# Partial Oxidation of Light Alkanes during $O_2$-$H_2$ Cell Reactions at Room Temperature

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The partial oxidation of light alkanes (methane, ethane, and propane) has been carried out successfully by applying an $O_2$-$H_2$ cell at ambient temperature and atmospheric pressure. The conversion of alkanes increased in the order of $CH_4 < C_2H_6 < C_3H_8$. The selectivity to useful oxygenates was the highest in the case of propane. The selectivity to acetone was higher than 65%.

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Partial oxidation of light alkanes such as methane, ethane, and propane into their oxygenates has been one of the most desired reactions from a standpoint of utilizing natural gas as a chemical feed stock.[1] However, catalytic oxidation of these light alkanes under mild reaction conditions has not been successful because a high activation energy is required for breaking their C-H bonds.[1] We have reported that the selective partial oxidations of benzene to phenol and of hexane to hexanol and hexanone occurred at room temperature in the liquid phase by reductively activating oxygen at the cathode during $O_2$-$H_2$ cell reactions.[2-4] The cathodes effective for these oxygenations were $SmCl_3$/graphite,[3] $Fe_2O_3\cdot$ Pd-black/CW[4] (CW= carbon whisker), and $CuSO_4$/CW.[5] We have suggested that a reductively activated oxygen (O*) on these cathode (Eq. 2) must be responsible for the oxygenations of benzene and hexane.[3-6]

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ (1)

Cathode: $O_2 + 2H^+ + 2e^- + M^{n+} \rightarrow O^*\text{-}M^{n+} + H_2O$ (2)

where, $M^{n+}$ represents the active site on the cathode such as $Sm^{3+}$, $Fe^{3+}$, and $Cu^{2+}$. However, the oxidations of methane, ethane, and propane have not been successful by applying the cathodes examined so far in the $O_2$-$H_2$ cell system. Therefore, the purpose in this work is to explore the cathodes and the reaction conditions suitable for the activation of methane, ethane, and propane into their oxygenates at ambient conditions by applying an $O_2$-$H_2$ cell.

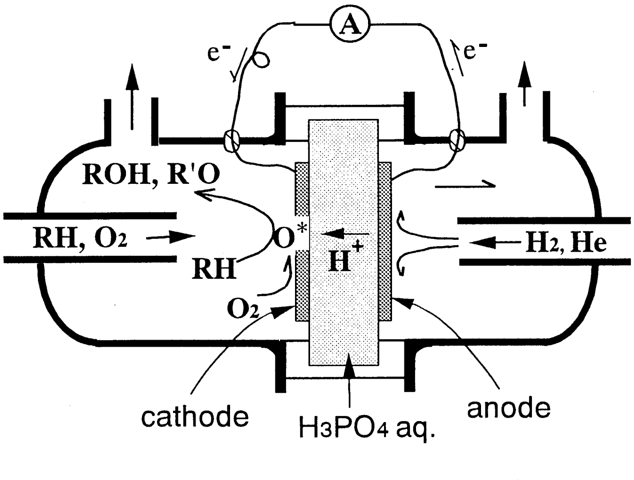

**Figure 1.** Diagram of the cell for the oxidation of light alkanes in the gas phase.

The reactor used in this work was of 10 cm length and 2.2 cm inner diameter. The schematic diagram of the cell and the principle of the reaction are indicated in Figure 1. A silica-wool disk (21 mm diameter, 2 mm thickness) containing aqueous solution of $H_3PO_4$ (1 M, 0.75 g) separates the anode and the cathode compartments. A detailed description of the cell-setup has been described elsewhere.[6] Light alkanes (methane, ethane, and propane, 50 kPa) and oxygen (51 kPa) were passed through the cathode compartment. Hydrogen (50 kPa) and water vapor (4 kPa, added to keep the electrolyte wet) were carried by He (47 kPa) in the anode compartment. The flow rate for both compartments was 10 $cm^3min^{-1}$.

The anode was prepared from a mixture of Pt-black (30 mg), graphite (70 mg), and Teflon powder (10 mg) by the hot-press method at 393 K. The cathode was prepared from the carbon whisker (50 mg) with and without additives ($Fe_2(SO_4)_3$, $FeCl_3$, $CuCl_2$, $CuSO_4$, $Cu_3(PO_4)_2$, Pd-black, $RuO_2$, $SmCl_3$, $SnCl_4$ and tetraphenyl porphyrins of Fe, Mn, Zn, Cu and Mg), and Teflon powder (35mg) by the same hot-press method. The specific surface area of the carbon whisker used (obtained from Asahi Chemical Industry Co.) was 22 $m^2/g$. The pore size distribution of this carbon material showed no micropores (pore diam>10 nm). The outer phase of the whisker was made up of graphite polycrystallites of 1 to 3 nm. The contents of additives were 20 mg in the case of $RuO_2$ and Pd-black and 1 mol% (metal base) in the case of metal salts tested. In the case of metal porphyrins, 6 mg dissolved in $CH_2Cl_2$ was impregnated in 50 mg of carbon whisker. The superficial surface area of the electrodes was 3.8 $cm^2$.

The oxidation of alkanes was started by shorting the circuit at 293 K or at 301 K. Steady state formation of the products in the effluent gas mixture was analyzed by an on-line gas chromatography with a FID except for $CO_2$. $CO_2$ was analyzed separately by sampling with a syringe using another gas chromatography with a TCD. The products dissolved in $H_3PO_4$ aq. in the silica-wool disk was negligibly small compared to the products detected in the gas phase.

The electrocatalytic functions of the additives described above have been tested first in the oxidation of propane at 293 K. It should be noted that no product was obtained under open-circuit conditions. The reaction was initiated by shorting the circuit. The products for the oxidation of propane were acetone and $CO_2$ for all the cathodes tested. The steady state current and the formations of acetone and $CO_2$ were usually obtained at 40 min after shorting the circuit. All the copper salts tested in this work as well as the Cu-tetraphenyl porphyrin enhanced remarkably the formation of $CO_2$ compared with the carbon whisker alone, but enhanced only slightly the acetone formation. Other metal-porphyrins enhanced only the formation of $CO_2$. The Pd-black increased the current remarkably due to the $O_2$-$H_2$

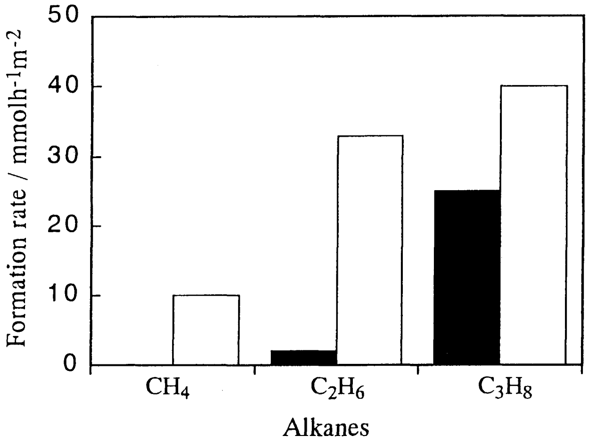

**Figure 2.** Oxidation of light alkanes during $O_2$-$H_2$ cell reactions. Cathode: Carbon whisker; P(alkane) = 51 kPa, $P(O_2)$ = 50 kPa. Anode : Pt-black /graphite; $P(H_2)$ = 50 kPa, $P(H_2O)$ = 4 kPa, P(He) =47 kPa.
■ , acetaldehyde for ethane and acetone for propane.
□ , carbon dioxide.

reaction, but reduced the oxidation of propane. The $SmCl_3$/CW, $FeCl_3$/CW, and $Fe_2(SO_4)_3$/CW cathodes decreased both rates of $CO_2$ and acetone formations compared to the cathode of carbon whisker alone. Therefore, we have concluded that the carbon whisker cathode without additives is the best one for the partial oxidation of propane into acetone.

The cathodes prepared from other carbon materials such as graphite, active carbon cloth, active carbon fiber, and carbon black were less active than the carbon whisker.

Figure 2 compared the rates of oxidation of methane, ethane, and propane on the carbon whisker cathode at 301 K. The rate of alkane oxidation increased as $CH_4 < C_2H_6 < C_3H_8$ as we expected. It should be noted that, although $CO_2$ is the main product, methane and ethane can be oxidized at 301 K. In contrast with the results of methane and ethane, the selectivity to the useful oxygenate (acetone) in the case of propane exceeded 65% on the basis of the propane reacted.

Figure 3 indicates the formation rates of acetone and $CO_2$, the current density (C.D.), and the oxidation efficiency (O.E.) for the formation of acetone as functions of the potential difference between the cathode and the anode ($\Delta E$). The oxidation efficiency of acetone was evaluated from the mole of the produced acetone divided by the mole of oxygen atoms reduced. The latter was calculated on the basis of the current assuming that two protons and two electrons are required for the reduction of an oxygen atom. As can be seen in Figure 3 the formation rates of both products increased as a decrease in $\Delta E$ from 0 to -0.4 V. Beyond this $\Delta E$, the formation rates decreased sharply, though the current density still increased. In this high negative $\Delta E$, the adsorption of propane might be blocked by the hydrogen pumped from the anode or by the water formed on the cathode. Under the conditions where the electric power output can be obtained, the oxidation efficiency is improved dramatically in this region with a decrease in the current density. The oxidation efficiency for the total products exceeded 50% at +0.3 V. This observation suggests that the intermediate active oxygen species, probably OH radical,[4] reacts efficiently with propane before being reduced deeply into water if we squeeze the current.

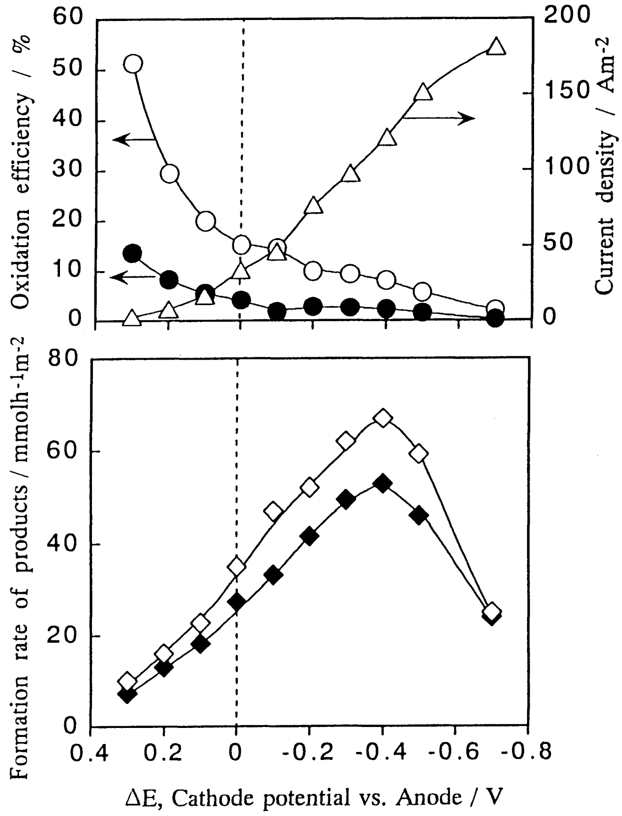

**Figure 3.** Effects of the Cathode potential vs. Anode on oxidation of propane.
Cathode: Carbon whisker; P(alkane) = 51 kPa, $P(O_2)$ = 50 kPa.
Anode : Pt-black /graphite; $P(H_2)$ = 50 kPa, $P(H_2O)$ = 4 kPa, P(He) =47 kPa.
Formation rate (◆, acetone; ◇, $CO_2$), Current density (△), Oxidation efficiency (●, acetone only; ○, acetone and $CO_2$).

## References and Notes

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