Oxidative Coupling of Methane on an ABO_3 Type Oxide with Mixed Conductivity

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Substituted $SrCoO_{3-\alpha}$ perovskite oxide show high selectivity (>98%) and stable activity for oxidative coupling of methane at 1023 K in the redox system; repeated reaction–oxidation cycles show a high tolerance in a reductive atmosphere; a particular lattice oxide ion is found to be responsible for the selective oxidation of methane.

Many catalysts for oxidative coupling of methane (OCM) have been reported.[1–5] However, the selectivity for C_2 hydrocarbons is poor owing to nonselective gas phase reactions induced by the catalyst surface. Membrane reactor systems which utilize solid electrolytes and catalyst electrodes have been reported as an advanced reaction method to achieve high selectivity because of the absence of oxygen gas.[6–8] We found that lattice oxygen of PbO is active for OCM[9] and proposed use of a PbO film membrane on a porous tube.[10–12] Over a PbO membrane the diffusion of oxide ion determines the overall reaction rate. Some perovskite type oxides, such as strontium-substituted $LaCoO_3$, show higher O^{2-} ion conductivity than stabilized zirconia in addition to high electronic conductivity.[13] Such a 'mixed conductor' is a suitable material for an OCM membrane because, in contrast to the solid-electrolyte stabilized zirconia, a counter electrode is not necessary since electrons are transferred through the oxide to compensate the charge transfer by oxide ion migration. In this study the methane oxidation activity of ABO_3 type mixed conductors was studied.

Several oxides were prepared by a codecomposition method. After aqueous solutions comprising of metal acetates and nitrates were evaporated, the mixtures of salts were decomposed in air at 873 K to produce the mixed oxides. The resulting powders were compressed into disks followed by firing at 1233 K and crushing into granules of 40–80 mesh. X-Ray diffraction patterns indicated that substituted $LaCoO_3$ have perovskite structures and that $SrCoO_{3-\alpha}$ has a brownmillerite structure.[14] In the case of substituted $SrCoO_{3-\alpha}$ the structures are not certain. The activities of the oxides were evaluated in a flow-type fixed-bed reactor made of quartz by a periodic reaction where methane and air were alternatively supplied for reaction and reoxidation, respectively. Argon was supplied as the purge gas after every step. In the reaction with methane, the surface of the oxide is in a similar environment to the reactant surface of a membrane reactor. Therefore the periodic reaction method is adequate to evaluate the potential of oxides for applications to membranes. The oxide granule (0.2 g, 40–80 mesh) was placed in the annular space between the inner and outer tube. Reaction temperatures were monitored by a thermocouple placed inside the inner quartz tube. The product was analysed by gas chromatography.

Table 1 Initial activity for methane conversion at 1023 K

Oxide	Methane conversion rate[a] C_2	CO_x	H_2	C_2 selectivity (%)
$LaCoO_3$	4.2	11.8	0	26.0
$LaCo_{0.9}Li_{0.1}O_3$	5.5	2.4	0	69.6
$LaCo_{0.9}Cr_{0.1}O_3$	1.1	18.5	0	5.4
$LaCo_{0.9}Mg_{0.1}O_3$	1.0	28.0	0.05	3.4
$La_{0.9}Pb_{0.1}CoO_3$	2.7	6.7	0.05	28.9
$La_{0.9}Sr_{0.1}CoO_3$	4.8	24.4	0	16.3
$La_{0.9}Ce_{0.1}CoO_3$	1.0	26.8	0.05	3.6
$SrCoO_3$	5.8	0.6	0.1	91.3
$SrCo_{0.8}Li_{0.2}O_3$	11.2	0.2	0.05	98.2
$SrCo_{0.8}Mg_{0.2}O_3$	5.5	0.3	0.05	95.7
$SrCo_{0.8}Sb_{0.2}O_3$	2.3	1.0	0.05	69.7
$SrCo_{0.8}Fe_{0.2}O_3$	2.8	6.7	0.15	29.5
$Sr_{0.8}Ce_{0.2}CoO_3$	2.4	0.2	0.05	94.1
$Sr_{0.8}La_{0.2}CoO_3$	1.2	0.2	0	85.2
$Sr_{0.8}Pb_{0.2}CoO_3$	2.2	2.4	0.05	48.4
$Pb_{0.02}Mg_{0.98}O$	1.0	0	0.06	>99

[a] mmol h^{-1} g^{-1}.

The oxides employed for the reaction were grouped into two classes, substituted $LaCoO_3$ and substituted $SrCoO_{3-\alpha}$. Fig. 1 shows the change in activity of $SrCo_{0.8}Mg_{0.2}O_{3-\alpha}$ upon recycling the methane feed. Results indicate high selectivity for C_2 hydrocarbons and excellent reproducibility.

It has been reported that two types of oxygen species exist in the lattice of $SrCoO_{3-\alpha}$.[14] By heating the oxide in helium, α-oxygen which was accommodated in oxide ion vacancies was

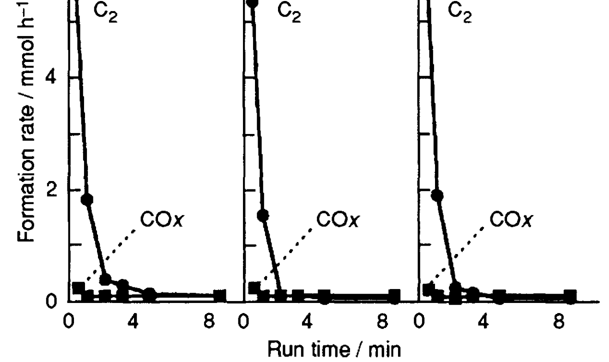

Fig. 1 Transient response of methane conversion at 1023 K on $SrCo_{0.8}Mg_{0.2}O_{3-\alpha}$; (*a*) first, (*b*) second and (*c*) third cycle

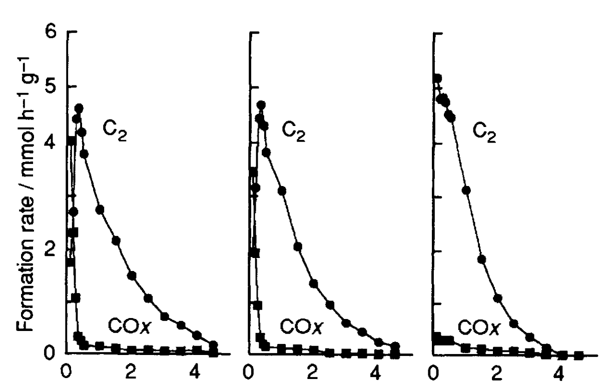

Fig. 2 Effect of Ar purge on methane conversion at 1023 K with $SrCoO_{3-\alpha}$ after 1 (*a*) and 30 min (*b*) at 1023 K, and after 30 min (*c*) at 1173 K

desorbed below 973 K while β-oxygen was desorbed at *ca.* 1023–1123 K. This process was accompanied by reduction of Co^{3+} to Co^{2+}.[15] We have found that a further oxygen desorption peak (γ-oxygen) appears at 1123–1273 K. In Fig. 2 the effect of pretreatment by Ar purge before the reaction is shown. After the purge at 1023 K for 1 and 30 min, no significant difference was observed, whereas only C_2 species were formed after the oxide was purged at 1173 K for 30 min. These observations suggest that γ-oxygen is responsible for C_2 formation and that β-oxygen leads to CO_x formation.

In Table 1 the initial activity of catalytic oxide in the first 30 seconds is summarized. When cobalt in the B site in ABO_3 type oxide is substituted by a basic element, the C_2 selectivity is improved. In the case of $SrCo_{0.8}Li_{0.2}O_{3-\alpha}$, the selectivity was as high as 98%. On the other hand, when lanthanum in the A site is substituted, the total activity tends to increase, but the selectivity decreases. All of the mixed oxides in Table 1 showed higher activity than the PbO–MgO catalyst,[5] and $SrCoO_{3-\alpha}$, $SrCo_{0.8}Li_{0.2}O_{3-\alpha}$ and $SrCo_{0.8}Mg_{0.2}O_{3-\alpha}$, are suitable for membrane materials and exhibit C_2 selectivity.

Further investigations are in progress to conduct the continuous reaction by use of a membrane reactor made of a mixed conductor oxide.

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