

## ♦ Oxidative Coupling of Methane by using a Membrane Reactor modified by Molten Salts

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Oxidative coupling of methane is successfully conducted with high selectivity (~90%, on  $\text{PbO-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$ ) by using a membrane reactor which is composed of a liquid membrane ( $\text{K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  or  $\text{KCl}$ ) and metal oxides.

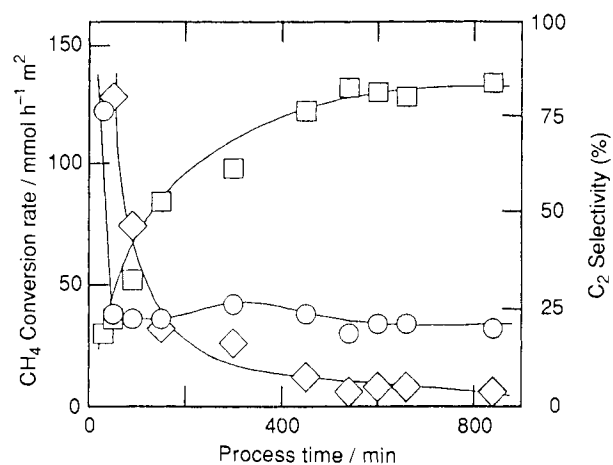
Methane conversion technologies have been studied by many investigators with the aim of developing a novel use of natural gas. So far, many catalysts for the oxidative coupling of methane have been developed.<sup>1-5</sup> The authors found that the lattice oxygen of lead oxide on an  $\text{MgO}$  carrier converted methane to  $\text{C}_2$  hydrocarbons with high selectivity.<sup>6</sup> Thus, the authors developed a membrane reactor made of a non-porous  $\text{PbO}$  film on a porous alumina tube, which exhibited the activity for  $\text{CH}_4$  oxidation and for oxide ion conductivity. Methane was continuously converted to  $\text{C}_2$  hydrocarbons with high selectivity (>90%) by the lattice oxygen of the  $\text{PbO}$  film.<sup>7,8</sup> However, this method has a serious problem in that it is very difficult to make a pinhole-free  $\text{PbO}$  film on the porous support materials.

In this study, the authors modified the  $\text{PbO}$  membrane reactor by molten alkali compounds to make the membrane reactors much easier to prepare. The oxidative coupling of methane was successfully conducted with the modified membrane reactors supported on the porous  $\text{SiO}_2\text{-Al}_2\text{O}_3$  tube.

Porous  $\text{SiO}_2\text{-Al}_2\text{O}_3$  tubes (o.d. 10 mm, i.d. 5 mm, length 300 mm) were employed as the supporting material of the

membranes. This supporting material was produced by pressing  $\text{SiO}_2\text{-Al}_2\text{O}_3$  particles (1  $\mu\text{m}$ ) and calcining the resulting tube at 1320 °C, the porosity of the tube is 0.3 and it consists of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ (1 : 2) and 3 wt% of other metal oxides (iron oxides,  $\text{CaO}$  and  $\text{MgO}$ ). The porous supports were coated with a methanol slurry of the membrane compounds (commercially available  $\text{PbO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{KCl}$ , supplied by Tokyo Kasei Ltd) and calcined at 800 °C. The coating zone was 50 mm in length and the rest of the porous tube was sealed by fused silica. The reactor was set in a fused alumina tube (i.d. 13 mm). Air was passed through the inside of the membrane reactor at 60  $\text{ml min}^{-1}$ , while methane was fed to the outside of the membrane at 85  $\text{ml min}^{-1}$ . The product gas was analysed by gas chromatography. Nitrogen and oxygen in the methane stream were monitored by a gas chromatograph and neither nitrogen nor oxygen was detected. This means that methane was converted only by the lattice oxygen of the membrane.

Fig. 1 shows the activity change with process time for the  $\text{PbO-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  membrane. Similar responses were observed on other membranes. Though the rate of  $\text{CH}_4$

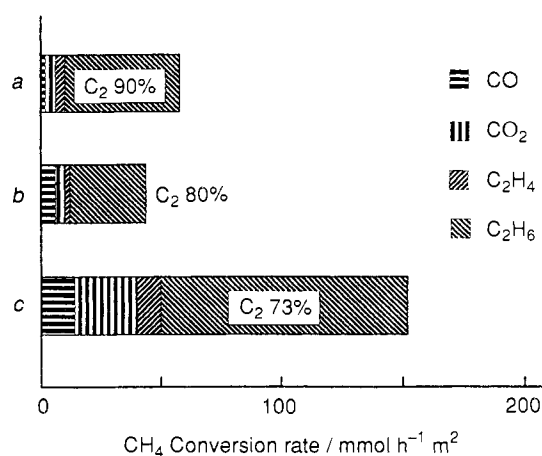


**Fig. 1** Activity change with process time for the  $\text{PbO-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  membrane at  $750^\circ\text{C}$ .  $\text{CH}_4$  conversion to  $\text{C}_2$  hydrocarbons:  $\circ$   $\text{CO}$  and  $\text{CO}_2$  and  $\square$   $\text{C}_2$  selectivity.

conversion to products over the membrane was high at the beginning of the reaction, the level decreased gradually with reaction time to reach a low steady state level within two or three hours. After use, the colour of the methane-side surface of the membrane turned grey and X-ray diffraction (XRD) peaks of Pb were observed. The initial high activity was caused by the lead oxide on the membrane surface, which was reduced to a level that was equal to that of oxygen transportation through the membrane. The driving force of oxygen transportation is the concentration gradient of lattice oxygen in PbO. For this membrane, the activation energy of  $\text{C}_2$  formation was  $40\text{ kcal mol}^{-1}$  ( $1\text{ cal} = 4.184\text{ J}$ ), which was a little lower than catalytic  $\text{CH}_4$  oxidation ( $50\text{--}60\text{ kcal mol}^{-1}$ ). This means that the reaction rate was influenced by the rate of oxide ion transportation.

In the case of the oxide membrane, the oxygen carrier is the oxide ion ( $\text{O}^{2-}$ ). Therefore, when the oxide ions are transferred from the air side to the methane side through the membrane, electrons must be transferred in the inverse direction. Molten salts may act as the conductor of these electrons. A detailed discussion of a kinetic model will be presented in the next paper.

The performance of the membranes used in this study are presented in Fig. 2. Higher activity of  $\text{C}_2$  formation was exhibited by the  $\text{Bi}_2\text{O}_3\text{-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  membrane, while the  $\text{PbO-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  membrane exhibits a higher selectivity ( $\sim 90\%$ ). The carbonate ion of molten alkali carbonates is well



**Fig. 2**  $\text{CH}_4$  conversion activity on the membranes: a,  $\text{PbO-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  (Pb 17 mol%, thickness  $90\ \mu\text{m}$ ); b,  $\text{PbO-KCl}$  (Pb 17 mol%, thickness  $160\ \mu\text{m}$ ); c,  $\text{Bi}_2\text{O}_3\text{-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  (Bi 17 mol%, thickness  $90\ \mu\text{m}$ )

known as an oxide ion carrier in a fuel cell. However, the reactivity of the  $\text{PbO-KCl}$  membrane was comparable to that of the  $\text{PbO-K}_{0.76}\text{Li}_{1.24}\text{CO}_3$  membrane. Thus, implying that PbO is responsible for the oxide ion transportation.

It was found that the metal oxide membrane was easily prepared when it was modified by alkali molten salts. The modified membranes exhibited higher selectivity and a stable activity for the oxidative coupling of methane.

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