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# Electrochemical Control for Oxidative Coupling of Methane over $LiNiO_2$ Using Solid Electrolytes

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The catalytic conversion of methane into ethylene and ethane over $LiNiO_2$ was improved considerably when the oxygen on the catalysts was removed electrochemically from the catalyst by oxygen pump through a stabilized zirconia electrolyte.

The oxidative coupling of methane is potentially an attractive method for the production of ethylene from natural gas. Since Keller and Bhasin[1] reported the synthesis of $C_2$ compounds ($C_2H_6$ + $C_2H_4$) by partial oxidation of methane over metal oxides, many groups[2] have published preliminary results on catalytic activity and $C_2$ selectivity for this reaction.

We have shown that Li-doped NiO gives fairly good yields of $C_2$ compounds and $C_2$ selectivity.[3] We now report an electrochemical method by which the catalytic activity and selectivity of the Li-doped NiO are improved appreciably. The catalyst is deposited on a stabilized zirconia solid electrolyte with gold film electrodes and is held under an externally applied potential.

The application of the electrochemical technique utilizing a stabilized zirconia solid electrolyte to the partial oxidation of ethylene was first demonstrated by Stoukides and Vayenas.[4] Hayakawa et al. applied this technique to the partial oxidation of propene.[5] We have reported the partial oxidation of methane over a $Bi_2O_3$/Ag-deposited zirconia electrolyte.[6] The reaction was controlled by electrochemically pumped oxygen through the zirconia electrolyte which acted as a separator for the reactants, i.e., methane and oxygen. The method used in this work is rather unusual in that the catalyst-deposited zirconia is suspended in a flow of gas mixture of methane and oxygen (Fig. 1). The Li(50 mol%)-doped NiO catalyst (58 mg), shown by X-ray diffraction analysis to be $LiNiO_2$, was coated on one side of the Au-deposited yttria-stabilized zirconia plate (20 x 15 x 0.4 $mm^3$). With the circuit open the $LiNiO_2$ acted as a regular catalyst for oxidative coupling of methane. However with an external voltage V applied between the two electrodes, $O^{2-}$ was pumped through the zirconia electrolyte to or from the catalyst depending on the polarity of the external voltage.

Figure 2 shows the formation rates of products, and the oxygen conversion, as functions of the current, and the corresponding externally applied voltages. Positive current means that the catalyst forms the anode, i.e., $O^{2-}$ is pumped to the catalyst in Fig. 1. A negative current involves the pumping of $O^{2-}$ from the catalyst to the right side of the zirconia. The results in Fig. 2 show that the

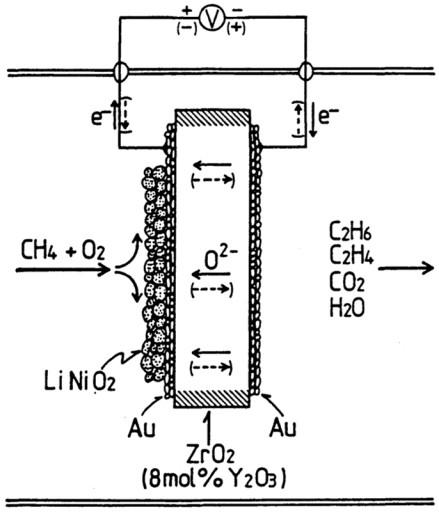


Fig. 1. Schematic diagram of the $LiNiO_2$-deposited zirconia electrolyte.

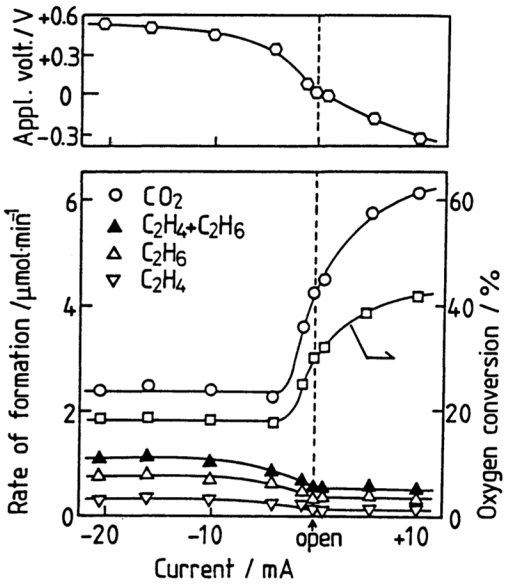


Fig. 2. Formation rates of the products as functions of the current. T=973 K, flow rate =20.3 ml $min^{-1}$, $P(O_2)$=3.9 kPa, $P(CH_4)$=23.5 kPa.

pumping of oxygen from the catalyst enhances the formation of $C_2$ compounds and reduces the deep oxidation of methane. The selectivity to $C_2$ compounds increased from 18% (open circuit) to 48% at the current of -16 mA. However, pumping of oxygen to the catalyst decreased the $C_2$ selectivity. The rate of $CO_2$ formation increased as the applied voltage was made more negative. The reproducibility of the data in Fig. 2, tested by changing the polarity of the external voltage, was within the experimental error of ±3%.

The favorable effect on oxidative coupling of methane when oxygen is pumped from the catalyst may be ascribed to the decrease in concentration of surface oxygen species which oxidize a reaction intermediate or $C_2$ compounds to $CO_2$. Oxygen pumping in the reverse direction increases the concentration of such species, hence increasing the rate of deep oxidation.

The advantage of this method is that it does not require a separator between anode and cathode. The method is simple and generally applicable for enhancing catalytic oxidations using a conventional flow system.

References

1) G.E. Keller and M.M. Bhasin, J. Catal., 73, 9(1982).
2) K. Otsuka, Sekiyu Gakkaishi, 30, 385(1987) and references therein.
3) K. Otsuka, Qin Liu, M. Hatano, and A. Morikawa, Chem. Lett., 1986, 903.
4) M. Stoukides and C.G. Vayenas, J. Catal., 1981, 70, 137.
5) T. Hayakawa, T. Tsunoda, H. Orita, T. Kayama, H. Takahashi, K. Takehira, and K. Fukuda, J. Chem. Soc., Chem. Commun., 1986, 961.
6) K. Otsuka, S. Yokoyama,and A. Morikawa, Chem. Lett., 1985, 319.

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