Bimetallic Catalysts for the Electro-oxidation of Hydrocarbon Fuels

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Start Date = 1 January 2004
Planned Completion = 31 December 2007
Research Goals and Objectives

Objective:
Synthesize heterobimetallic complexes and evaluate them as catalysts for methanol electrooxidation as a model for direct utilization of hydrocarbons in fuel cells.

Crucial Questions:
• Can the function of bulk Pt/Ru alloy be reproduced in a simple complex using much less precious metal?
• Can simple complexes immobilized on anodes serve as electrocatalysts for fuel cells?
• Can cheaper, more readily available, more active first row transition metals be used in catalysts?
Relevance to Current State-of-the-Art

- For direct utilization of hydrocarbon fuels in fuel cells, state of the art is DMFC with Pt/Ru surface serving as anode catalyst.

Relevance to NASA

- Future direct use of hydrocarbon fuels in fuel cells will require new catalysts and understanding of the reactions involved.
Budget, Schedule and Deliverables

Budget
• $40,000 for the grant period 10/1/05 to 3/31/07

Deliverables
• 1st Quarter: oxidation data from previously prepared Fe/Pt, Fe/Pd and Fe/Au catalysts and comparison to Ru/Pt, Ru/Pd, Ru/Au analogues
• 2nd Quarter: modified carbon paste electrodes with neutral catalysts
• 3rd Quarter: bulk electrolysis data from modified carbon paste electrodes
• 4th Quarter: new Ru/Pt, Ru/Pd, Ru/Au, Fe/Pt, Fe/Pd and Fe/Au catalysts with charged ligands
• 5th Quarter: modified Nafion electrodes with charged catalysts
• 6th Quarter: bulk electrolysis data from modified Nafion electrodes
Anticipated Technology End Use

• Results on single molecule catalysts and use of more active first row transition metals could be generally relevant to direct utilization of hydrocarbons in fuel cells
Accomplishments and Results

Methanol as a model for more complex hydrocarbon fuels

- Complex oxidation mechanism

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow -2e^- \rightarrow \text{CH}_2\text{O} + 2\text{H}^+ \\
\text{CH}_2\text{O} & \rightarrow -2e^- \rightarrow \text{CO} + 2\text{H}^+ \\
\text{CO} + \text{H}_2\text{O} & \rightarrow -2e^- \rightarrow \text{CO}_2 + 2\text{H}^+ \\
\text{CH}_2\text{O} + \text{H}_2\text{O} & \rightarrow -2e^- \rightarrow \text{HCOOH} + 2\text{H}^+ \\
\text{HCOOH} & \rightarrow -2e^- \rightarrow \text{CO}_2 + 2\text{H}^+
\end{align*}
\]

- Requires activation of C-H bonds

\[
\begin{align*}
\text{CH}_2\text{O} + 2\text{CH}_3\text{OH} & \rightarrow \text{CH}_2(\text{OCH}_3)_2 + \text{H}_2\text{O} \\
\text{HCOOH} + \text{CH}_3\text{OH} & \rightarrow \text{HCO}_2\text{CH}_3 + \text{H}_2\text{O}
\end{align*}
\]
Accomplishments and Results

Synthesis of Charged Catalysts for Modified Electrodes

- Positive charge facilitates incorporation into Nafion for preparation of modified electrodes
Accomplishments and Results

Synthesis of First and Second Row Metal Catalysts for Comparison

- Catalytic behavior of 1st row metal (Fe) can be compared to 2nd row (Ru)
Accomplishments and Results

Ru and Fe heterobimetallic complexes

\[
\begin{align*}
\text{Ru} & \quad \text{Ru} & \quad \text{Ru} & \quad \text{Ru} & \quad \text{Ru} & \quad \text{Ru} \\
\text{OC} & \quad \text{OC} & \quad \text{OC} & \quad \text{OC} & \quad \text{OC} & \quad \text{OC} \\
\text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} \\
\text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2
\end{align*}
\]

\[\nu_{\text{co}} = 1958 \text{ cm}^{-1}\]

\[
\begin{align*}
\text{Fe} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} & \quad \text{OC} & \quad \text{OC} & \quad \text{OC} & \quad \text{OC} \\
\text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{P} \\
\text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2 & \quad \text{PPh}_2
\end{align*}
\]

\[\nu_{\text{co}} = 1939 \text{ cm}^{-1}\]

\[\nu_{\text{co}} = 1992 \text{ cm}^{-1}\]

\[\nu_{\text{co}} = 1980 \text{ cm}^{-1}\]

\[\nu_{\text{co}} = 1947 \text{ cm}^{-1}\]

\[\nu_{\text{co}} = 1984 \text{ cm}^{-1}\]

\[\nu_{\text{co}} = 1972 \text{ cm}^{-1}\]

\[\nu_{\text{co}} = 1949 \text{ cm}^{-1}\]
Accomplishments and Results

Cyclic Voltammetry

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Accomplishments and Results

Bulk Electrolysis: Product Evolution for Electrooxidation of Methanol by Ru/Pt and Ru/Pd Heterobimetallic Complexes

DMM = CH$_2$(OCH$_3$)$_2$
2 e$^-$ oxidation

MF = HCO$_2$CH$_3$
4 e$^-$ oxidation

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DMM = CH₂(OCH₃)₂
2 e⁻ oxidation

MF = HCO₂CH₃
4 e⁻ oxidation
Accomplishments and Results

Summary

- Heterobimetallic Ru/Pt, Ru/Pd, Ru/Au, Fe/Pt, Fe/Pd and Fe/Au complexes have been synthesized

- Cationic Ru/Pt and Ru/Pd complexes have been prepared for incorporation into Nafion films for fabrication of modified electrodes

- These heterobimetallic complexes have been demonstrated to be catalysts for the electrochemical oxidation of methanol

- Fe/Pt and Fe/Pd binuclear complexes are more active catalysts than their Ru/Pt and Ru/Pd analogues
Future Plans

• Fabricate carbon paste electrodes modified with neutral catalysts

• Fabricate modified electrodes using Nafion films impregnated with cationic catalysts

• Test modified electrodes for electrooxidation of methanol

• Continue synthesis of catalysts bearing first row metals
  – additional Fe/Pt, Fe/Pd, Ru/Ni, Fe/Ni complexes designed

• Evaluate performance of new catalysts for electrooxidation of methanol as a model for hydrocarbon systems