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14. ABSTRACT
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Oxidative C-C Bond Cleavage for Alkane Fuel Cells

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2013	ACS Catalysis Lectureship for the Advancement of Catalytic Science
2013	Herbert C. Brown Award for Creative Research in Synthetic Methods
2012	Member, National Academy of Sciences

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Adele Pacquette	1.00	
Justin Oberst	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Dr. Tyler Wilson	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Andrew Gewirth	0.00	No
John F. Hartwig	0.00	Yes
FTE Equivalent:	**0.00**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report for Period 07/01/2011 – 06/30/2013

Overview of research activities:

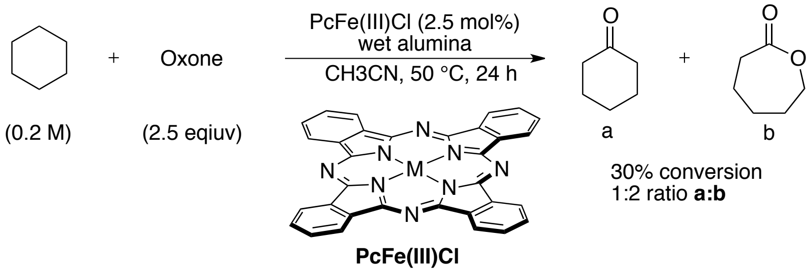
The work under support of DARPA for the period of 07/01/2012 – 06/30/2013 focused on the identification of organotransition metal catalysts that can oxidize alkanes to esters using mild oxidizing agents and on the oxidation of alcohols for use of the alkane oxidation products in fuel cells. Progress on these two research paths during the no costs extension period are described below.

Progress Reports

Studies toward oxidative C-C bond cleavage and electrochemical oxidation of alkanes.

In the previous funding period (07/01/2011 – 06/30/2012), we demonstrated proof of concept for cyclohexane oxidation with concomitant C-C bond fragmentation using Fe and Ru-based phthalocyanine catalysts in combination with wetted-alumina as a co-catalyst and Oxone as the stoichiometric oxidant (Scheme 1). Control studies using wetted-alumina and Oxone with and without Fe phthalocyanine established that, although the transition metal complexes are essential for effecting the initial C-H oxidation, they do not catalyze by themselves the subsequent oxidation of ketones to esters. However, they are compatible with known catalysts for ketone oxidation to esters, and we have shown that the two catalysts can work in combination for the first oxidation of an alkane to an ester.

Scheme 1. Oxidation of Cyclohexane to Caprolactone with PcFe(III)Cl



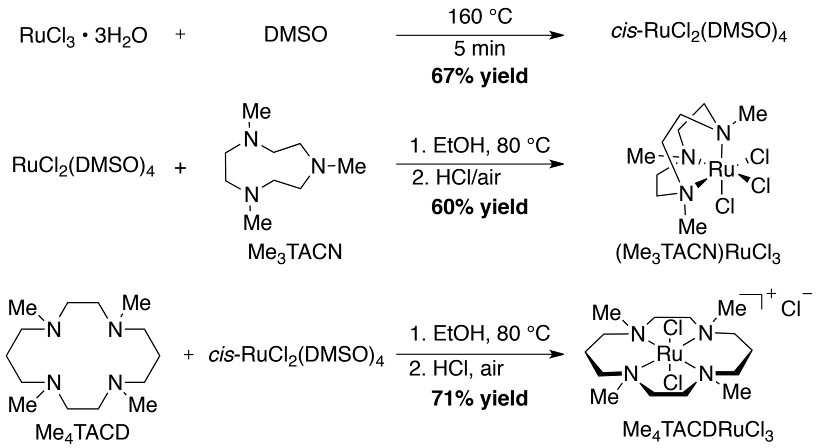
The two major problems that needed to be addressed in this funding period were: (1) overcoming the reduction in catalyst activity observed for the Fe and Ru phthalocyanine catalysts when supported on electrodes and (2) identifying new catalysts systems or reaction conditions that can achieve C-H oxidation using milder oxidants that more closely approximate the oxidation potentials achievable in an electrochemical cell. In short, these results identified some promising Fe and Ru based catalyst systems for further study under electrochemical conditions, and in each case we were able to ship samples to Prof. Gewirth's lab in Illinois for testing on supported electrodes. The results obtained for homogeneous oxidations of cyclohexane are presented in the following sections.

Oxidation with Ru-based Catalysts:

Ruthenium tetraoxide is a well-known oxidant in organic chemistry and has previously been used for the oxidation of a wide-variety of C-H bonds.[1] Although accompanying C-C bond oxidation is not usually observed in these systems, it has been reported in at least one case involving the oxidation of a tertiary C-H bond adjacent to a cyclic ether.[2] Ruthenium tetraoxide is most-commonly used as a stoichiometric oxidant, generated from equimolar amounts of $RuCl_3$ and $NaIO_4$. More recently, Dubois and McNeill have reported a milder and more selective oxidation of tertiary and benzylic C-H bonds using catalytic $RuCl_3$ in combination with $KBrO_3$ as the stoichiometric oxidant.[3] In a follow-up publication Dubois also described a highly chemoselective catalyst for tertiary C-H bond oxidations, which utilized a 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN) ligated $RuCl_3$ as the pre-catalyst.[4] The active species in these reactions is thought to be $(Me_3TACN)RuO_2$, formed from the reaction of $(Me_3TACN)RuCl_3$ with ceric ammonium nitrate (CAN) and silver perchlorate.

The precedence by Dubois and others suggested that RuO_4 and related species could be promising catalyst for the oxidation of cyclohexane in either homogenous or electrochemically driven reactions. However, oxidation of 2° C-H bonds utilizing catalytically generated ruthenium oxide species is not well described. Therefore the synthesis of a few ruthenium based catalyst for testing under homogeneous reaction conditions with different oxidants was undertaken first (Scheme 2).

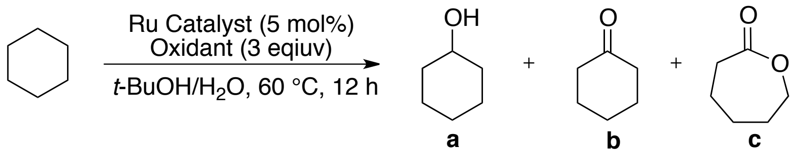
Scheme 2. Synthesis of Ruthenium Chloride Complexes



The reaction of triazacyclononane with dichlorotetrakis(dimethylsulfoxide)ruthenium(II) and subsequent air oxidation in concentrated hydrochloric acid solution afforded $(Me_3TACN)RuCl_3$ in good yield (Scheme 2). In an analogous reaction, $(Me_4TACD)RuCl_3$ was prepared in good yield starting from 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4TACD).[5] The cis-complex of DMSO and ruthenium dichloride was prepared from $RuCl_3$ following the method of Wilkinson.[6]

Screening of ruthenium-based catalysts for oxidation of cyclohexane under homogeneous conditions was conducted using methods similar to those reported by Dubois for tertiary C-H bond oxidations. Hence, a solution of cyclohexane in *t*-BuOH and water was treated with 5 mol% of ruthenium catalyst and 3 eqiuv of oxidant at 60 °C for 12 h (Table 1). A number of oxidants, varying in oxidation potential from weak to strong, were tested under these reaction conditions. Consistent with the literature reports, reactions conducted with potassium bromate gave the highest conversions, yielding cyclohexanone as the major product. $RuCl_3$ was the most reactive catalyst tested, followed closely by $(Me_3TACN)RuCl_3$. The catalyst derived from Me_4TACD was nearly unreactive with all oxidants examined, which could result from a more sterically congested site of oxidation imparted by the cyclotetradecane core of the ligand. Interestingly, $(Me_3TACN)RuCl_3$ demonstrates activity towards cyclohexane oxidation, even with weaker oxidants such as *t*-butyl hydroperoxide (Table 1, entry 15). This promising result suggested that $(Me_3TACN)RuCl_3$ would be a good candidate for electrochemically driven oxidations at lower potential. Therefore the preparation of $(Me_3TACN)RuCl_3$ was repeated on a larger scale and the material was shipped to the Gewirth lab for electrode deposition and testing.

Table 1. Oxidant Screen for Cyclohexane Oxidation with Ru-based Catalysts



Entry	Catalyst	Oxidant	Conversion[1]	a:b:c ratio[2]
1	$RuCl_3\cdot 3H_2O$	$KBrO_3$	66%	1:99:0
2	$RuCl_3\cdot 3H_2O$	Oxone	5%	1:2:0
3	$RuCl_3\cdot 3H_2O$	*m*-CPBA	<2%	n/a
4	$RuCl_3\cdot 3H_2O$	*t*-BuO_2H	<2%	n/a
5	$RuCl_3\cdot 3H_2O$	NaOCl	52%	1:2:0
6	$RuCl_3\cdot 3H_2O$	2,6-Cl_2Pyr-O	<1%	n/a
7	$RuCl_2\cdot(DMSO)_4$	$KBrO_3$	26%	1:99:0
7	$RuCl_2\cdot(DMSO)_4$	Oxone	10%	1:4:0
8	$RuCl_2\cdot(DMSO)_4$	*m*-CPBA	<1%	n/a
9	$RuCl_2\cdot(DMSO)_4$	*t*-BuO_2H	13%	1:3:0
10	$RuCl_2\cdot(DMSO)_4$	NaOCl	40%	2:1:0
11	$RuCl_2\cdot(DMSO)_4$	2,6-Cl_2Pyr-O	<1%	n/a
12	$(Me_3TACN)RuCl_3$	$KBrO_3$	60%	1:99:0
13	$(Me_3TACN)RuCl_3$	Oxone	15%	1:1:0
14	$(Me_3TACN)RuCl_3$	*m*-CPBA	5%	1.5:1:0
15	$(Me_3TACN)RuCl_3$	*t*-BuO_2H	20%	1:99:0
16	$(Me_3TACN)RuCl_3$	NaOCl	12%	1:10:0
17	$(Me_3TACN)RuCl_3$	2,6-Cl_2Pyr-O	<1%	n/a
18	$(Me_4TACD)RuCl_3$	$KBrO_3$	<5%	n/a
19	$(Me_4TACD)RuCl_3$	Oxone	<5%	n/a
20	$(Me_4TACD)RuCl_3$	*m*-CPBA	<5%	n/a
21	$(Me_4TACD)RuCl_3$	*t*-BuO_2H	<5%	n/a

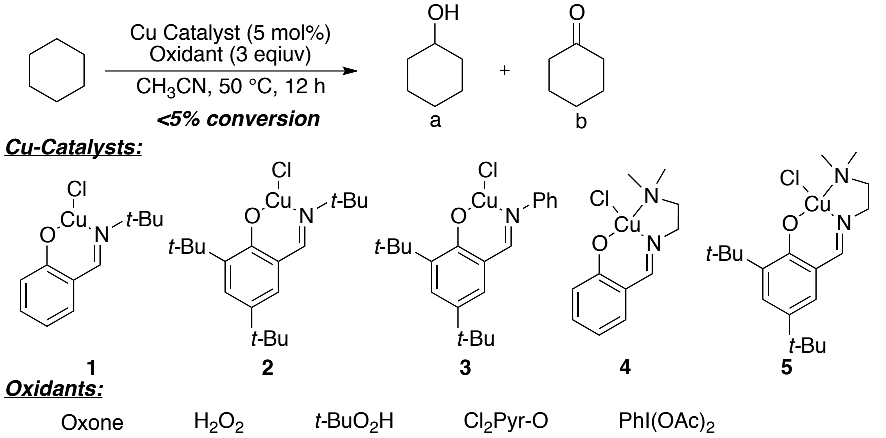
[1,2] Determined by GC integration.

Oxidation with Cu-based Catalysts:

Copper has long been recognized as one of the key transition metals used by biological systems for metalloenzyme-catalyzed redox processes. For example, current studies on methane monooxygenase have suggested that the metal co-factor involved in the C-H activation is a cluster of two copper ions.[7] Copper is also known as a versatile reagent for oxidative coupling reactions in organic chemistry and more recently for oxidative functionalizations of C-H bonds.[8] Unpublished studies in these laboratories have shown that Cu(II) metal complexes ligated by an aromatic Schiff bases can be used for C-H activation/amination reactions of cyclohexanes.

Although no direct precedent for oxidation of cyclohexane with Cu-based catalyst was available it seemed prudent to screen the catalyst already available in the Hartwig labs against known oxidants. Copper catalysts **1-5** were examined with the same set of oxidants and under identical reaction conditions as used in the studies conducted for Ru-based catalysts (Scheme 3). Unfortunately, only trace amounts of oxidation products could be detected by gas chromatography even when strong oxidants such as oxone or potassium bromate were employed. Weaker oxidants such as *t*-butyl hydroperoxide and 2,6-dichloropyridine *N*-oxide also led to low conversion suggesting that catalyst deactivation by ligand oxidation was not the sole reason for the low activity observed in this system.

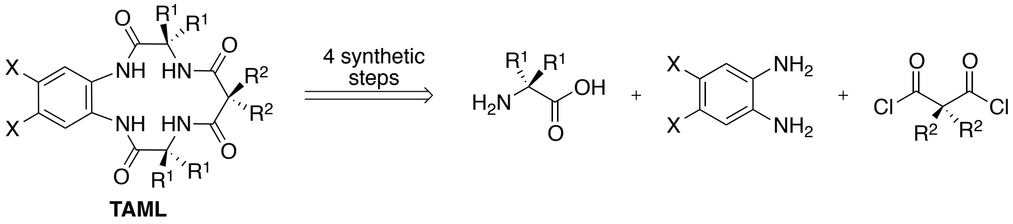
Scheme 3. Oxidant Screen for Cyclohexane Oxidation with Cu-Based Catalysts.



Oxidation with FeTAML Catalysts:

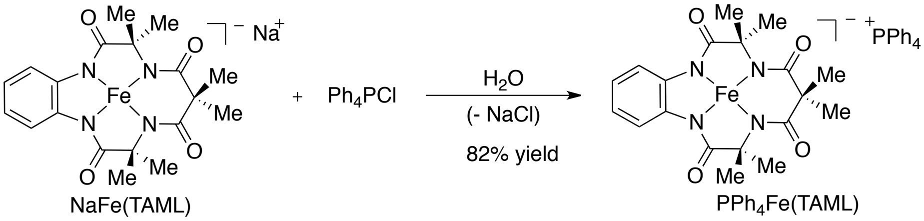
The tetra-amido macrocyclic ligands (TAML) were developed by Collins and co-workers as synthetic mimics of peroxidase enzymes.[9] Metal complexes of these ligands with Fe have shown extraordinary activity towards oxidation of organic molecules and have primarily been developed for cleaning waste streams via oxidative degradation of potentially toxic chemicals.[10] Surprisingly, the use of Fe(TAML) based ligands as catalysts for site selective C-H oxidation in organic synthesis is largely undeveloped. A major advantage of the TAML based catalysts, compared to related porphyrin or phthalocyanine catalysts, is the ease and modularity of their synthesis and their resistance toward oxidative degradation. The TAML ligands can be prepared in four high yielding synthetic steps from three simple building blocks (Scheme 4).[11] Varying the substituents on the building blocks provides access to organic-soluble catalysts, different electronic states at the metal center, and the ability to block potential sites of undesired ligand oxidation.

Scheme 4. Synthesis of TAML Catalysts



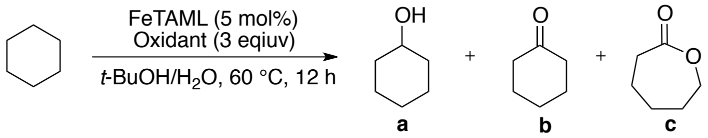
To test FeTAML ligands for cyclohexane oxidation under homogeneous conditions, a commercial sample of the sodium salt of the parent FeTAML catalyst was purchased from GreenOx Catalysts, Inc. Due to the limited solubility of the sodium salt in organic solutions, a cation exchange reaction with tetra-phenylphosphonium chloride was performed providing the soluble Ph_4PhFe(TAML) catalyst in good yield (Scheme 5).[12]

Scheme 5. Synthesis of Organic-Soluble FeTaml Catalyst



For consistency, the FeTAML catalyst was examined for cyclohexane oxidation under the same conditions used to examine Cu- and Ru-based catalysts. Consequently, a solution of cyclohexane in *t*-BuOH/H_2O was treated with 5 mol% of FeTAML catalyst and 3 equiv of oxidant. The reactions were heated to 60 °C and monitored for conversion by GC over a 12 h period (Table 2). For stronger oxidants, such as $KBrO_3$ and oxone, very little conversion was observed which could be a result of ligand degradation by oxidation. However, with milder oxidants such as *t*-butyl hydroperoxide good conversion to cyclohexanone was observed for both the sodium and tetra-phenylphosphonium salts of FeTAML. In addition to *t*-butyl hydroperoxide, the oxidants sodium perchlorate and (diacetoxyiodo)benzene reacted with low to moderate conversion. The reactions conducted with the FeTAML catalysts resulted in the highest yields observed to date for cyclohexane oxidation using mild peroxide oxidants. Both salts of the FeTAML catalyst were shipped to Prof. Gewirth's lab for testing in electrochemically driven oxidations.

Table 2. Oxidant Screen for Cyclohexane Oxidation with FeTAML Catalysts



Entry	Catalyst	Oxidant	Conversion[1]	a:b:c ratio[2]
1	NaFe(TAML)	$KBrO_3$	<1%	n/a
2	NaFe(TAML)	Oxone	<1%	n/a
3	NaFe(TAML)	*m*-CPBA	2%	1:99:0
4	NaFe(TAML)	*t*-BuO_2H	57%	1:99:0
5	NaFe(TAML)	NaOCl	30%	2:1:0
6	NaFe(TAML)	H_2O_2	<1%	n/a
7	NaFe(TAML)	2,6-Cl_2Pyr-O	<1%	n/a
8	NaFe(TAML)	CAN	<1%	n/a
9	Ph_4PFe(TAML)	*t*-BuO_2H	50%	1:99:0
10	Ph_4PFe(TAML)	H_2O_2	<1%	n/a
11	Ph_4PFe(TAML)	2,6-Cl_2Pyr-O	<1%	n/a
12	Ph_4PFe(TAML)	*m*-CPBA	5%	1:99:0
13	Ph_4PFe(TAML)	$PhI(OAc)_2$	10%	1:99:0

[1,2] Determined by GC integration.

Conclusions for the oxidation of alkanes.

In conclusion, we identified two new catalysts scaffolds that show promise for electrochemically driven oxidations at lower potentials. Both the (Me$_3$TACN)RuCl$_3$ and FeTAML catalysts give moderate to good conversions of cyclohexane oxidation to afford cyclohexanone using *tert*-butyl hydroperoxide as the stoichiometric oxidant under homogeneous reaction conditions. FeTAML catalysts were the most reactive catalysts tested to date. Given their ease of synthesis and the ability to fine-tune the ligand structure, these catalysts represent a promising candidate for future studies on alkane oxidation.

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Mo-V-O based electrocatalysts for low temperature alcohol oxidation

In parallel with studies on alkane oxidation in Hartwig's laboratory, studies on alcohol oxidation were conducted in Gewirth's laboratory. This combination of studies address a strategy for alkane fuel cells comprising the oxidation of alkanes at high potential to generate alcohols and oxidation of the alcohol at low potential in an alcohol fuel cell. Alcohol fuel cells are widely studied electrochemical devices. These systems are used due to the ease of storage and high theoretical mass energy density of liquid alcohols. There is a growing interest in alcohol oxidation electrochemistry due to its role in renewable energy technologies. At present, the most active alcohol oxidation catalyst in acidic media is based on the precious metal Pt. However, it is accepted that Pt alone is not sufficient to oxidize alcohols at a reasonable rate due to poisoning by reaction intermediates such as CO. Also it is necessary to improve alcohol oxidation at low temperatures.

Molybdenum-based oxides have been extensively researched for several decades.[1]The selective oxidation of light alkanes into oxygenated products has attracted interest recently.[2] Mo-V-O based catalysts have been utilized in the oxidation reactions such as benzene to maleic anhydride, acrolein to acrylic acid, and propane to acrylic acid.[3] Selective alkane oxidation has been observed at elevated temperatures above 300 ^{0}C on these catalysts. However, electrooxidation of alcohols at low temperatures has not yet been studied.

In this report, the Mo-V-O based catalyst is prepared hydrothermally. The effect on the catalytic activity by metal substitution, such as Nb and Te, is investigated. The catalytic activity for the oxidation of alcohols such as, cyclohexanol, butanol, propanol, ethanol, and methanol is studied electrochemically. The studies are conducted at low temperatures, 25-60 ^{0}C. The efficiency of alcohol oxidation by the catalyst is based on the nature of the oxidative products. Results show that these materials are effective dehydrogenation catalysts.

The diffraction pattern of the material prior to calcination was indexed to $(V_{0.07}Mo_{0.93})_5O_{14}$ (JCPDS 00-031-1437) with a tetragonal structure. The characteristic peak at $2\theta \sim 22.2^0$ associated with a Mo_5O_{14} type structure[6] was observed in this pattern. After calcination, there were structural changes to yield a triclinic $Mo_{0.97}V_{0.95}O_5$ (JCPDS 04-015-6540) product. This product is consistent with that first determined by Plyasova et al.[10] The characteristic peak for the product structure at $2\theta \sim 22.0^0$ was reported by Roussel et. al and cannot be mistaken with the one at 22.2^0 of Mo_5O_{14} type structure found in the material prior to calcination.[6]

Mo-V-O electrocatalyst

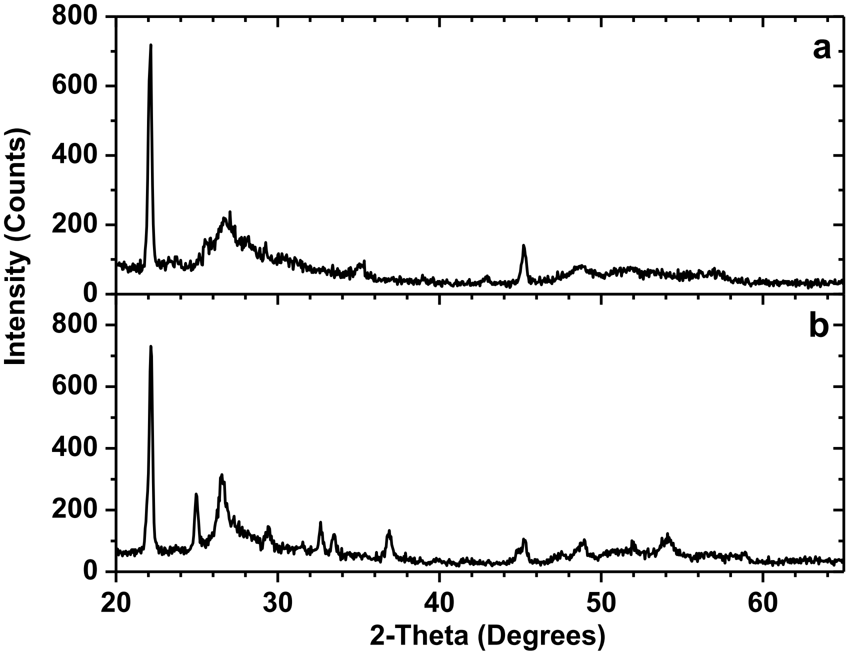

Figure 1: Powder X-ray diffraction pattern before calcination (a) and after calcination under nitrogen flow (b)

Figure 1 shows the powder X-ray diffraction data of the material obtained both before (Fig. 1a) and after

Before calcination the hydrothermal synthesis product exhibits a Mo_5O_{14} structure. However, calcination changes the structure to one similar to V_2O_5. The interatomic distances of the calcined material are close to those found in V-Mo compounds following isomorphous replacement of Mo^{6+} by V^{5+}.[10] V substitution after secondary heat treatment was also observed to transform a orthorhombic (M1) structure to a V-substituted Mo_5O_{14} type variant.[4] XPS shows that the V/Mo ratio increases following calcination. The origin of this increase may be decomposition of the starting reagent $(NH_4)_6Mo_7O_{24}.4H_2O$ to MoO_3 at 500 °C,[6] which may be removed from the calcined product.

Figure 1 shows that calcination improves the crystallinity of the material as evidenced in the sharper, well defined peaks observed in the material after calcination. Additionally, calcination led to a better match with the index pattern. The crystallite size following calcination determined by Rietveld refinement was 34.3 nm.

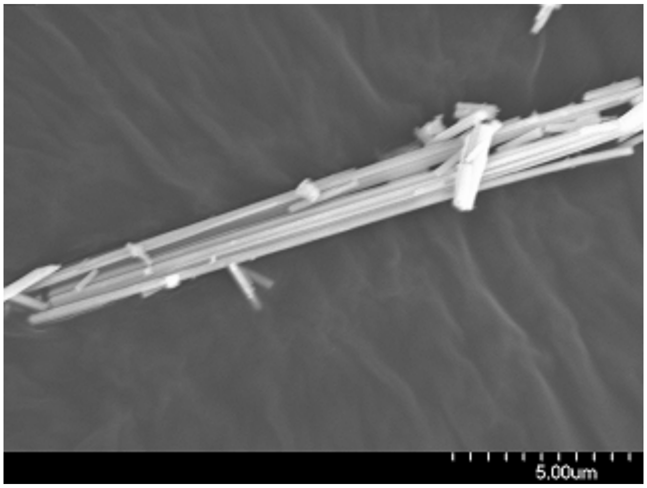

Figure 2: SEM micrograph illustrating the morphology of the calcined$Mo_{0.97}$ $V_{0.95}O_5$

Figure 2 shows a representative SEM image of the product$Mo_{0.97}V_{0.95}O_5$. The image shows rod-shaped or fiber-like crystallites about15 μm in length. The rod-shaped crystallites are consistent with shapes observed previously in Mo-V-O[1] and Mo-V-M-O oxides.[8]

Mo-V-Te-O electrocatalyst

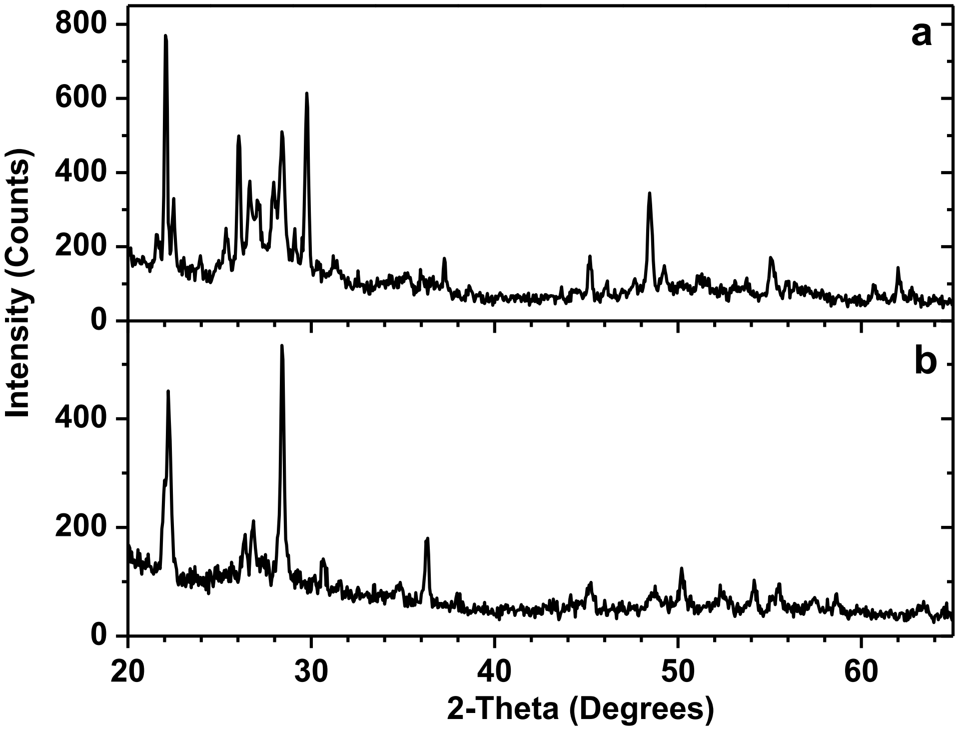

Figure 3: Powder X-ray diffraction pattern before calcination (a) and after calcination under nitrogen flow (b)

We also investigated the effect of Te addition on the catalytic activity of the Mo-V-O materials. Figure 2 shows the powder X-ray diffraction data of the hydrothermal synthesis product obtained before calcination and the material obtained after calcination. The precursor was a mixture of unreacted TeO_2, V_4O_9 and desired product $(TeO_{0.77}Mo_{0.33}\ V_{1.67})\ O_{14}$. Calcination completed the reaction and a mixture of $(TeO_{0.77}Mo_{0.33}\ V_{1.67})\ O_{14}$ and $TeO_{0.33}Mo_{0.75}\ V_{0.25}O_x$ was obtained.

Alcohol Oxidation

Cyclohexanol Oxidation

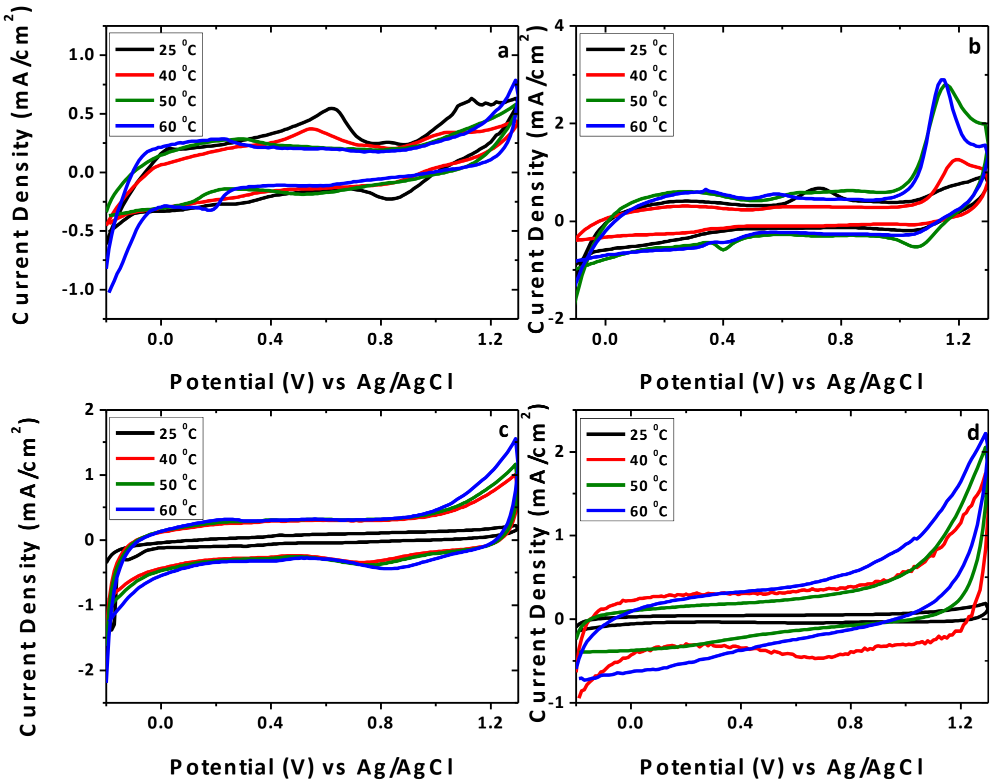

Figure 4: Cyclic voltammetry curves of $Mo_{0.97}\ V_{0.95}O_5$/Vulcan in 0.5 M H_2SO_4 (a), $Mo_{0.97}\ V_{0.95}O_5$/Vulcan in 0.5 M H_2SO_4/0.15 M $C_6H_{11}OH$ (b) Vulcan in 0.5 M H_2SO_4 (c) and Vulcan in 0.5 M H_2SO_4/0.15 M $C_6H_{11}OH$ (d) at different temperatures 25^0C (black), 40^0C (red), 50^0C (green), 60^0C (blue). Scan rate $10mVs^{-1}$

Figure 4a shows first cycle CVs from $Mo_{0.97}\ V_{0.95}O_5$ supported on Vulcan XC-72 in 0.5 M H_2SO_4 obtained at a scan rate of 10 mVs^{-1} at different temperatures. The voltammetry exhibits differences and variation due to variation in the preparation of the ink The voltammetry at 25 °C (black line) exhibits features associated with the Mo(IV/VI) redox couple around 0.6 V and the V(IV/V) couple around 1.0 V. As the temperature is increased, the Mo and V couples become less pronounced, and features associated with hydrogen evolution around 0 V and nascent oxygen evolution around 1.3 V are observed. These same features can be seen in voltammetry obtained from Vulcan XC-72 alone (Figure 4c). The increase in capacity with temperature seen in Fig. 4c may be associated with water and/or sulfate incorporation in the carbon at higher temperatures; a similar effect has been observed in phosphoric acid electrolyte.

Addition of 0.15 M cyclohexanol to the solution yields different features in the voltammetry obtained from the $Mo_{0.97}$ $V_{0.95}O_5$ based electrode. As shown in Fig. 4b, there is a well-defined oxidative feature found at ca. 1.1 V, which increases in intensity as the temperature approaches 60 C. The increase in activity at higher temperatures is in contrast to that seen in Figure 4 (a) without added cyclohexanol, where the current density in this region is some 2.5 mA/cm^2 less. Also by way of contrast, Fig. 4d shows the effect of added cyclohexanol on a bare Vulcan XC-72 electrode. There is a modest (ca. 0.4 mA/cm^2) at 1.1 V with the addition of cyclcohexanol.

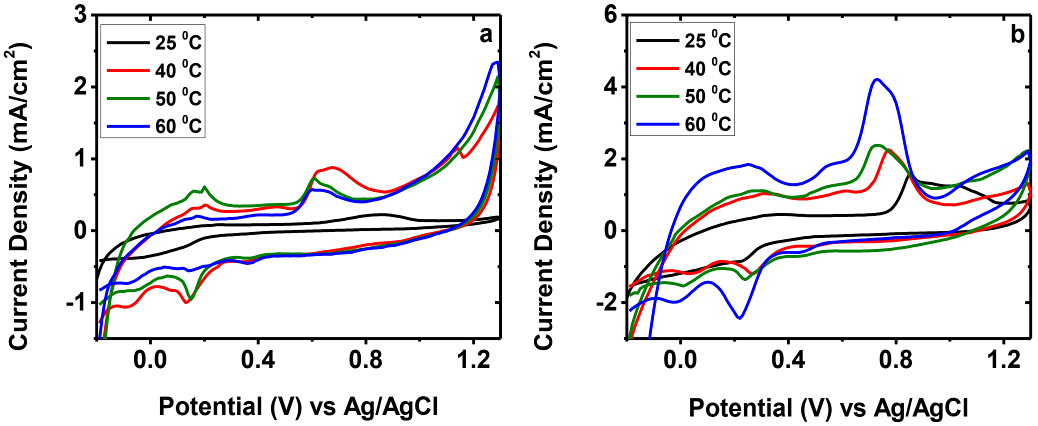

Figure 5: Cyclic voltammetry curves of Mo-V-Te-O/Vulcan in 0.5 M H_2SO_4 (a) or 0.5 M H_2SO_4/0.15 M $C_6H_{11}OH$ (b) at different temperatures 25^{0}C (black), 40^{0}C (red), 50^{0}C (green), 60^{0}C (blue). Scan rate 10mVs^{-1}

Figure 5a shows CVs from Mo-V-Te-O supported on Vulcan XC-72 in 0.5 M H_2SO_4 obtained at a scan rate of 10 mVs^{-1}. At room temperature features similar to those found for the $Mo_{0.97}$ $V_{0.95}O_5$ associated with the Mo(IV/VI) redox couple around 0.6 V are observed. However, the redox properties associated with V(IV/V) couple around 1.0 V are not observed. Fig. 5b shows the increase in oxidative activity in the presence of cyclohexanol.

GCMS Analysis to determine products

Cyclohexanol oxidation

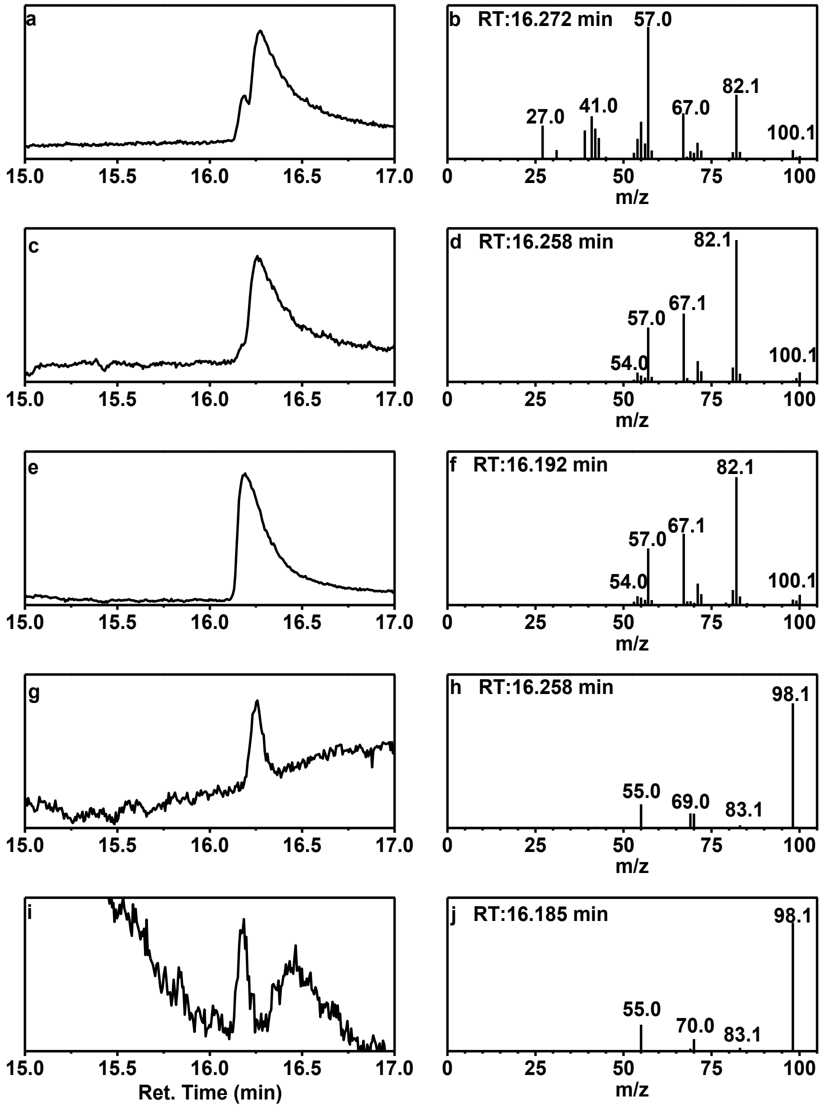

Figure 6: GCMS analysis of 0.5 M H_2SO_4/0.15 M $C_6H_{11}OH$ blank (a,b) and solutions after cyclic voltammetry studies in 0.5 M H_2SO_4/0.15 M $C_6H_{11}OH$ for $Mo_{0.97}$ $V_{0.95}O_5$/Vulcan at
6 ^{0}C(c,d), 40 ^{0}C(e,f), 50 ^{0}C(g,h) and 60 ^{0}C(i,j)

Figure 6 shows the chromatograms and mass spectra after the CV was collected for $Mo_{0.97}$ $V_{0.95}O_5$ supported on Vulcan XC-72 in 0.5 M H_2SO_4/0.15 M $C_6H_{11}OH$. The peak at retention time 16.27 min in the blank corresponds to cyclohexanol. At the lower temperatures of 25 ^{0}C and 40 ^{0}C, the cyclohexanol peaks were present at 16.26 min and 16.19 min respectively. At 50 ^{0}C and 60 ^{0}C, the peaks at 16.26 min and 16.19 min have masses which match that of cyclohexanone. This cyclohexanone product was not found in solutions exposed to Vulcan carbon absent the catalyst. The tables below show products obtained from different alcohols for both the Mo$_{0.97}$ V$_{0.95}$O$_5$ (Table 1) and Mo-V-Te-O (Table 2) materials.

Table 1: Summary of GCMS analysis results

Alcohol	Product		
	Mo$_{0.97}$ V$_{0.95}$O$_5$	Pt	Vulcan
Cyclohexanol	Cyclohexanone	-	-
Butanol	Butanal	1-Butene	-
Ethanol	Methyl Formate	Acetaldehye	-

Table 2: Summary of GCMS analysis results for Mo-V-Te-O

Alcohol	Product
Cyclohexanol	Cyclohexanone
Butanol	Butanal
Ethanol	Formaldehye

In conclusion, we show that the Mo-V-O catalysts dehydrogenate alcohols at relatively mild temperatures in acid solution. Heteroatom substitution increases the activity and stability of the material.

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