

Selective Oxidation in Supercritical Carbon Dioxide Using Clean Oxidants

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We have systematically investigated heterogeneous catalytic oxidation of different substrates in supercritical carbon dioxide (SC-CO₂). Three types of catalysts, a metal complex {*cis*-[Fe-(dmp)₂(H₂O)₂](CF₃SO₃)₂} (dmp = 2,9-dimethyl-1,10-phenanthroline), 0.5% platinum γ -alumina, and 0.5% palladium γ -alumina, were used at a pressure of 200 bar, at temperatures from 60 to 150 °C, and for 3–18 h for partial oxidation of organic substrates. The metal–oxo catalyst used gave as high as 3.9% conversion of cyclohexene to its oxides and epoxides, with the major products being the ketone and alcohol. The oxidation of cyclohexene strongly depended on the concentration of oxygen, whereas length of reaction (3–18 h) and temperature (60–150 °C) were shown to be less significant on the conversion and selectivity of the reaction. Oxidation of cyclohexene over Pd and Pt/Al₂O₃ catalysts resulted in a mixture of dehydrogenation and oxygenated products.

Introduction

Oxidation of hydrocarbons by molecular oxygen is a key process in the chemical industry. Small, partially oxygenated hydrocarbons are used as building blocks in the manufacture of plastics and synthetic fibers. Many oxygenates play a role as intermediates in the synthesis of fine chemicals. But reactions that use O₂ as the primary oxidant often produce a large amount of unwanted byproducts. In particular, autoxidation of small alkanes, alkenes, or aromatics is inherently unselective, whether conducted in the gas or liquid phase or catalyzed by transition.^{1–4} Current processes for the production of these highly desired oxygenates involve stringent conditions which may include high temperatures and pressures, strong acids, free radicals (halogenated starting materials), and/or corrosive oxidants. Most of the current processes used have low energy efficiencies and selectivities as well as generate environmentally hazardous waste and byproducts. One major reason that selectivities are low is that the desired products (such as carbonyls or alcohols) are more easily oxidizable by O₂ than the parent hydrocarbon. Over-oxidation can be minimized only by keeping conversions low, a serious disadvantage from a chemical processing standpoint. Therefore, a major challenge in this field is to find reaction pathways that afford the primary product with high selectivity at high conversion of the hydrocarbon. In addition to low conversions and poor selectivities, heterogeneous oxidation could involve diffusion and mass-transfer problems.¹ The problem of product separation could also be critical.

Selective oxidation of organic compounds in supercritical fluid solvents at mild conditions as a means for direct synthesis of valuable oxygenates has become of considerable importance. The objective of our project is to assess the potential benefit of the replacement of organic solvents traditionally used in heterogeneous

catalysis with environmentally benign supercritical fluids, by identifying a list of the top processes that provide opportunities for pollution prevention. This research focuses on development of synthetically useful reactions as an alternative for existing methodology that uses undesirable toxic solvents. In particular, we are focusing on oxidation reactions because of the high toxicity of the reagents (stiochiometric oxidants) and the wide range of potential applications. The metal–oxo catalyst used was a biomimetic complex that contains ligand and metal centers that have high oxidation potentials and possess multiple oxidation states. The activation of these inorganic metal precursors using molecular oxygen (clean oxidant) generates high valent metal–oxo species capable of activating the inert saturated hydrocarbon. These metallo-oxidants (green oxidants) are being investigated for their ability to effectively and selectively oxidize alkanes in SC-CO₂ into their corresponding oxygenates at temperatures < 80 °C and pressure < 22 MPa. In addition, the activity and selectivity were compared with those of other conventional metal catalysts.

The success of chemical synthesis depends on the ability of chemists to devise and use catalysts and reagents that will affect reactions selectively, both as to the specific atom attacked and as to the stereochemical outcome of the process. Clearly the best approach is to develop processes with very high single-pass yields. Often this is not possible, and therefore, byproducts and waste products are formed. Although, the usefulness of supercritical fluids for extraction, as cleaning solvents, and for analytical methodologies has been well established, their use for reactions and other processes is a far less explored area of research. Solvent properties have a pivotal role in controlling the course and rate of chemical reactions.^{5–9} Supercritical fluids have the advantage of varying solvent properties, for example, with changes in pressure, especially near the mixture critical point. Thus, it is important to understand how they can influence the reaction rate, conversion, and reaction pathways. The change of properties of supercritical fluids with pressure and temperature can be

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expected to direct chemical pathways and influence reaction rates, which can result in fast and selective reactions. Many reactions in SCF solvents have been reported.^{10,11} The use of a supercritical fluid medium for catalytic^{12–15} and noncatalytic reactions^{16–23} has successfully been demonstrated. SC carbon dioxide has proven to be a workable, and in some cases superior, solvent for polymerizations,^{24–28} electrophilic reactions,^{29,30} enzymatic transformation,^{31–35} and other reactions.^{36–38}

Heterogeneous catalysis is a particularly promising area for SC-CO₂ in terms of economics, selective gains, and ease of catalyst separation. An increase in reaction rates in the SCF phase may be due to efficient production of free radicals at lower viscosities and their enhanced rate of diffusion as compared to diffusion in the liquid phase. Reaction rates are generally slow for solid-catalyzed reactions of liquids due to mass-transfer limitations in the catalyst pores or from the liquid to the catalyst. Using a supercritical fluid medium, some of the diffusion-controlled heterogeneous reactions can be carried out homogeneously by dissolving both the reactant and catalyst in a single fluid phase. It is also possible to devise a suitable reaction-separation scheme to improve the selectivity to the desired product. One of the main problems in solid-catalyzed gas-phase reactions is the fouling of the catalyst through coke formation. This problem could be minimized if SCFs are used for the reaction medium.

Selective Oxidation in SC-CO₂

The use of catalytic oxidation has significant industrial importance in the United States, where more than 31% of the catalytic production of organic chemicals corresponds to oxidation catalysis. In the conventional process, these free radical reactions are carried out in the liquid phase with either air or oxygen as the coreactant. The reactions are in general autocatalytic, and a catalyst only helps in reducing the induction period. Various catalysts have been used for selective oxidations of different substrates in SC-CO₂, including cumene,^{20,23} cyclohexane,^{39,40} sulfur,⁴¹ Pd(II) for methyl acrylate,⁴² [Fe(TFPP)Cl] and IER for cyclohexene,^{43,44} molybdenum hexacarbonyl for alkenes,⁴⁵ and Pt/TiO₂ for ethanol and acetaldehyde.

Reactions of catalytic oxidation can be divided into two categories:⁴⁷ (1) electrophilic oxidation, proceeding through the activation of oxygen, such as the addition of oxygen to the double bond, resulting in the formation of epoxides, or the oxyhydration of the double bond to form respective saturated ketones (The end-products of total oxidation are CO₂ and H₂O.) and (2) nucleophilic oxidation, in which activation of the hydrocarbon molecule is the first step, followed by consecutive steps of nucleophilic oxygen addition and hydrogen abstraction. Examples of nucleophilic oxidation are the abstraction of hydrogen in the process of oxidative dehydrogenation of alkenes to dienes or the dehydrodimerization of dehydrocyclization.

Catalytic properties of oxidation reactions involve a redox mechanism between reactant molecules and surface active sites, as represented in the schematic in Figure 1.⁴⁸ Such a scheme necessitates a catalyst that contains a redox couple (e.g. transition metal ions) and that exhibits high electrical conductivity to favor electron transfer and a high lattice oxygen anion mobility within the material to ensure the reoxidation of the

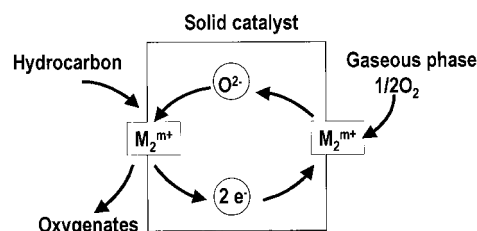


Figure 1. Schematic of the Mars and van Krevelen mechanism.

reduced catalyst. The catalyst has two active sites in order for this mechanism to work: a site which oxidizes the substrate and another site for oxygen reduction. According to this mechanism, the substrate is oxidized by the solid and not directly by molecular oxygen of the gaseous phase. The role of such dioxygen is to regenerate or maintain the oxidized state of the catalyst. The oxygen introduced in the substrate stems from the lattice. Oxygen is reported to be a better free radical initiator in the SC phase.⁴⁷

The use of metal complexes for oxidation of organic substrates is a subject of intensive research. The synthesis, reactivity, and electrochemical properties of a large number of ruthenium complexes have been extensively studied.^{49–53} The reactivity of oxygen is governed by its preference to react as a two-electron oxidant rather than a one-electron oxidant.^{54,55} There has been extensive work done on the oxidation of alkenes and alkanes with dioxygen and hydrogen peroxide.

Using the ideology of the previously described heme and non-heme catalysts, it was the goal of this research to develop a robust catalytic system capable of oxidizing hydrocarbons with hydrogen peroxide or dioxygen under relatively mild conditions (> 150 °C and 100 atm) while maintaining environmental stewardship. The catalysts are designed to be simple and are based on enzymes and proteins found in the human body and nature. These biomimetic complexes “mimic” the reactive center of enzymes and eliminate the ancillary portions normally found on an enzyme or protein. These novel catalysts are comprised of two important components, the ligand system and the metal center. The ligand systems (polypyridyl) are designed to be simple, robust, rigid, tunable, and oxidatively resistant as well as to utilize nontoxic elements: N, O, H, C, S, and P. The metal centers are chosen for their ability to maintain large oxidation potentials, possess multiple oxidation states, and have no or minimal toxicity. When the two portions are combined, a robust inorganic catalytic precursor results.

The objective of this work was to study heterogeneous catalytic oxidation of alkanes and alkenes in supercritical carbon dioxide to synthesize the respective aldehydes, ketones, and epoxides at mild conditions. The effectiveness of both conventional and new green oxidation catalysts was tested. The effects of temperature, reaction time, and oxygen concentration on the yield and selectivity were investigated.

Experimental Section

Materials and Methods. Two types of catalyst were used for this study. The first type was two noble metal catalysts (0.5% Pd/ γ -Al₂O₃ and 0.5% Pt/ γ -Al₂O₃) obtained from Engelhard Corporation. The catalysts had a nominal BET surface area of 100 m²/g. The second

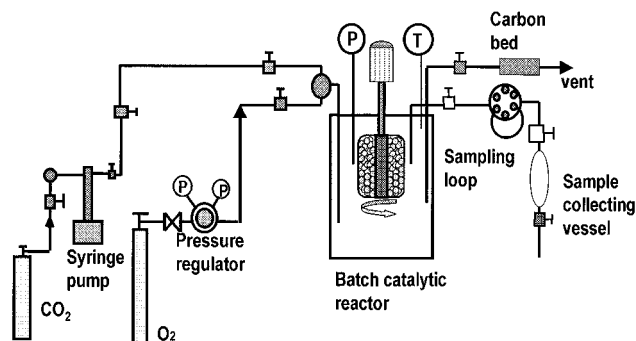


Figure 2. Schematic of the experimental apparatus.

type of catalyst was $\{cis-[Fe(dmp)_2(H_2O)_2](CF_3SO_3)_2\}$, where $dmp = 2,9$ -dimethyl-1,10-phenanthroline. The raw materials for synthesizing the metal-oxo catalyst, $FeCl_2 \cdot 4H_2O$, 2,9-dimethyl-1,10-phenanthroline, $NaCF_3SO_3$, and $LiCl$, were received from Aldrich. The substrates, other reagents (acetonitrile, acetone), and 30% hydrogen peroxide (aqueous) were all used as received from Fisher Scientific (ACS Grade). Acetonitrile was distilled over P_2O_5 and stored over 4 Å molecular sieves.

Synthesis of Catalyst. The catalyst cis -iron(II)bis(aquo)bis(2,9-dimethyl-1,10-phenanthroline)bis(trifluoromethanesulfonate), $\{cis-[Fe(dmp)_2(H_2O)_2](CF_3SO_3)_2\}$, was synthesized using a modification of a prior method.⁵⁶ 2,9-Dimethyl-1,10-phenanthroline (4.5 g, 24 mmol) was added to 150 mL of deionized H_2O at 90 °C and allowed to stir vigorously for 20 min under nitrogen. Upon complete dissolution of the ligand, 2.5 g (12 mmol) of $FeCl_2 \cdot 4H_2O$ was added, and the resulting solution was then stirred for 2 h. The solution was then filtered (hot), and the filtrate was immediately added dropwise to a chilled saturated $NaCF_3SO_3(aq)$ solution (25 mL of $H_2O/9$ g of $NaCF_3SO_3$). The resulting precipitate was allowed to stand in ice for 2 h and was filtered. The product was dried under vacuum at 60 °C overnight.

Batch Experiment. Isothermal oxidation reactions were conducted using a 500 mL stainless steel batch reactor from Pressure Products Industries (FC series). Due to the difficulty of achieving constant temperatures because of the lower surface-to-volume ratio, studies were conducted at low concentrations to achieve an adequate approach to isothermal operation. Solid-supported catalysts loaded in a spinning dynamic basket (Pressure Products Inc.) were used (Figure 2). The supported catalyst was loaded in the dynamic basket followed by a known amount of substrate (10 mL). The temperature of the reactor was monitored and controlled using a PID controller. The reactor was then filled with a known amount of oxygen based on the set pressure. When the reactor reached the set temperature, a syringe pump (ISCO, LC-260), with the jacket kept at 4 °C, was used to pump liquid CO_2 and bring the reactor to the required set pressure. The intense stirring of the basket was intended to remove all bulk mass-transfer effects and to ensure that the experiments only measured kinetic effects. Repeated sampling of the product formation was done using a six-port heated manual Valco valve to monitor the course of the reaction. Spinning catalyst in a basket removed mass-transfer problems and increased heat transfer from the catalyst. With such a system the effects of both mass and particle size on reaction rate and pore diffusion were studied. Experiments were conducted at the temperatures 60 and 100 °C (± 4 °C), a pressure of 207 bar (± 9 bar), a density of

0.497 or 0.735 g/mL, a reaction time of 3–18 h (± 0.1 h), a basket speed of 600 rpm (± 15 rpm), and a O_2 /substrate ratio of 0.57–2.86 mole ratio. Conversions were calculated according to the following method:

$$\gamma_i = (M_{i,feed} - M_{i,notconverted})/M_{i,feed} \quad (1)$$

where γ_i is conversion of component i and M_i is moles of component i .

Sample Analysis. For product formation analysis, gas and liquid samples were collected and analyzed using a Hewlett-Packard gas chromatograph (GC) equipped with a mass selective detector (6890/5973). This instrument enabled both qualitative and quantitative characterization. A quadrupole mass filter detector generated the ions via electron impact ionization corresponding to an electron energy of 70 eV. Separation of products was achieved with a HP-capillary column (HP-5 30 m \times 0.25 mm \times 0.25 mm) with a split/splitless heated injection port. An injection size of 1.0 μ L with three repetitive injections for reproducibility was the norm. Collected gas samples were kept in an 80 °C oven before analysis to prevent condensation. A 1.0 mL gas syringe was used to sample from the gas container for direct injection to the GC. At the end of each run the reactor was cooled to 12 °C and the CO_2 was vented out and the remaining liquid samples were collected for GC analysis. Formations of mono- or diacids were qualitatively analyzed with an LC/MS (Finnigan LCQ MS/DS Bundle). Quantitative analysis of reactants and products was obtained by analyzing response factors of known quantities.

Results and Discussion

Catalyst Development and Synthesis. Iron-containing complexes including heme and non-heme enzymes are reported to effectively oxidize alkenes and alkanes under a variety of conditions.^{57–59} The development of a catalytic system to mimic a variety of biological systems has been the subject of intense investigation. Cytochrome P-450,⁶⁰ peroxidases, catalases, and high-valent iron-oxo porphyrin complexes, all involving a two-electron oxidation, produce a reactive intermediate necessary for hydrocarbon oxidation.^{61,62}

The use of iron porphyrins as model catalysts has allowed for further understanding of the significant steps involved in many enzymatic oxidation reaction mechanisms.⁶³ More recently, Machii et al.⁵⁷ demonstrated the use of a $(TMP)Fe^{III}(RCO_2)$, where TMP is 5,10,15,20-tetramesitylporphyrin, complex for the epoxidation of norbornene and α -methylstyrene at -78 °C with a variety of peracids. This research has suggested the $O=Fe^{IV}(TMP) \pi$ -cation radical as being the active oxidant for the epoxidation reaction.

Catalysts based on iron complexes in the absence of porphyrins have also been investigated. Leising et al.⁵⁹ demonstrated the reactivity of (μ -oxo) diferric complexes with t -BuOOH for the activation of cyclic hydrocarbons in acetonitrile. The μ -oxo diferric complex was synthesized in an effort to model the dinuclear sites found in non-heme iron enzymes. The $[Fe(TPA)_2O(OAc)](ClO_3)_3$, where TPA is tris(2-pyridyl)methylamine and OAc is acetate, complex is a robust catalyst for the activation of cyclohexane under ambient temperature and pressure. The oxidation products produced include cyclohexanol, cyclohexanone, and (*tert*-butylperoxy)-cyclohexane. Leising et al. suggested that the formation

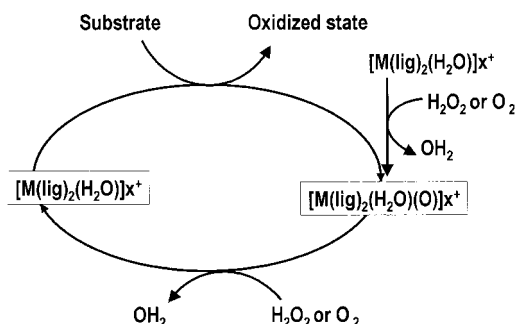


Figure 3. Desired reaction pathway for the oxidation of hydrocarbons.

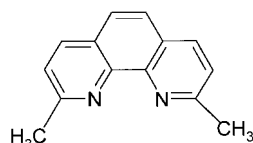


Figure 4. Structure of 2,9-dimethyl-1,10-phenanthroline.

of the alcohol and ketone occurs by catalyst-initiated decomposition of *t*-BuOOH to afford a high-valent metal-oxo complex via a heterolytic pathway. Additional research presented by Shu et al.⁶⁴ was directed toward the further investigation of these non-heme iron centers. Furthermore, Que proposed a high-valent $\text{Fe}_2-(\mu\text{-O})_2$ diamond core structure, which is believed to be the key oxidizing species of methane monooxygenase (MMO). Further research using iron-coordinated ligand type complexes has also been reported. Hague and Sawyer⁵⁷ have reported a number of iron(II) complexes $[\text{Fe}^{\text{II}}\text{L}_x]$: $\text{Fe}(\text{DPAH})_2$, where DPAH_2 is 2,6-dicarboxylpyridine, $\text{Fe}^{\text{II}}(\text{PA})_2$, where PA is picolinic acid, and $\text{Fe}^{\text{II}}(\text{bpy})^{2+}$, where bpy is 2,2'-bipyridine. Each of these complexes with the addition of a reductant, $[\text{DH}_2]$: PhNHNHPh for example, is able to catalytically activate O_2 (1 atm) for the hydroxylation of phenol and substituted phenol. Results provided indicate the mechanism of oxidation proceeds via a Fenton like intermediate.

Activation of the catalyst precursor occurs upon addition of hydrogen peroxide and/or molecular oxygen (clean oxidants) to generate a high-valent metal-oxo species. These catalytic metallo-oxidants or green oxidants are able to effectively and selectively oxidize a multitude of organic substrates (e.g. alkanes and alkenes) into their corresponding oxygenates at low temperatures ($<150^\circ\text{C}$) and pressures ($<2\text{--}100\text{ atm}$). Figure 3 demonstrates the desired catalytic oxidation reaction pathway.

The synthesis of an iron "analogue" based on the *cis*- $[\text{Ru}(\text{dmp})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ ⁶⁴ complex is the focus of this research. By altering the metal center, it is anticipated a more robust and efficient catalyst will result. The ligand was not altered due to its ability to impart *cis* geometry,⁶⁴ with respect to the two remaining coordination sites, when the metal is coordinated by two dmp, where dmp is 2,9-dimethyl-1,10-phenanthroline, ligands (Figure 4). This geometry, the result of steric hindrance created by the methyl groups α to the nitrogen atoms, results in the *cis* isomer being a more powerful oxidant when compared to the *trans* counterpart.^{65,66} The lesser oxidizing power of the *trans* isomer, measured to be on the order of 35 kcal mol^{-1} , is attributed to the lower energy of the HOMO d_{xy} .⁶³ Additional benefits of this ligand include its ability to prevent the condensation

of hydroxo- or oxo-bridged dinuclear species when two ligands are present on the metal center, thus decreasing the catalyst effectiveness.

The approach taken in this research was to develop a catalyst that possesses properties pertaining to either metal-oxo formation via oxygen or metal-oxo formation via peroxides. This developed catalyst could also possess a mechanism of regeneration with dioxygen to generate a high-valent metal-oxo complex, necessary for alkane oxidation.⁵⁴ The catalyst must also be able to perform the key step, generation of a strongly oxidizing high-valent metal center.⁵⁵

The desired reaction pathway, illustrated in Figure 3, exhibits the need for a metal center, which can be activated by hydrogen peroxide or molecular oxygen to form the mono-oxo species. This activated complex may be a powerful enough oxidant to activate the substrate or be further oxidized by hydrogen peroxide or dioxygen to generate a di-oxo species, a complex with greater oxidizing strength than the mono-oxo species. However, the formation of the di-oxo species is dependent on the metal center. Upon delivery of its one or two oxygen atoms, the reduced metal center could be reoxidized by hydrogen peroxide or oxygen to regenerate the mono- or di-oxo species, thereby closing the catalytic cycle.

Two control runs were conducted to determine whether oxidation can occur with dioxygen alone and if the metal-oxo complex has catalytic activity without activation with H_2O_2 . No product formations were observed after a 5 h run. The oxidation of many organic molecules, including saturated hydrocarbons, by metal-oxo catalyst is thermodynamically allowed in the presence of oxygen at low temperatures (Table 1). These catalysts have been promising for oxidation of alkanes and epoxidation of small olefins. The homolytic pathway is desired for activation of the metal center dioxygen or hydrogen peroxide. This pathway normally involves the following transition metal couples: $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$, $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{V}}$, $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$, $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$, $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$, and $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$.⁵⁵ Characteristics of this reaction include the production of a free radical intermediate, oxidation occurring in the outer-sphere via bimolecular steps, and noncoordination of the substrate.






Catalytic oxidation of various feed substrates (using a *cis*- $[\text{Fe}(\text{dmp})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ complex) was made at 207 bar CO_2 and 100°C using oxygen as an oxidant in a batch reactor. Reactions were run for a period of 6–18 h in a stirred reactor. The results of these runs are shown in Table 2. Partial oxidation of alkanes and alkenes to ketones, alcohols and aldehydes, and acetates was shown to be effective in SC-CO_2 .

Cyclohexene was chosen as a model compound because it showed higher conversions than the alkanes tested. Cyclohexene is widely used as a molecular probe in studies involving catalyst preparation and assessment.^{67,68} The possibility of radical oxidation and epoxidation makes it an interesting compound to study selective reaction in SC-CO_2 . We found three major allylic oxidation products of cyclohexene, (I) 2-cyclohexene-1-ol, (II) 2-cyclohexene-1-one, (III) 4-hydroxy-2-cyclohexene-1-one, and two epoxidation products, (IV) cyclohexene oxide and (V) 7-oxybicyclo[4.1.0]heptan-2-one (Table 3). The alcohol is derived from radical oxidation, whereas products III, IV, and V are higher oxidation products. Although a small amount of products IV and V was detected, showing that the catalyst supports epoxidation, there was very little cyclohexene oxide detected.

Table 1. Experimental Conditions and Results of Oxidation of Hydrocarbons in SC-CO₂ Solvent with the *cis*-[Fe(dmp)₂(H₂O)₂] (CF₃SO₃)₂ Complex as a Catalyst






substrate	oxidant/ pressure (bar)	total pressure (bar)	temp (°C)	reaction time (h)	products
cyclohexene	O ₂ /2.7	207	100	8	2-cyclohexene-1-ol 2-cyclohexene-1-one
1-octene	O ₂ /2.7	207	100	7	1-octene-3-one 2-octenal
toluene	Air/6.2	207	100	8	benzaldehyde
cyclohexane	O ₂ /2.7	207	100		cyclohexanol cyclohexanone
ethanol	O ₂ /2.7	207	100	7	ethyl acetate

Table 2. Cyclohexene Oxidation in SC-CO₂ with *cis*-[Fe(dmp)₂(H₂O)₂](CF₃SO₃)₂ Complex

Run	Reaction Conditions (°C/hr/bar- O ₂)	%Product					Substrate Conversion (%)	Turn Over number*
								
1	100 / 6 / 5.5	34.7	58.4	0.0	5.4	1.4	3.98	96.8
2	100 / 6 / 13.8	37.2	59.5	0.1	3.3	-	3.36	80.7
3	100 / 6 / 27.6	31.2	63.0	0.0	2.2	3.6	1.42	36.3
4	100 / 12 / 5.5	35.7	60.7	0.0	0.3	3.2	2.79	70.1
5	100 / 18 / 5.5	24.6	75.4	0.0	0.0	0.0	0.52	13.9
6	60 / 6 / 5.5	30.6	62.0	0.0	4.3	3.1	2.33	59.1
7	100/12/200	25.6	71.3	0.1	0.4	2.7	2.06	55.2

* Turnover counts ketone as 2 and oxabicyclo[4.1.0]heptan-2-one and hydroxyl-cyclohexane-1-one as 3 each, assuming that the reaction follows progressive oxidation.

Table 3. Effects of Catalyst on Cyclohexene Oxidation in SC-CO₂

Catalyst	O ₂ Bar / °C	% Conversion	% Products				
							
0.5% Pd on γ-Al ₂ O ₃	4.8/100	0.43	5.2	15.1	2.5	39.5	37.6
0.5% Pt on γ-Al ₂ O ₃	4.8/100	0.17	16.4	19.6	3.5	55.2	5.21

This product composition was different from that of other studies of liquid-phase oxidation of cyclohexane on a palladium catalyst, which showed large amounts of dehydrogenation and disproportionation products,⁶⁹ or in SC-CO₂ using a homogeneous chlorinated metal-porphyrin catalyst.⁴² The turnover number, number of moles of oxidation per mole of catalyst, was calculated as TON = {I + IV + 2(II) + 3(III + IV)} per mole of catalyst, to account for the multiple oxidation products II, III, and IV.

These initial experiments indicate that the concentration of oxygen is a more significant process variable than reaction time and temperature. Longer reaction periods gave a lower yield, indicating the possibility of overoxidation to CO₂. Increasing temperature from 60 to 100 °C resulted in an increase in product formation, although the increase was not significant.

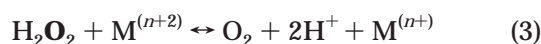
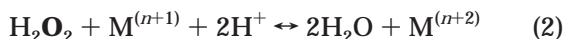
Selectivity. Catalytic oxidation of a hydrocarbon molecule requires finding a compromise between many opposing factors, which include the thermodynamics, the kinetics, and the effects of the catalyst on multiple-pathway consecutive reactions.⁴⁷ Thermodynamics favors the ultimate formation of carbon dioxide and water; therefore, all partial oxidation products are intermedi-

ates derived by kinetics control of the reaction. The hydrocarbon-oxygen mixture can react along many different pathways in the network of competing and consecutive reactions, and therefore the catalyst must strictly control their relative rates, accelerating the sequence of steps leading to the desired products and hindering formation of unwanted byproducts. The C-H bonds in the initial reactants are usually stronger than those in the intermediate products, which makes these intermediates prone to rapid further oxidation. All oxidation reactions are strongly exothermic, and efficient heat removal must be secured to control the temperature and prevent overoxidation as well as catalyst damage. For the oxidation of cyclohexene, the metal-oxo catalyst favored the formation of ketone, in a 2:1 ratio over that of the alcohol. There were few epoxidation products (Table 2). Oxidation of cyclohexene over Pd and Pt/Al₂O₃ catalysts resulted in a mixture of dehydrogenation and oxygenated products.

The hydrogen abstraction or "rebound" mechanism produces an alkyl free radical. The free radical produced in the first step of the mechanism is the result of the *cis*-{M(O)₂}²⁺ (when M = Ru) or {M(O)}²⁺ (when M = Fe) moiety abstracting a hydrogen atom from the alkane

to produce a reduced metal-hydroxide species. The active metal center, $M^{(x+2)}=O$ functions as a free radical which is capable of abstracting a hydrogen atom from the hydrocarbon. The second step proceeds with the transfer of the hydroxyl ligand to the formed radical to yield the hydroxylated product. The catalytic cycle involves regeneration of the high-valent metal center by oxidation with O_2 or H_2O_2 .

In peroxide activation the hydrogen peroxide can act as both a reductant and an oxidant, as shown in eqs 2 and 3.



Peroxide reduction and metal oxidation, eq 2, are involved in substrate oxidation by a high-valent metal-centered oxidant mechanism.^{54,55} The metal undergoes the two-electron change shown in eq 2, but the product is an oxo-metal complex. Catalysis (or peroxide activation) by the metal complex occurs when the oxidized metal complex, peroxo-metal, or oxo-metal species is kinetically more reactive than peroxide in the oxidation of substrate. In addition, depending on the potentials, the oxidized complex may oxidize H_2O_2 as shown in eq 3.

Conclusion

The results presented above have demonstrated the effectiveness of the use of a metal-oxo catalyst to oxidize cyclohexene in SC- CO_2 . Although the reaction conditions were not optimized, the conversions and selectivities measured were encouraging. The turnover numbers are anticipated to improve when process conditions are optimized. Ruthenium-based catalysts have been shown to catalyze epoxidation and cleavage of alkenes with dioxygen and hydrogen peroxide.⁶⁶ However, these catalysts were not tested in SC- CO_2 . More work is being conducted to enhance the selectivity of the catalyst and develop more active catalysts that are not iron based.

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