrates that when coated with the phosphonic acid, the core Fe_3O_4 particles can withstand acidic, oxidizing environments.

We decided to further investigate the ability of our catalyst to oxidize other aromatic alcohols. From this point on we chose to only pursue catalyst **5b**, because of its overall better performance and simpler synthesis and analysis. Table 2 shows the results of using catalyst **5b** under the Minisci condition to oxidize aromatic alcohols. Under these conditions, 5 mol % **5b** chemoselectively oxidized both electron-rich and electron-poor primary benzylic alcohols to the respective aldehydes, in 1–2.5 h, with high selectivities and yields. Typically, little to no acylation or over-oxidized side products were detected. In particular, the phenol, 4-hydroxy-3-nitrobenzyl alcohol, smoothly oxidized to the aldehyde with little acylation side product. Oxidation of secondary alcohols 1-phenylethanol and 1-indanol required 2.5 h to reach completion, but they were still cleanly oxidized to the ketones in high yields. Oxygen and sulfur-containing heterocyclic alcohols were also oxidized with high yields and selectivity. Surprisingly, sulfur-containing alcohols selectively oxidized to the aldehyde and did not over-oxidize to sulfoxide or sulfone derivatives. Oxidation of cinnamyl alcohol and 2-pyridinemethanol required 7 mol % **5b** to reach completion; however, selectivities for the aldehyde were lower. The low selectivity for the oxidation of 2-pyridinemethanol is likely caused by formation of the pyridinium salt which makes the ring highly electron deficient and decreases the oxidation rate.[25]

Table 2. Aerobic oxidation of alcohols catalyzed by **5b** under the Minisci conditions.[a]

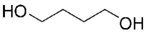
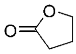
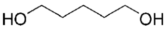
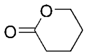
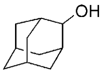
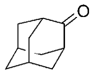
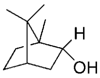
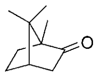
Entry	Alcohol	*t* [h]	Conv. [%]	Select. [%]	Yield [%][b]
1	benzyl alcohol	1	>99	>99	85
2	1-phenylethanol	2.5	96	99	90
3[c]		2.5	>99	90	86
4[c]	4-methylbenzyl alcohol	1	>99	>99	98
5[c]	4-methoxybenzyl alcohol	1	>99	97	94
6	4-bromobenzyl alcohol	2	>99	>99	95
7	4-nitrobenzyl alcohol	2	>99	>99	98
8		2	>99	>99	91
9	4-(methylthio)benzyl alcohol	1	96	97	86
10		1	>99	>99	91
11		2	>99	>99	95
12[c,d]		2.5	>99	80[e]	–
13[d]		1	>99	73	–

[a] Alcohol (1 mmol), **5b** (0.05 mmol, 5 mol %), $Mn(NO_3)_2{\cdot}6H_2O$ (0.05 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.05 mmol), 50 % AcOH in α,α,α-trifluorotoluene (2 mL), heat to 50 °C and stir open to air; conversions and selectivities determined by GC/MS. [b] Yields of isolated products. [c] TsOH added (0.10 mmol). [d] 7 mol % **5b**. [e] 20 % acylation side product.

Several attempts to oxidize an alkyl alcohol, 1-octanol, under the Minisci conditions at 10 mol % **5b** resulted in only moderate conversions (54 %) and selectivities (62 %). The reactivity of alkyl alcohols under Minisci conditions tends to be lower than that of benzyl alcohols, so often higher catalyst loadings are used to achieve good conversions.[12h,f,14a,b] A possible reason for the low reactivity of alkyl alcohols can be gleaned from mechanistic work by Minisci et al.[25] They found that under acidic conditions, deprotonation of the α-proton adjacent to the hydroxy group was rate limiting. Based on this explanation, the lower reactivity of 1-octanol, as compared to benzyl alcohol, is likely due to the less acidic nature of the α-proton on 1-octanol, which impedes completion of the oxidation cycle.

Switching to the Anelli conditions, 5 mol % **5b** was able to cleanly and quantitatively oxidize 1-octanol to 1-octanone in 30 min (Table 3). As shown in Table 3, under Anelli con-

Table 3. Oxidation of alcohols catalyzed by **5b** using hypochlorite.[a]

Entry	Substrate	Product	*t* [h]	Conv. [%]	Select. [%]	Yield [%][b]
1	1-octanol	1-octanal	0.5	>99	>99	90
2	2-octanol	2-octanone	2	>99	>99	98
3[c]			0.5	>99	>99	97
4[c]			0.5	>99	>99	99
5			1	98	>99	97
6			2	>99	91[d]	90

[a] Alcohol (1 mmol), **5b** (0.05 mmol, 5 mol %), in CH_2Cl_2 (3 mL) sonicate 30 s and cooled to 0 °C. KBr (0.33 mmol), $NaHCO_3$ (0.48 mmol, 50 mg mL^{-1} NaOCl) and 11 % NaOCl (0.8 mL, 1.5 mmol) added and the suspension was stirred at 0 °C; conversions and selectivities determined by GC/MS. [b] Yields of isolated products. [c] 2.5 mmol NaOCl added. [d] 9 % ring-opened side product, 2-(2,2,3-trimethylcyclopent-3-enyl)acetaldehyde.

ditions **5b** was able to fully oxidize hindered and unhindered secondary alcohols to their respective ketones in high yields. Symmetric alkyl diols also smoothly underwent one-pot oxidation and cyclization to lactones with 2.5 equiv NaOCl.[14c] Under the Anelli conditions, **5b** could be recycled up to eight times for the oxidation of 1-octanol, with consistent conversions of >99 % and selectivities ≥96 % (see the Supporting Information). On the ninth cycle, the catalytic activity of **5b** dropped sharply (21 % conversion, 93 % selectivity). A detailed leaching study shows that on average, 8 % of the total immobilized TEMPO is lost after one reaction cycle with washing (see the Supporting Information). The isolated supernatant from a reaction of **5b** with 1-hexanol was found to have low levels of residual catalytic activity, which suggests the supernatant is responsible for at best 38 % of the conversion of 1-octanol, of which 54 % was 1-octanal. Further comparisons of the activity of the supernatant, heterogeneous **5b**, and homogeneous reactions with **3** demonstrate the majority of catalytic activity comes from **5b** SPNs. (There is also evidence for synergistic effects of leached iron from the particles and TEMPO; see the Supporting Information for full details.) In summary, neither the leached TEMPO nor homogeneous **3** gave the high conversions and good selectivities that were obtained with the particles. Furthermore, the TEMPO-coated particles were more reactive and more easily recovered and recycled.

Conclusion

We have developed two simple methods to synthesize TEMPO-coated SPN catalysts for the selective oxidation of alcohols. The chemistry and processes used to construct the catalysts are high yielding and simple, require inexpensive materials, and result in good TEMPO loadings. The catalysts efficiently and chemoselectively oxidize alcohols (primary, secondary and hindered ones) to their carbonyl analogues, under both Minisci and Anelli conditions, with excellent yields and selectivities using low catalyst loadings. TEMPO-coated SPNs are quickly and efficiently recovered from solution using hand-held magnets. This allowed particles to be easily recycled over 20 times under the Minisci conditions and up to eight times under Anelli conditions, while maintaining good to high conversions and selectivities. A detailed leaching study on particles under Minisci conditions showed that the phosphonic acid coated particles remain stable under the highly acidic oxidizing conditions. The loss of particle catalytic activity occurs mostly due to very slow deactivation of TEMPO on the particles, and leaching of very small amounts of catalyst. Particle leaching studies under Anelli conditions showed that on average 8 % of **3** leached per reaction. A more detailed look at the active components in a typical reaction showed that immobilization of **3** to SPNs is important for having good substrate conversions and product selectivities. Therefore, it is indeed useful to immobilize **3** on SPNs, even though the particles are only recyclable eight times under these conditions.

While both of the TEMPO-immobilization approaches demonstrated in this work were successful, approach B, which separates the click reaction from the catalyst immobilization step, allowed faster immobilization of TEMPO and direct quantitative analysis of TEMPO loadings, and produced more stable TEMPO-coated SPNs with larger magnetic susceptibilities. It also ensured little catalyst was wasted or lost during the immobilization process. This slight modification to the approach developed Chouhan et al.[23] also ensures that the only molecule on the particle surface is the catalyst and eliminates the need to block unreacted functionalities. This modified approach provides a straightforward path for the immobilization of many other types of catalysts to oxide SPNs, and could be particularly useful for the immobilization of expensive and complex asymmetric catalysts that operate under neutral or acidic environments.

Experimental Section

General conditions: Fe_3O_4 superparamagnetic nanoparticles,[17] 3-azidopropylphosphonic acid,[23] and 2,2,6,6-tetramethyl-4-(prop-2-ynyloxy)piperidin-1-oxyl[14a] were synthesized following literature procedures. THF was dried over $MgSO_4$ prior to use. All other chemicals purchased were reagent grade and used as received. ^1H, ^{13}C, and ^{31}PNMR spectra were obtained by using either a Bruker AV300 spectrometer or Bruker ARX400 spectrometer. Spectra were referenced to $CDCl_3$ ($\delta(^1H) = 7.26$ ppm), $CDCl_3$ ($\delta(^{13}C) = 77.0$ ppm) or CD_3OD ($\delta(^1H) = 3.29$ ppm), CD_3OD ($\delta(^{13}C) = 47.9$ ppm), or 85 % H_3PO_4 in H_2O ($\delta(^{31}P) = 0$ ppm). High-resolution mass spectral data were acquired on a Waters LCT Premier XE time of flight mass spectrometer, and elemental analysis was performed on a Thermo Scientific Flash 1112 series elemental analyzer. (The percent error in nitrogen measurements was determined when calibrating the instrument and ranged between 1–5 %. Measurements were precise to at least three significant figures.) FT-IRs were recorded by using pressed KBr pellets, or thin liquid films between AgCl plates on a Jasco FT/IR-420. Magnetic measurements of particles were made by using a Quantum Design MPMS 5XL Super Quantum Interference

Device (SQUID) magnetometer. Transmission electron microscopy (TEM) images were taken on a FEI CM120 operating at 120 kV. Reaction conversions and selectivities were quantified by using an Agilent 6890–5975 GC/MS with autosampler, equipped with a HP-5 column. TEM images, particle recycling tables, particle leaching studies, experimental procedures for synthesis of bare $Fe_{3e}O_4$ particles and Cu/C, and detailed spectroscopic data for all isolated compounds are contained in the Supporting Information.

Diethyl 3-azidopropylphosphonate: A 100 mL round-bottom flask was charged with diethyl 3-bromopropylphosphonate (10.1 mmol), dry NaN_3 (20.2 mmol), and dry acetone (15 mL), and refluxed under argon for 24 h. The reaction mixture was filtered over a pad of celite and the celite washed several times with dry acetone. The organic liquid was concentrated in vacuo to give a clear/light brown oil (97 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.09$ (m, 4H; CH_2), 3.37 (t, $^3J(H,H) = 6.40$ Hz, 2H; CH_2N_3), 1.67 (m, 4H; CH_2), 1.32 ppm (t, $^3J(H,H) = 7.04$ Hz, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 61.7$ (d, $^2J(C,P) = 7$ Hz, 2C), 51.6 (d, $^2J(C,P) = 16$ Hz, 2C), 23.6 (d, $^2J(C,P) = 119$ Hz, 2C), 22.5 (d, $^2J(C,P) = 27$ Hz, 2C), 16.5 ppm (d, $^2J(C,P) = 6$ Hz, 2C); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = 30.7$ ppm (s, 1P); IR: $\tilde{\nu} = 2993$, 2983, 2937, 2910, 2873, 2104, 1444, 1392, 1369, 1350, 1247, 1163, 1097, 1029, 960, 785, 543 cm^{-1}.

3-Azidopropylphosphonic acid (1): Prepared according to a method previously reported.[17] Briefly, a 100 mL round-bottom flask was charged with diethyl 3-aizdopropylphosphonate (5 mmol), acetonitrile (20 mL), and the mixture cooled to –5 °C with continuous argon purging. TMSBr (25 mmol) was added dropwise over 10–15 min with continuous argon purging and vigorous stirring. The reaction mixture was then warmed to room temperature and stirred under argon for 24 h. The resulting mixture was concentrated in vacuo and then a 9:1 mixture of MeOH/H_2O (10 mL) was added. The resulting solution was stirred at room temperature for an additional 24 h. The reaction mixture was concentrated in vacuo, co-evaporated again with dry toluene and then fully dried in a vacuum desicator overnight to yield a yellow gummy/oil product (99 %). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 3.39$ (t, $^3J(H,H) = 6.64$ Hz, 2H; CH_2N_3), 1.79 ppm (m, 4H; CH_2); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): $\delta = 51.4$ (d, $^2J(C,P) = 17$ Hz, 2C), 24.6 (d, $^2J(C,P) = 139$ Hz, 2C), 22.5 ppm (d, $^2J(C,P) = 4$ Hz, 2C); ^{31}P NMR (162 MHz, CD_3OD, 25 °C): $\delta = 28.8$ ppm (s, 1P); IR: $\tilde{\nu} = 2948$, 2881, 2842, 2110, 1652, 1250, 1163, 1020, 943 cm^{-1}.

2,2,6,6-Tetramethyl-4-(prop-2-ynyloxy)piperidin-1-oxyl (2): An oven-dried 100 mL round-bottom flask was charged with *t*BuOK (30 mmol) and dry THF (20 mL), placed under an argon atmosphere, and cooled to 0 °C. 4-Hydroxy-TEMPO (23 mmol) was dissolved in dry THF (10 mL), injected into the flask, and stirred for 1 h at 0 °C. Propargyl bromide (30 mmol, 80 % in toluene) was added slowly to the flask and the reaction mixture warmed to room temperature and stirred for an additional 24 h. The reaction mixture was opened to air, and de-ionized (DI) H_2O (2 mL) added. The mixture stirred for an additional 15 min and then all the solvent was removed in vacuo. The resulting viscous liquid was subjected to silica gel flash chromatography by using ethyl acetate/hexanes (3:7) to yield an orange crystalline solid (65 %). IR: $\tilde{\nu} = 3439$, 3232, 2995, 2973, 2937, 2870, 1631, 1465, 1379, 1365, 1350, 1311, 1269, 1242, 1219, 1176, 1086, 1020, 734, 692, 555 cm^{-1}; elemental analysis calcd (>99 %) $C_{12}H_{20}NO_2$: C 68.54, H 9.59, N 6.66; found: C 68.42, H 9.55, N 6.71.

Phosphonic acid functionalized TEMPO (3): A 25 mL round-bottom flask was charged with **1** (2 mmol), **2** (2.2 mmol), Cu/C catalyst (224 mg), and dioxane (3.5 mL). The flask was placed in a 60 °C oil bath and Et_3N (2.2 mmol) was added while stirring. The flask was capped and stirred for 24 h at 60 °C. The resulting slurry was filtered over a pad of celite and the celite washed with methanol. The organics were concentrated in vacuo to yield an orange oil. The oil was subjected to silica flash chromatography on a very short column, using ethyl acetate to first flush the column of unreacted alkyne, and then methanol to flush the product from the column. The collected methanol was concentrated in vacuo to yield a gummy orange solid (76 %). IR: $\tilde{\nu} = 3435$, 3139, 2976, 2940, 2877, 2678, 1635, 1463, 1379, 1363, 1242, 1219, 1178, 1157, 1083, 1053, 906, 551, 478 cm^{-1}. MS (ESI): *m*/*z* (%): Product exists as a mixture of pure product, and Et_3NH^+, Na^+ salts: 399.17 (17) $[M^+ + Na + 2H]$, 377.19 (100) $[M^+ + 2H]$, 194.06 (15) $[C_8H_{13}NO_4P^+]$, 102.13 (30) $[C_6H_{10}N^+]$. MS(ESI) calcd for $C_{15}H_{28}N_4O_5P$ $[M^+ + 2H] = 377.1948$; found 377.1945. Note: See Supporting Information for high-resolution mass spectrum with assigned peaks.

Azide-coated particles (4): A 14.8 mL glass vial was charged with of **1** (600 mg), crushed bare Fe_3O_4 nanoparticles (600 mg), chloroform (6 mL), and methanol (0.6 mL). The vial was tightly capped and the mixture sonicated for 2 h at room temperature. The resulting particles were separated by using a hand-held rare-earth magnet and the supernatant decanted. The particles were washed three times with methanol and dried in a vacuum desicator to yield **4** as a light brown powder. Azide loadings, determined by elemental analysis of the nitrogen content, ranged from 2.40–2.93 mmol g^{-1}. IR (KBr): $\tilde{\nu} = 2958$, 2933, 2870, 2111, 1633, 1066, 580 cm^{-1}.

Catalyst 5a made by using Approach A: A 10 mL round-bottom flask was charged with **4** (1 equiv N_3, typically 0.70 mmol N_3), **2** (1.1 equiv, 0.77 mmol), $CuSO_4 \cdot 6H_2O$ (0.05 equiv, 0.04 mmol), sodium ascorbate (0.15 equiv, 0.11 mmol), Et_3N (2 equiv, 1.40 mmol), and degassed 1:1 *t*Bu/H_2O (3 mL). The suspension was stirred under ambient conditions at room temperature for 24 h. The solvent was then removed in vacuo and the particles were washed three times with dichloromethane/diethyl ether (1:1) and then three times with diethyl ether using a hand-held rare-earth magnet to separate the particles after each wash. The particles were then dried in a vacuum desicator to yield a light brown powder. TEMPO loadings determined by elemental analysis of the nitrogen content range from 0.71–1.08 mmol g^{-1}. IR (KBr): $\tilde{\nu} = 2993$, 2977, 2935, 2854, 1643, 1066, 580 cm^{-1}.

Catalyst 5b made by using Approach B: A 14.8 mL glass vial was charged with **3** (800 mg), crushed bare Fe_3O_4 nanoparticles (800 mg), chloroform (8 mL), and methanol (0.8 mL). The vial was tightly capped and the mixture sonicated for 2 h at room temperature. The resulting particles were separated by using a hand-held rare-earth magnet and the supernatant decanted and saved. Particles were washed four times with dichloromethane/diethyl ether (1:1), and the supernatant saved. Particles were dried in a vacuum desicator to yield **5b** as a dark brown/black powder. TEMPO loadings determined by elemental analysis of the nitrogen content range from 0.30–0.73 mmol g^{-1}. The collected supernatant was concentrated in vacuo to afford **3**, which was not attached to the particles. This material could be reused to make another batch of **5b**. TEMPO loadings determined by elemental analysis of the nitrogen content range from 0.50–0.93 mmol g^{-1}. IR (KBr): $\tilde{\nu} = 2993$, 2977, 2935, 2854, 1643, 1066, 580 cm^{-1}.

General procedure for aerobic oxidation of alcohols by 5a or 5b with Mn^{II}/Cu^{II} co-catalysts: In general, a 10 mL round-bottom flask was charged with **5a** or **5b** (0.05 mmol, 5 mol %), alcohol (1 mmol), $Mn(NO_3)_2 \cdot 6H_2O$ (0.05 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.05 mmol), and 50 % acetic acid in α,α,α-trifluorotoluene (2 mL). The mixture was sonicated for 15 s and then heated to 50 °C in an oil bath under vigorous stirring. The reaction was stirred open to the air at 50 °C for 1–2.5 h. The catalyst was then collected at the side of the flask using a held-held rare-earth magnet, and the supernatant carefully decanted. Particles were then washed three times with dichloromethane (5 mL) and the collected organics were washed two times with saturated $NaHCO_3$ (20 mL), two times with DI H_2O (20 mL), dried over Na_2SO_4, and filtered over a pad of celite. The organics were then concentrated in vacuo to yield the corresponding carbonyl compound.

General procedure for catalyst recycling experiments using Mn^{II}/Cu^{II} co-catalysts: A 10 mL round-bottom flask was charged with **5a** or **5b** (0.025 mmol, 5 mol %), benzyl alcohol (0.5 mmol), $Mn(NO_3)_2 \cdot 6H_2O$ (0.025 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.025 mmol), and 50 % acetic acid in α,α,α-trifluorotoluene (1 mL). The mixture was sonicated for 15 s and then heated to 50 °C in an oil bath under vigorous stirring. The reaction was stirred open to the air at 50 °C for 1 h. After 1 h, particles were collected at the side of the reaction flask using a hand-held rare-earth magnet and a 10 uL aliquot was taken for GC/MS analysis. The reaction medium was carefully decanted and the particles washed two times with acetone, two times with dichloromethane, and then reused immediately or stored capped at 0 °C.

General procedure for aerobic oxidation of alcohols by 5b with sodium hypochlorite: In general, a 14.8 mL vial was charged with **5b** (0.05 mmol, 5 mol %), alcohol (1 mmol), and dichloromethane (3 mL). The mixture was sonicated briefly for 20–30 s and then cooled to 0 °C under vigorous stirring. KBr (0.33 mmol), $NaHCO_3$ (0.48 mmol, 50 mg mL^{-1} NaOCl), and 11 % NaOCl (0.8 mL, 1.5 mmol) were added sequentially and the mixture stirred for 0.5–2 h at 0 °C. The particles were then magnetically collected at the side of the vial using a hand-held rare-earth magnet and the supernatant carefully decanted. The particles were washed three times with dichloromethane (5 mL) and the collected organics were passed over a pad of celite. The organics were then washed once with DI H_2O (30 mL), dried over Na_2SO_4, and concentrated in vacuo to yield the corresponding carbonyl compound.

General procedure for catalyst-recycling experiments using NaOCl: A 14.8 mL vial was charged with **5b** (0.025 mmol, 5 mol %), alcohol (0.5 mmol), and dichloromethane (2 mL). The mixture was sonicated briefly for 20–30 s and then cooled to 0 °C under vigorous stirring. KBr (0.17 mmol), $NaHCO_3$ (0.24 mmol, 50 mg mL^{-1} NaOCl), and 11 % NaOCl (0.4 mL, 0.75 mmol) were added sequentially and the mixture was stirred for 0.5 h at 0 °C. The particles were then magnetically collected at the side of the vial using a hand-held rare-earth magnet, and a 10 uL aliquot was taken for GC/MS analysis. The reaction medium was carefully decanted and the particles were washed two times with DI H_2O, two times with acetone, two times with dichloromethane, and then reused immediately or stored capped at 0 °C.

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