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Efficient Chemoselective Reduction of *N*-Oxides and Sulfoxides Using a Carbon-Supported Molybdenum-Dioxo Catalyst and Alcohol

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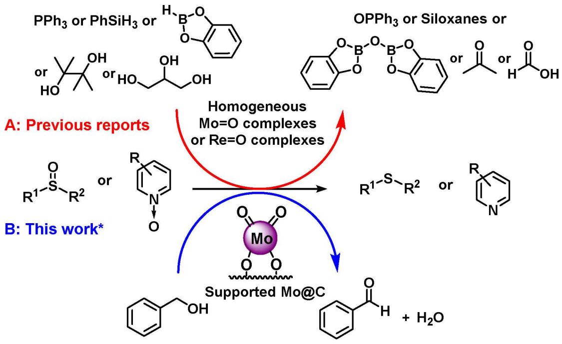
The chemoselective reduction of a wide range of *N*-oxides and sulfoxides with alcohols is achieved using a carbon-supported dioxo-molybdenum (**Mo@C**) catalyst. Of the 10 alcohols screened, benzyl alcohol exhibits the highest reduction efficiency. A variety of *N*-oxide and both aromatic and aliphatic sulfoxide substrates bearing halogens as well as additional reducible functionalities are efficiently and chemoselectively reduced with benzyl alcohol. Chemoselective *N*-oxide reduction is effected even in the presence of potentially competing sulfoxide moieties. In addition, the **Mo@C** catalyst is air- and moisture-stable, and is easily separated from the reaction mixture and then re-subjected to reaction conditions over multiple cycles without significant reactivity or selectivity degradation. The high stability and recyclability of the catalyst, paired with its low toxicity and use of earth-abundant elements makes it an environmentally friendly catalytic system.

Introduction

The chemoselective reduction of oxygenated compounds, such as *N*-oxides and sulfoxides, is of great importance from both a synthetic and biological standpoint.[1–3] The reduction of such compounds has typically been carried out with low-valent metal ions[2,4] or precious metal catalysts[5–8] in the presence of an excess of sacrificial reducing agents such as metal hydrides,[9] hydrogen halides,[10] organosulfur reagents,[11] and phosphorus containing reagents.[12] These sacrificial reducing agents are often highly toxic, and are known to produce large quantities of waste. Recent advances using high-valent transition metal catalysts have been reported, in which metal ions are combined with reducing agents such as PPh_3,[5,13] silanes,[8,14,15] boranes,[16] or high pressures of H_2 (Scheme 1, A).[7,17] Despite these advances in synthetic methodology, many of these systems still require highly toxic additives, stoichiometric sacrificial reducing agents, a rigorously air-/moisture-free environment, and harsh reaction conditions that are not suitable for many functionalized substrates. Furthermore, the fundamental problem of separating catalysts from the reaction mixture has not always been addressed, and potential catalyst recyclability has also not been thoroughly investigated. For these reasons, recent studies have focused on the development of more sustainable and environmentally friendly strategies.[18,19]



*Conditions: 1.0 mmol substrate, 1.25 mmol, $PhCH_2OH$, 2 mol% Mo@C, 1.0 mmol mesitylene as internal standard, 2 mL anisole as solvent, 500 rpm, 120 °C

Scheme 1. Various methods of Reducing *N*-Oxides and Sulfoxides.

Molybdenum-oxo based catalysts have attracted a considerable attention due to their low toxicity, earth abundance, and versatility in various reaction systems.[20] One promising methodology of interest to us involves the use of alcohols as a greener reducing agent. The Sanz group has reported the use of pinacol for the reduction of sulfoxides[21] and heteroaromatic *N*-oxides[19] using a homogeneous $MoO_2Cl_2(DMF)_2$ catalyst. In addition to pinacol, glycerol[22] and mercaptopropyl-functionalized silica gel[23] have also proven effective in this methodology for the reduction of sulfoxides.

Although the investigation of homogeneous dioxo-molybdenum(VI) catalyzed deoxygenation has yielded many advances in recent years, the study of their heterogeneous counterparts has received considerably less attention. Compared to homogeneous catalytic processes, heterogeneous catalysts offer several advantages including higher thermal stability and recyclability.[24] Recent work from the Marks group has shown that single-site dioxo-molybdenum species grafted on high

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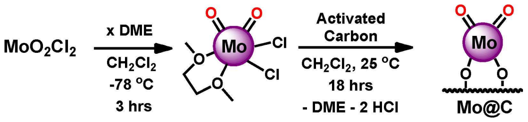
surface area activated carbon, **Mo@C**, is a highly active catalyst for alcohol oxidation,[25] transesterification,[26] as well as reductive carbonyl coupling.[27] Therefore, we reasoned that in the presence of alcohols **Mo@C** might also be competent for catalyzing reductions.

In this report, we describe an ecofriendly heterogeneous catalytic system for the chemoselective reduction of pyridine *N*-oxides and sulfoxides (Scheme 1, B). This system operates under mild conditions with an inexpensive single-site supported Mo catalyst that is both air- and moisture-stable (Scheme 2).



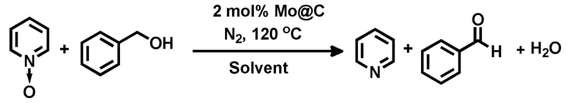
Scheme 2. Synthesis of **Mo@C**. For characterization details see ref. 26.

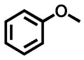
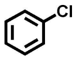
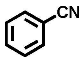
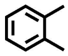
Results and Discussion

Optimization of Reaction Conditions

Initial experiments were carried out using pyridine *N*-oxide as a model substrate (Table 1, Entry 1). In the presence of 2 mol% **Mo@C**, the reaction of 1 equiv. of pyridine *N*-oxide with a slight excess of benzyl alcohol in anisole affords complete conversion of the starting material to pyridine within 3 h at 120 °C. As expected, no significant conversion takes place in the absence of Mo (**carbon** only) when pyridine *N*-oxide is subjected to identical reaction conditions. An investigation of temperature as well as catalyst loading effects were also conducted using the same conditions as Table 1 entry 1. With 1 mol% **Mo@C**, 95% conversion is achieved after 6 h. Decreasing the temperature to 105 °C achieves >99% conversion after 20 h (Table 1, Entry 2–4). These milder reaction conditions still achieve full conversion of the starting material, although slightly longer reaction times are necessary.

Table 1. Solvent screening.[a]



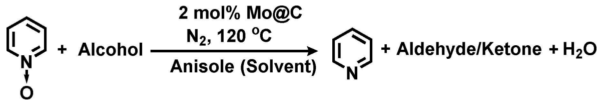
Entry	Solvent	*t* [h]	Conversion
1		3	>99%
2[b]		20	<1%
3[c]		6	95%
4[d]		20	>99%
5		3	>99%
6		3	>99%
7		3	>99%

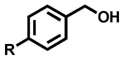
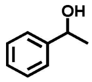
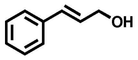
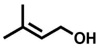
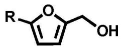
[a] Conditions: 1.0 mmol pyridine *N*-oxide, 1.25 mmol benzyl alcohol, 2 mol% **Mo@C**, 1.0 mmol mesitylene, 2.0 mL solvent, 500 rpm, 120 °C. [b] Carbon support alone. [c] 1 mol% Mo@C. [d] 105 °C.

A solvent screen was next conducted in order to compare the effects of anisole, chlorobenzene, benzyl nitrile, and o-xylene. All solvents examined afford full conversion and excellent yields in 3 h (Table 1). Additionally, solvent-free conditions were investigated and a similar conversion to product is observed. Note that because of the nature of the activated charcoal used as the carbon support, strong adsorption of substrates and products is unavoidable under both solvated and solvent-free conditions. Consultation of the solvent selection guide developed by ACS Green Chemistry Institute and others,[28,29] paired with the superior substrate solubility in anisole led us to pursue further investigations using this ecofriendly solvent.[29,30]

In order to better understand the electronic and steric effects of the reducing agent, 10 alcohols were screened for their efficiency (Table 2). Compared to benzyl alcohol, the reduction was found to proceed more slowly in the presence of electron poor or sterically hindered alcohols. It is worth highlighting that when furfuryl alcohol is used as the reducing agent, the reduction of pyridine *N*-oxide is achieved at a comparable rate as benzylic alcohols (>99% in 6 h, Table 2, Entry 5). The introduction of functional groups to furfuryl alcohol did not affect the reaction rate as illustrated in Table 2 Entry 5. Considering the wide availability of biomass-derived furfuryl alcohol,[31] this result further demonstrates the great potential of our system as a green chemical process.

Table 2. Alcohol screening.[a]



Entry	Alcohol		*t* [h]	Conversion
1		R=H	3	>99%
		R=CH_3	3	98%
		R=CF_3	6	84%
2			20	>99%
3			6	>99%
4			6	>99%
5		R=H	6	>99%
		R=CHO	6	>99%
		R=NO_2	6	>99%
		R=CH_3	6	>99%

[a] Conditions: 1.0 mmol pyridine *N*-oxide, 1.25 mmol alcohol, 2 mol% **Mo@C**, 1.0 mmol mesitylene, 2.0 mL anisole, 500 rpm, 120 °C.

Most of the alcohols are stoichiometrically converted to the corresponding aldehydes (Table S1 and Table S2 Entry 1–3, >90% selectivity) except for 3-methyl-2-buten-1-ol, furfuryl alcohol, and 5-methylfurfuryl alcohol (Table S2, Entry 4 and 5). For 3-methyl-2-buten-1-ol (Table S2, Entry 4), 3-methyl-2-butenal is the only product detected by ^{1}H-NMR and GC-MS and accounts for 67% of the consumed alcohol. The negative mass balance may reflect strong adsorption of the aldehyde on the surface of the activated carbon. For furfuryl alcohol and 5-methylfurfuryl alcohol (Table S2, Entry 5), aldehydes (65–69% selectivity), dehydrated ethers (4–5% selectivity), and trace amounts of 2-methylfuran or 2,5-dimethylfuran (2% selectivity) were observed. The furan derivatives may be due to the low stability of the corresponding aldehydes and alcohols, which are known to undergo deoxygenation.[32] Again, incomplete mass balance is observed in these two cases and may reflect strong adsorption of the aldehydes on the activated carbon.[33]

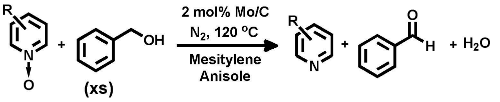
Substrate Functional Group Tolerance

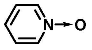
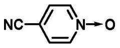
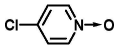
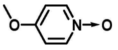
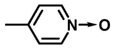
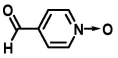
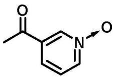
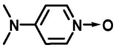
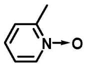
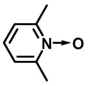
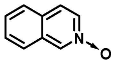
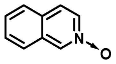
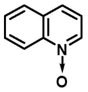
With optimal reaction conditions in hand, benzyl alcohol as reducing agent, anisole as solvent, 2 mol% Mo at 120 °C, the reduction of a representative selection of pyridine *N*-oxides was examined. These results are detailed below (Table 3).

Excellent conversion of *N*-oxide substrates and high selectivity towards the corresponding reduced products are observed regardless of the electronic nature of their substituents (Table 3, Entries 1–8). Additionally, reductions of various quinolone and isoquinoline *N*-oxides also proceed efficiently (Table 3, Entries 11–13). Moreover, the introduction of sterically demanding groups in close proximity to the *N*-oxide functionality do not have any major detrimental effect on the outcome of the reaction, as illustrated by the reactions of 2-methyl and 2,6-dimethyl pyridine *N*-oxide (Table 3, Entries 9–10). Note that the catalyst retains excellent chemoselectivity towards N–O moieties in the presence of halogens and additional reducible functionalities such carbonyls and cyano groups (Table 3, Entries 2–3, 6–7). The broad substrate tolerance of the present catalytic system offers an attractive alternative to chemoselectively reduce pyridine and its derivatives, which is known to be a challenging task.[3]

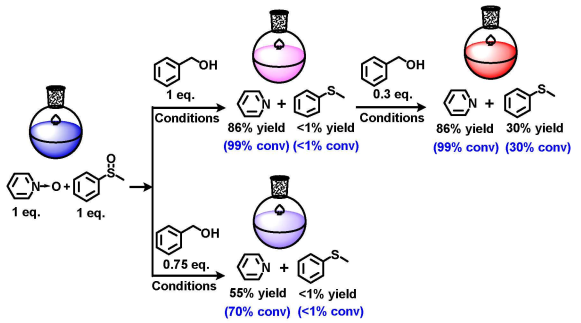
In previous reports of *N*-oxide reduction, particularly those using strong reducing agents, concurrent reduction of sulfoxide moieties is frequently observed, such as with $PhSiH_3/MoO_2Cl_2$, H_2/MoO_2Cl_2, and the $Fe/CO_2/H_2O$ system reported by the Romao, Royo, and He groups respectively.[14,17,34] Given the chemo-selective nature of our catalyst described above, we were intrigued to explore whether the heterogeneous **Mo@C** system can differentiate between *N*-oxide and sulfoxide reduction within the same reaction flask (Scheme 3). Interestingly, when a one pot competition reaction between pyridine *N*-oxide and methyl phenyl sulfoxide is conducted using a slight excess of benzyl alcohol, monitoring of the reaction mixture shows that the sulfoxide remains intact until complete conversion of pyridine *N*-oxide is achieved. Following the complete reduction of the *N*-oxide, thioether is detected as the only product from the sulfoxide reduction (Figure 1A). A similar experiment under benzyl alcohol starved conditions also confirms that **Mo@C** does not concurrently reduce both *N*-oxide and sulfoxide

Table 3. Scope of *N*-oxide substrate reduction.[a]



Entry	Substrate	*t* [h]	Conversion (Yield)
1		3	> 99% (85%)
2		6	> 99% (86%) (75%)[c]
3		6	> 99% (96%)
4		6	> 99% (93%) (78%)[c]
5		3	92% (81%)
6		3	> 99% (95%)
7		6	> 99% (92%)
8		3	95% (86%) (71%)[c]
9		3	> 99% (92%)
10		6	88% (77%)
11		6	> 99% (90%) (84%)[c]
12[b]		6	> 99% (89%)[c]
13		3	96% (85%) (79%)[c]

[a] Conditions unless otherwise specified: 1.0 mmol of substrate, 2 mol% of Mo (59 mg of 3.23 wt% **Mo@C**), 1.25 mmol benzyl alcohol, 1.0 mmol mesitylene (internal standard), 2.0 mL anisole, 500 rpm, 120 °C. Conversions and yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard; products also confirmed by ^{13}C NMR spectroscopy and GC-MS. During the reaction, the chemical shift of the *N*-oxides in the ^{1}H NMR spectra change slightly, but the integration is not influenced. For a more detailed analysis, see SI. [b] Preparative scale reaction. [c] Isolated yield.



Conditions: 2 mol% Mo@C, N_2, 120 °C, mesitylene, anisole

Scheme 3. Sulfoxide-*N*-oxide competition reactions.

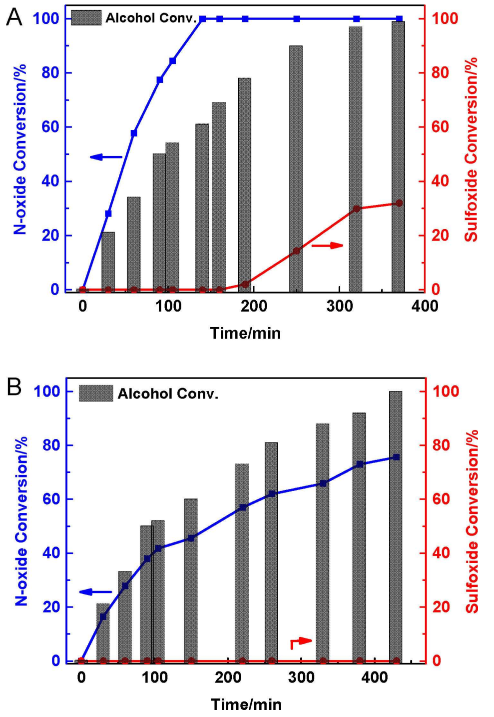


Figure 1. Sulfoxide and *N*-oxide competition reactions. Conversion of *N*-oxide (blue), methyl phenyl sulfoxide (red), and benzyl alcohol (gray) over time under alcohol sufficient (**A**) and starved (**B**) conditions at 120 °C. Conversions were determined by ^{1}H NMR integration against mesitylene as internal standard.

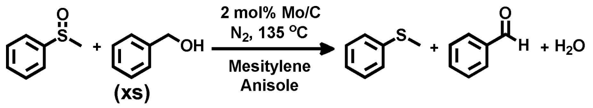
(Figure 1B), as only *N*-oxide reduction products are observed under these conditions. Similar selectivity results are observed at 135 °C (SI, Scheme S1 and Figure S2).

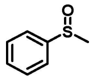
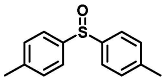
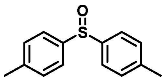
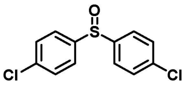
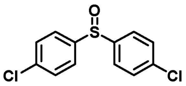
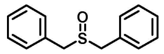
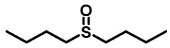
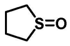
With these catalytic *N*-oxide results in hand, we next extended the scope of this catalytic reduction protocol to sulfoxides. An initial investigation was done with methyl phenyl sulfoxide. After optimizing reaction conditions, 96 % conversion in 3 h at 135 °C was achieved (Table 4, Entry 1). Next, the survey was expanded to other aliphatic and aromatic sulfoxides. In general, the **Mo@C** catalyst achieves excellent conversion to the corresponding thioether (Table 4, Entry 2–8) and retains the chemoselectivity over halogens, carbonyls, cyano groups, and C–C multiple bonds that was previously observed in the reduction of *N*-oxides (Table S3). These results show that **Mo@C** with alcohol serves as a broad and environmentally friendly system for chemoselective reduction.

Catalyst Recyclability

As noted above, homogeneous analogues of **Mo@C** have been reported to affect operationally similar reduction reactions. In order to ensure that the present system is indeed catalyzed by a heterogeneous Mo-dioxo species rather than leached homogeneous molecular Mo species, a number of control experiments were conducted.

Table 4. Scope of sulfoxide substrate reduction.[a]



Entry	Substrate	*t* [h]	Conversion (Yield)
1		3	96 % (96 %)
2		20	87 % (87 %)
3[b]		20	85 % (72 %)[c]
4		20	96 % (96 %)
5[b]		20	95 % (80 %)[c]
6		6	94 % (89 %)
7		20	90 % (90 %)
8		6	90 % (90 %)

[a] Conditions unless otherwise specified: 1.0 mmol of substrate, 2 mol % of Mo (59 mg of 3.23 wt % **Mo@C**), 1.25 mmol benzyl alcohol, 1.0 mmol mesitylene (internal standard), 2.0 mL anisole, 500 rpm, 135 °C. Conversions and yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard; products also confirmed by ^{13}C NMR spectroscopy and GC-MS. [b] Preparative scale reaction. [c] Isolated yield.

Upon comparing the elemental analyses of both spent and fresh catalyst the Mo loading remains essentially unchanged (3.2 wt.% fresh versus 3.1 wt.% spent). Additionally, ICP analysis of the reaction solution reveals that only trace amounts of Mo (< 13 ppm) leach from the supported catalyst into the reaction solution under typical reaction conditions. The trace amount of Mo in solution was determined to be catalytically insignificant via hot filtration experiments also conducted under optimized reaction conditions (Figure S1). Furthermore, recycling experiments show that the catalyst can be used 4 times without any significant decline in activity or selectivity (Figure 2A and B). The surface Mo of the spent catalyst was next characterized by XPS (Figure 2C) and PXRD (Figure 2D). No variation in the Mo binding energy is observed between the spent and fresh catalyst, indicating that the nature of the surface bound Mo species remains unchanged. The Mo 3d5/2 peak is found to be 232.6 eV with a spin orbit splitting of 3.1 eV. These results are in good agreement with previously reported XPS data[26] and support our hypothesis of the existence of a Mo(VI) dioxo species.

Preliminary Empirical Rate Law Investigation

A preliminary investigation of the empirical rate law for the **Mo@C** catalyzed reduction was conducted using pyridine *N*-

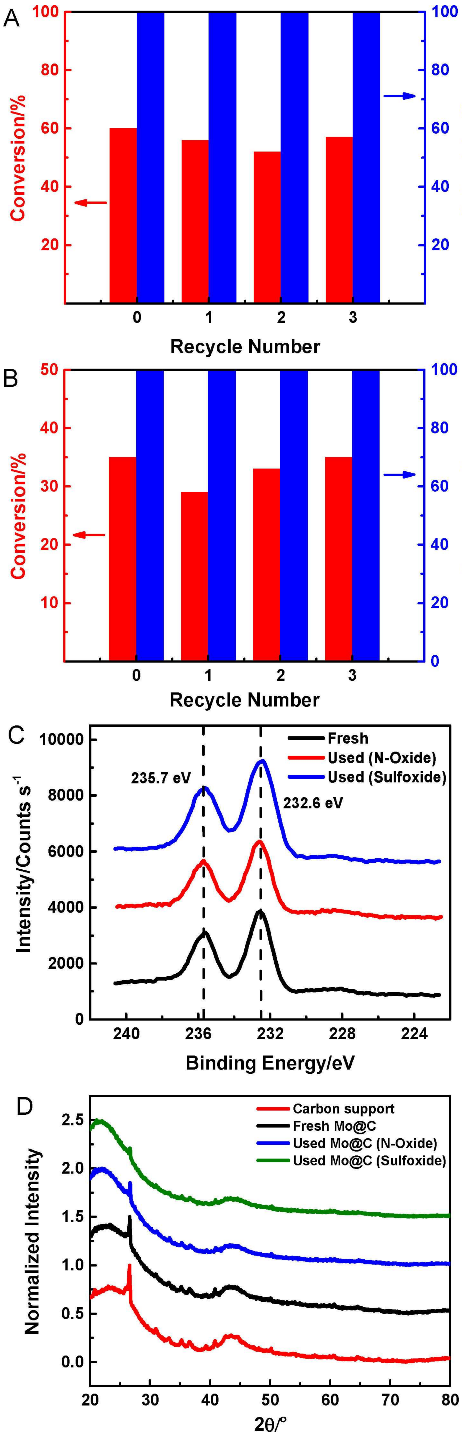


Figure 2. Recycling experiments illustrating conversion and selectivity from pyridine *N*-oxide to pyridine (**A**) and methyl phenyl sulfoxide to methyl phenyl sulfide (**B**) using the recycled **Mo@C** catalyst. Mo(3d5/2) XPS spectra of **Mo@C** before (black) and after (red and blue) reactions (**C**). PXRD spectra of carbon support (red) and **Mo@C** before (black) and after (blue and green) reactions(**D**).

oxide and methyl phenyl sulfoxide as model substrates respectively. The reaction was monitored via ^{1}H NMR using mesitylene as an internal standard. The initial reaction rates at different concentrations were measured at conversions below 25%. Again, because of the highly porous nature of the activated carbon support there is potential for the substrates and products to competitively adsorb on the catalyst surface (SI). This makes an accurate rate law challenging to deduce. Nevertheless, under the present conditions the overall rate for *N*-oxide reduction is found to be zero-order in pyridine *N*-oxide concentration, first-order in benzyl alcohol concentration, and fractional order in Mo content (Figure S3). However, for sulfoxide reduction, the overall rate is found to be zero-order in methyl phenyl sulfoxide concentration, and fractional order in both benzyl alcohol and Mo content (Figure S4). While detailed interpretation is frequently not straightforward in heterogeneous systems where the reaction occurs at the liquid-solid interface, the measured reaction orders suggest that both alcohol and Mo may be involved in the turnover-limiting step. Deoxygenation by H_2 produced from direct alcohol oxidation can be excluded since no deoxygenated products are observed under 50 psi of H_2 in the absence of alcohol (see Experimental).

Conclusions

We report a heterogeneous **Mo@C** catalyst demonstrating both high activity and selectivity in the reduction of *N*-oxides and sulfoxides when paired with alcohol reducing agents. The high functional group tolerance has been demonstrated by the chemoselective reduction of challenging substrates bearing C=C, C≡C, C≡N, C=O, halides, and S=O functional groups. The ease with which sterically hindered substrates undergo reduction is also noteworthy. The high stability, wide availability, recyclability, and low toxicity of the **Mo@C** catalyst and the reducing agents further support this system as an ecofriendly and robust catalytic system. We envision that the operational simplicity of this protocol allows for its use by not only experienced heterogeneous catalytic chemists, but also chemists that do not typically utilize heterogeneous catalysis.

Experimental Section

General Considerations

Activated carbon (06-0100, Lot#2562087) was purchased from Strem Chemicals. The reagents 3-acetylpyridine *N*-oxide, 4-chloropyridine *N*-oxide, 4-(dimethylamino)pyridine *N*-oxide hydrate, 2,5-lutidine *N*-oxide, 4-methoxypyridine *N*-oxide, 2-methylpyridine *N*-oxide, 4-nitropyridine *N*-oxide, 4-chlorophenyl sulfoxide, dibenzyl sulfoxide, and tetramethylene sulfoxide were purchased from TCI America. All other starting materials and solvents were purchased from Sigma-Aldrich. All chemicals were used as received and without further purification unless otherwise noted. Mo@C was prepared and fully characterized previously by this laboratory from (dme)Mo(=O)$_2$Cl$_2$ (dme = 1,2-dimethoxyethane) and activated carbon.[26]

Analytical Measurements

^{1}H and ^{13}C NMR spectra were recorded at Integrated Molecular Structure Education and Research Center (IMSERC) at Northwestern

University with a 500 MHz Bruker Avance III HD system equipped with a TXO Prodigy probe, a 400 MHz Bruker Avance III HD Nanobay system equipped with SampleXpress autosampler, or a 500 MHz Varian Inova-500 spectrometer. Chemical shifts (δ) for ^1H and ^{13}C are referenced to TMS. Mesitylene was used as an internal standard unless otherwise noted. GC/MS analyses were recorded at IMSERC at Northwestern University with an Agilent 7890 GC-TOF equipped with a 30 meter DB-5 column. An initial temperature of 75 °C was held for 2 min before applying a ramp rate of 20 °C/min up to 300 °C. The temperature was then held at 300 °C for an additional 10 min. ICP analysis of the catalyst Mo metal loading was performed by Galbraith Labs (Knoxville, TN). ICP analysis of the reaction solution was recorded at Quantitative Bio-element Imaging Center (QBIC) at Northwestern University with a Thermo iCAP 7600 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Powder X-ray diffraction (PXRD) experiments were carried out in the J. B. Cohen facility at Northwestern University using a Rigaku Ultima diffractometer.

Catalytic Reduction

In a typical experiment, pyridine *N*-oxide (0.095 g, 1.0 mmol, 1.0 equiv) or methyl phenyl sulfoxide (0.140 g, 1.0 mmol, 1.0 equiv), benzyl alcohol (0.135 g, 1.25 mmol, 1.25 equiv), mesitylene (0.14 mL, 1.0 mmol, 1.0 equiv), anisole (2.0 mL), **Mo@C** (0.059 g, 2 mol% Mo) and a magnetic stir bar were added to a single neck Schlenk flask in air. A reflux condenser was attached with a port to house N_2. The solution was degassed then placed under N_2. While stirring at 500 rpm, the flask was lowered into an oil bath at 120 °C. Samples were periodically collected and analyzed via NMR spectroscopy to monitor the course of the reaction. Conversion and selectivity were calculated by ^1H NMR spectroscopy through integration against the internal standard. All reported products area known compounds and were compared to published $^1H/^{13}C$ NMR values when possible and verified by GC/MS when appropriate.

Product Purification for *N*-Oxides

After the reaction, the reaction mixture was cooled to room temperature and the crude mixture was treated with 1 M aqueous HCl solution (5 mL). During extraction, the catalyst remained in the organic layer, which was discarded. The aqueous layer was washed with DCM (5×1 mL), neutralized with 1M aqueous NaOH solution (6 mL), and extracted with DCM (3×2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure. The corresponding pyridines were obtained in pure form with ^1H-NMR spectra (agreeing with the literature[35,36]) presented in the Supporting Information.

Product Purification of Sulfoxides

After the reaction, the reaction mixture was cooled to room temperature and the crude mixture was filtered through a silica bed to remove the catalyst and washed with hexanes (3×5 mL). Then the collected filtrate was placed under vacuum to remove hexanes and anisole at room temperature and the crude product further purified by column chromatography using hexanes as the eluent. The solvent was evaporated under vacuum. The purified product is slightly air-sensitive and was stored under inert atmosphere. The corresponding sulfides were obtained in pure form with ^1H-NMR spectra (agreeing with the literature[2]) presented in the Supporting Information.

Preparative Scale Reduction

On a preparative scale, isoquinoline *N*-oxide (1.161 g, 8 mmol) was subjected to the catalytic reduction conditions with benzyl alcohol at 120 °C with 2 mol% Mo metal loading. After 6 h, the reaction mixture was cooled to room temperature, treated with 1M aqueous HCl solution, washed with DCM, neutralized with 1M aqueous NaOH solution, and then extracted with DCM. Isoquinoline was recovered as yellow oil in 89% isolated yield after removal of solvent in vacuo. Similar reduction procedures were performed with p-tolyl sulfoxide (1.152 g, 5 mmol) and 4-chlorophenyl sulfoxide (1.356 g, 5 mmol) at 135 °C. After 20 h, the reaction mixtures were cooled to room temperature, filtered through a silica bed, placed under vacuum to remove solvent, and further purified by column chromatography. The corresponding sulfides were recovered as white solids in 72% and 80% isolated yields respectively after removal of solvent in vacuo, with ^1H-NMR spectra (agreeing with the literature[2,36]) presented in the Supporting Information.

Catalyst Recycling

After the initial reaction, the reaction mixture was filtered using a Buchner funnel and the **Mo@C** catalyst was then collected and washed with anisole (3×3 mL) and hexanes (2×3 mL). The catalyst was then allowed to air dry. The recyclability test was then performed for reduction of pyridine *N*-oxide and methyl phenyl sulfoxide under the same conditions detailed above. Four sequential catalytic runs were performed.

Hot filtration Procedure

Mo@C (0.594 g), anisole (2.0 mL), mesitylene (1.4 mL), benzyl alcohol (0.135 g), and a magnetic stir bar were added to a single neck Schlenk flask equipped with a reflux condenser. The solution was degassed, heated to 120 °C under nitrogen for 1 h, then filtered into another flask while still hot via cannula filter. After cooling to rt, pyridine *N*-oxide (0.095 g, 1.0 mmol) was added to the flask and heated to 120 °C for 3 h. The solution remained colorless, and no benzaldehyde or pyridine peaks were observed in the ^1H NMR spectrum.

Competition Experiment for Reduction of Sulfoxides and *N*-Oxides

Pyridine *N*-oxide (0.095 g, 1.0 mmol, 1 equiv), methyl phenyl sulfoxide (0.140 g, 1.0 mmol, 1.0 equiv), benzyl alcohol (0.140 g, 1.3 mmol, 1.3 equiv, or 0.081 g, 0.75 mmol, 0.75 equiv), mesitylene (0.14 mL, 1.0 mmol), anisole (2.0 mL), **Mo@C** (0.059 g, 2 mol% Mo) and a magnetic stir bar were added to a single neck Schlenk flask in air. A reflux condenser was attached with a port to house N_2. The solution was degassed and then placed under N_2. While stirring at 500 rpm, the flask was lowered into an oil bath at 120 °C. Samples were periodically collected and analyzed via NMR spectroscopy to monitor the course of the reaction. Conversion and selectivity were calculated by ^1H NMR through integration against the internal standard.

Control Experiments Using H_2 as a Reductant

Pyridine *N*-oxide (0.095 g, 1.0 mmol, 1.0 equiv), mesitylene (0.14 mL, 1.0 mmol), anisole (2.0 mL), **Mo@C** (0.059 g, 2 mol% Mo) and a magnetic stir bar were added to a round bottom heavy wall pressure vessel in air. The solution was degassed and then placed under 50 psi H_2(g). While stirring at 500 rpm, the flask was lowered into an oil bath at 120 °C and heated for 3 h. Samples were collected and analyzed via NMR spectroscopy to monitor the course of the reaction. Pyridine *N*-oxide deoxygenation by H_2 produced from direct alcohol oxidation was ruled out because no deoxygenated product was observed under 50 psi of H_2 without alcohol addition.[7,17, 25]

Control Experiments Under Air

Pyridine *N*-oxide (0.095 g, 1.0 mmol, 1.0 equiv), mesitylene (0.14 mL, 1.0 mmol), anisole (2.0 mL), **Mo@C** (0.059 g, 2 mol% Mo) and a magnetic stir bar were added to a round bottom heavy wall pressure vessel in air. While stirring at 500 rpm, the flask was lowered into an oil bath at 120 °C and heated for 3 h. Samples were collected and analyzed via NMR spectroscopy before and after the reaction. A negligible decrease in reaction rate is observed for the reduction of pyridine *N*-oxide under air compared to the reaction under inert atmosphere, showing the air- and moisture- stability of this catalytic system.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Chemoselective · *N*-oxide and Sulfoxide Reduction · Carbon-supported Dioxo-Molybdenum · Environmentally Friendly · Heterogeneous Catalysis

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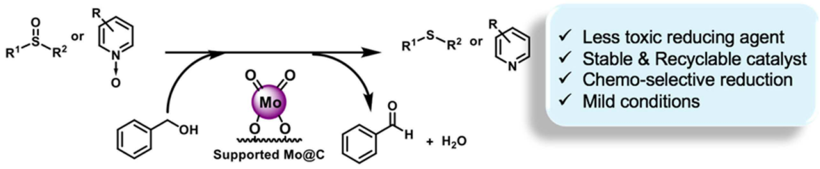

Mo@C makes it: The chemoselective reduction of a wide range of *N*-oxides and sulfoxides with alcohols using a carbon-supported dioxo-molybdenum catalyst is reported. The high stability, earth abundance, and recyclability of the catalyst, paired with its low toxicity represents an environmentally friendly catalytic system.

J. Li, S. Liu, Dr. T. L. Lohr,*
*Prof. Dr. T. J. Marks**

1 – 9

Efficient Chemoselective Reduction of *N*-Oxides and Sulfoxides Using a Carbon-Supported Molybdenum-Dioxo Catalyst and Alcohol