Catalytic Conversion of Light Alkanes -- Proof of Concept Stage

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CONTRACT INFORMATION

Contract Number	DE-FC21-90MC26029
Contractor	Sun Company, Inc. Research and Development Department P.O. Box 1135 Marcus Hook, PA 19061 (610) 859-1731
Contractor Business Manager	Allen W. Hancock
Principal Investigator	James E. Lyons
METC Project Manager	Rodney D. Malone
Period of Performance	November 1, 1993 to October 31, 1994
Schedule and Milestones	

N D J F M A M J J A S O

Phase IV C₁-C₄ Research

- Synthesize 2nd Generation Cat.
- Design and Synth. 3rd Gen. Cat.
- Test 2nd and 3rd Gen. Cat. for C₁-C₄ activity

---(complete)
----- (complete)
----- (complete)

Phase V Process Dev. i-C₄ -->TBA

- Determine Commercial Targets
- Achieve for One-Step Route
- Achieve for Two-Step Route

----- (complete)

----- (complete)

Phase VI C₁-C₃ Research

- Modify 3rd Gen. Cat for C₃
- Test 3rd Gen. Cat for C₃ ox
- Design More Active Catalyst
- Synthesize Family of MAC's

-/-

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MASTER

OBJECTIVES

The objective of the work presented in this paper is to develop new, efficient catalysts for the selective transformation of the light alkanes in natural gas to alcohols for use as liquid transportation fuels, fuel precursors and chemical products. There currently exists no direct catalytic air-oxidation process to convert these substrates to alcohols. Such a one-step route would represent superior useful technology for the utilization of natural gas and similar refinery-derived light hydrocarbon streams. Processes for converting natural gas or its components (methane, ethane, propane and the butanes) to alcohols for use as motor fuels, fuel additives or fuel precursors would not only add a valuable alternative to crude oil but would produce a clean-burning, high octane oxygenate which would be a major component of reformulated gasoline (RFG).

BACKGROUND INFORMATION

Natural gas is an abundant resource that can provide an inexpensive feedstock for production of C_1 - C_4 alcohols. The low molecular weight alcohols, methanol, ethanol, isopropyl alcohol and tert-butyl alcohol have seen application both as alternative fuels and in reformulated gasoline. The ethers that are made from these alcohols: methyl-tert-butyl ether, MTBE, ethyl-tert-butyl ether, ETBE, diisopropyl ether, DIPE, and tert-amyl methyl ether, TAME, are major oxygenate components of RFG. These oxygenates have high blending value octane numbers, BVON, and good gasoline properties. Of these, MTBE has seen the most widespread use and the most rapid growth in RFG.

Working with ideas generated from recent

understanding of biological systems responsible for enzymatic oxidations, Sun has developed a number of new catalyst systems for the direct oxidation of light alkanes to alcohol-rich oxygenate mixtures (1-40). The relative ease of oxidation of natural gas components with our catalyst systems has been found to be: isobutane>propane>ethane>methane. For this reason, the first oxidation reaction to reach the proof-of-concept stage was the oxidation of isobutane to TBA. TBA has been used as a high-octane fuel component and is the major precursor to MTBE. MTBE has excellent fuel properties. Among these are the apparent reduction of CO emissions from automotive exhaust. MTBE is currently the oxygenate of choice for RFG.

Field butanes have historically found a large number of liquid fuel precursor applications. Traditionally, this C_4 component was blended into gasoline for octane and vapor pressure. Light hydrocarbons, however, whether from natural gas or petroleum refining are rejected in large part from the gasoline pool in response to environmental regulations of vapor pressure emissions. After isomerization, the isobutane can be dehydrogenated to isobutylene which is a precursor to alkylate and MTBE - both high octane, clean-burning RFG components. Dehydrogenation is costly, however. Direct oxidation of isobutane to TBA is a way to avoid this expensive process step. The TBA produced is a viable high octane fuel oxygenate and a precursor to MTBE as well. Sun catalytic technology, therefore is able to convert a C_4 stream into a fuel oxygenate without requiring a costly dehydrogenation step.

Thus, in summary, the direct reaction of a light alkane with air or oxygen to give an alcohol-rich oxidate would: a) utilize an inexpensive feedstock unacceptable for liquid transportation fuel use, b) produce a material that would have superior gasoline performance properties such as driveability and high octane, and c) produce a clean-burning

alternative to conventional gasoline for use in areas that fail to meet air quality standards.

PROJECT DESCRIPTION

During the stage at which this work ended, our program consisted of two phases which were running concurrently, a research phase and a proof-of-concept phase. The function of the research phase is to design synthesize and perform laboratory tests on new materials in order to enhance the catalytic properties of the suprabiotic systems generated in our laboratories. Increases in catalytic activity and process selectivity as well as extensions of structure-activity relationships are examined. The research phase is intended to provide the process development phases with catalysts having superior properties for light alkane oxidation. The second concurrent phase, is the proof-of-concept phase. In this phase process development of oxidations which have succeeded in the research phase are carried out in a pre-pilot PDU. At the conclusion of the cooperative agreement we were developing a process for the conversion of isobutane to TBA. We have identified two routes for this transformation: a one-step route directly from isobutane to TBA, and a two-step route in which the isobutane is oxidized first to tert-butyl hydroperoxide and then transformed into TBA catalytically. This paper will present the results of these activities.

RESULTS

One Step Oxidation of Isobutane to TBA.

There are currently no efficient catalysts for the direct oxidation of isobutane to TBA, eq. 1. Cobalt salts and complexes have been used

(41) but in order to achieve good rates, high catalyst concentrations are needed as well as high temperature. Under these conditions poor selectivity is achieved. In the research phase of our work we have designed, synthesized, and tested a family of metal complexes that are very effective catalysts for the selective low temperature oxidation of isobutane to TBA. These catalysts, the perhaloporphyrinatometal complexes, were designed based on biomimetic considerations. The halogen ligands on the periphery of the porphyrin ring withdraw electrons from the metal center, increase the M(III)/M(II) reduction potential and enhance the alkane oxidation activity. We have further shown that iron perhaloporphyrins have the greatest activity of any of the metalloporphyrins studied. Figure 1 shows that as the degree of electron withdrawal (number of halogens on the porphyrin macrocycle) increases, the reduction potential of a series of iron porphyrin complexes increases and the activity of the catalysts steadily increases. Table 1 shows that these perhaloporphyrin catalysts are effective soluble catalysts in neat isobutane and give unprecedented rates and selectivities for converting isobutane to TBA.

The same iron perhaloporphyrin complexes that were found to be effective for the direct oxidation of isobutane to TBA were also shown to be excellent catalysts for the decomposition of t-butylhydroperoxide, TBHP, to TBA, Figure 2, Table 2. Again, perhaloporphyrin complexes were over an order of magnitude more active than previously known catalysts. The same relationship was found between Fe(III)/Fe(II) reduction potential as in the direct oxidation reaction, Table 3. Since TBHP is made commercially by non-catalytic oxidation of isobutane (42), our work suggested the possibility of a competitive two-step route from isobutane to TBA, eq. 2, 3.

Figure 1. Catalyst Activity vs. Redox Potential

Figure 2. TBA from TBHP

Table 1. Iron Haloporphyrin - Catalyzed Isobutane Oxidation

Catalyst	T. °C	T. Hrs	Charge to Reactor		Conversion	Select	
			$i-C_4H_{10}$	O_2	$i-C_4H_{10}\%$	TBA % ^b	TON ^c
$Fe(TPPF_{20}-\beta-Br_8)Cl$	80	3	1870	53	17	87	10,660
	80	3	1862	100	28	83	17,150
	80	3	1865	47	14	91	8,420
	25	71.5	1862	53	22	92	13,560
$Fe(TPPF_{20})OH$	24	143	1871	53	18	95	12,150

^a Isobutane oxidized by an oxygen - containing gas (75 ATM, diluent = N_2), liq. phase (180 ml), 3 hours. O_2 added as used

^b (Moles TBA/mols liquid product) x 100

^c Models (TBA + acetone) produced/mole catalyst used

Table 2. Conversion of TBHP to TBA

<u>Catalyst</u>	<u>Time Hours</u>	<u>t-BuO₂H</u>	<u>Product, Molar Sel., %</u>		
		<u>Conv., %</u>	<u>t-BuOH</u>	<u>(t-BuO)₂</u>	<u>(CH₃)₂CO</u>
Fe(ACAC) ₃	2.3	<5	67	tr	32
Fe(TPP)Cl	1.9	27	82	7	11
Fe(TPPF ₂₀)Cl	3.3	72	87	10	3
Fe(TPPF ₂₀ β-Br ₈)Cl	1.9	95	90	8	2
Fe(TPPF ₂₀ β-Cl ₈)Cl	3.3	100	90	8	2

^a The catalyst, 2 x 10⁻⁴ mmoles, in 2.4 ml p-xylene was rapidly added to a stirred solution of 10 ml t-BuO₂H (90%) in 48 mls benzene. O₂ evolved was measured manometrically and liquid samples taken periodically and analyzed by standardized gc

Table 3. Electron Affinity Reduction Potential and Catalytic Activity

<u>Species</u>	<u>EA (eV)</u>	<u>E_{1/2} (V) vs. SCE</u>	<u>TO iC₄-ox^a</u>	<u>TBA⁻Yield_b TBHP-dec</u>
Fe(TPP)Cl	2.15	-.29	0	4.8
Fe(TPPF ₂₀)Cl	3.14	+.08	1160	16.0
Fe(TPPF ₂₀ βCl ₈)Cl	3.35	+.29	1800	67.2

^a Moles O₂ taken up in 60°C oxidations of isobutane after 6 hours

^b Yield of TBA from TBHP decomposition in 0.5 hours

Since both of these reactions work so well, we determined to proceed with evaluating the concept of potentially commercial routes from isobutane to TBA using both the one-step and the two-step processes. Together with a joint R&D partner we set proprietary hypothetical

commercial targets for each process. The concept was proven, therefore, if our catalytic processes met these criteria. We first examined the direct one-step oxidation route. Our process concept is shown schematically in Figure 3. Using our best perhaloporphyrin complex as a catalyst we met all targets except that of catalyst cost. Efforts using new catalysts with lower costs failed to meet rate and selectivity targets. Efforts to lower the cost of manufacture of the

Figure 3. Isobutane Oxidation - One Step Process

perhaloporphyrin complexes failed to achieve costs that were even close to what was needed. When the project ended we had found a way to make the inexpensive, first row metals including iron, far more active for oxidation of an alkane, than had ever been observed. How to do this with a low-cost ligand system is the one remaining technical problem with the one-step route.

Figure 4 shows a schematic flow diagram of the proposed two step process for manufacture of TBA. Catalyst cost again was a problem for the iron perhaloporphyrins. In this case, however we were able to find proprietary new catalyst systems that met the catalyst cost criterion. At the conclusion of the cooperative agreement we had met or exceeded all of the performance criteria for a two-step process. Table 4 summarizes our progress vs goals up until the end of the project in October, 1994.

CONCLUSIONS

During the period of the cooperative agreement we have uncovered a family of catalysts which have shown unprecedented activity for the oxidation of alkanes to alcohol-rich oxidates. These catalysts have a ligand system which confers unusually high oxidation activity to inexpensive first row transition metals, especially iron. If less expensive analogs can be produced, they should ultimately have great practical value in converting natural gas components to fuel oxygenates. Isobutane can be converted to TBA in excellent selectivity at acceptable rates for a practical process if catalyst cost can be lowered. In the case of the conversion of isobutane to TBA we have found a two step route through the hydroperoxide that could have value in a retrofit of an existing plant.

Figure 4. Isobutane Oxidation - Two Step Process

Table 4. Isobutane to TBA - Proof -of-Concept Criteria For New Retrofit Process

Process Mode 2

Rate:	Proprietary	(Achieved)
Catalyst cost:	<\$100/lb	(Achieved)
TBA selectivity:	≥85%	(Achieved)
(2) Conversion:	99%	(Achieved)

Process Mode 1

Rate:	Proprietary	(Achieved)
Catalyst cost:	5¢/gal. TBA	(Not achieved)
TBA selectivity:	≥85%	(Achieved)
Conversion:	50%	(Achieved)

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