Oxidative Dimerization of Methane over Cerium Mixed Oxides and Its Relation with Their Ion-conducting Characteristics

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Selectivities for ethene and ethane formation during oxidative dimerization of methane over cerium mixed oxide catalysts $Ce_{1-x}Yb_xO_{2-0.5x}$ and $SrCe_{1-x}Yb_xO_{3-0.5x}$ appear to be related to the nature of their ionic conduction, decreasing with oxygen ion mobility while increasing with proton mobility.

Oxidative coupling of methane, particularly with air, has been studied because of its potential in producing useful higher hydrocarbons such as ethene.[1] Investigations on catalyst materials have mainly concentrated on oxides, or mixed oxides, of alkali earth,[2] transition,[3] rare earth,[4] and group IIIA—VA metals.[5] It is known that some oxides conduct owing to oxygen ion mobility,[6] while others conduct due to proton mobility.[7] This transport of oxygen or hydrogen could influence the oxidation reaction through oxygen supply from, or hydrogen removal to, the catalyst. This communication deals with the oxidative dimerization of methane in two systems, CeO_2–Yb_2O_3 and SrO–CeO_2–Yb_2O_3, which are known to be good ion conductors but with mobility of different ionic species, *i.e.* O^{2-} and H^+, respectively.[8,7]

The cerium and zirconium mixed oxides used in this work were prepared from reagent grade chemicals (>99.9% purity) by intimate mixing, pelletizing, and heating at 1573 K for 12 h in air. The pellets were powdered, pelletized again, and heated under the same conditions. They were finely powdered before use as catalysts. The surface area of the catalysts was measured by a conventional Brunauer–Emmett–Teller (B.E.T.) nitrogen absorption method.

Powder *X*-ray diffraction (x.r.d.) showed that $Ce_{1-x}Yb_xO_{2-0.5x}$ and $SrCe_{1-x}Yb_xO_{3-0.5x}$ had single structures, confirmed to be of fluorite and perovskite type, respectively. With increasing Yb_2O_3 content, *e.g.* $x = 0.50$, other peaks started to appear on the x.r.d. patterns, *e.g.* $SrYb_2O_4$ was present and gave a major peak for $x = 1.00$ in the oxide $SrCe_{1-x}Yb_xO_{3-0.5x}$, *i.e.* $SrO{\cdot}(Yb_2O_3)_{0.5}$.

The reactions were carried out with 0.60 g of the catalyst in a conventional fixed-bed quartz tube reactor (10 mm o.d.) at 873—1023 K. The catalyst was used after preheating in helium at 873 K for 2 h. Products were analysed by gas chromatography, and the selectivites for C_2H_4 and C_2H_6 production

Table 1. Product distribution and C_2H_4 and C_2 yields.[a]

Catalyst	B.E.T. area/ $m^2 g^{-1}$	Selectivity/%				Yield/%	
		CO	CO_2	C_2H_4	C_2H_6	C_2H_4	(C_2)
CeO_2	3.5	≃0	87.3	11.4	1.3	3.6	(4.0)
$Ce_{0.95}Yb_{0.10}O_{1.95}$	0.9	3.6	93.5	≃0	2.9	Trace	(0.73)
Yb_2O_3	6.7	26.5	29.0	22.5	22.0	6.4	(12.6)
SrO[b]	3.1	9.5	28.1	45.7	16.7	11.6	(15.8)
$SrCeO_3$	1.2	≃0	50.7	22.6	26.7	10.0	(21.8)
$SrCe_{0.90}Yb_{0.10}O_{2.95}$	1.4	≃0	39.9	36.1	24.0	19.0	(31.6)
ZrO_2	11.8	28.8	63.6	7.5	0.10	1.8	(1.9)
$Zr_{0;90}Yb_{0.10}O_{1.95}$	2.3	50.8	48.0	0.69	0.51	0.11	(0.26)

[a] Amount of catalyst = 0.60 g, reaction gas mixture He : CH_4 : O_2 = 12 : 2 : 1, flow rate = 50 ml min^{-1}, temperature = 1023 K.
[b] Prepared by heating $SrCO_3$ at 873 K for 12 h *in vacuo*.

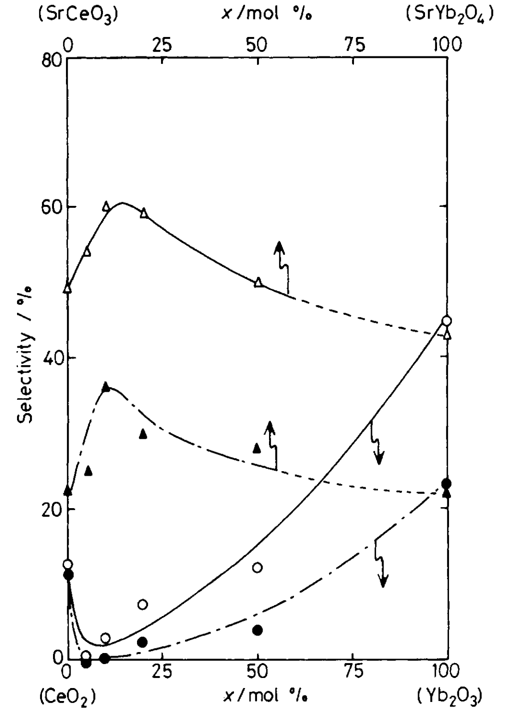

Figure 1. Selectivity for C_2 (○,△) and C_2H_4 (●,▲) in oxidative dimerization of methane over cerium mixed oxide catalysts in the groups $Ce_{1-x}Yb_xO_{2-0.5x}$ (○,●) and $SrCe_{1-x}Yb_xO_{3-0.5x}$ (△,▲). See Table 1 for other conditions.

were evaluated as percentage of carbon atoms in these hydrocarbons produced per total methane molecules converted.

Products from the oxidative coupling of methane were CO, CO_2, C_2H_4, C_2H_6, and H_2O only (see Table 1). It is noteworthy that the yield of C_2 product, particularly C_2H_4, over the $SrCe_{1-x}Yb_xO_{3-0.5x}$ mixed oxides is considerably higher than with other mixed oxides, or SrO.

The dependence of the selectivities for formation of C_2H_4 and C_2, on the Yb_2O_3 concentration in the cerium mixed oxides, $Ce_{1-x}Yb_xO_{2-0.5x}$ and $SrCe_{1-x}Yb_xO_{3-0.5x}$ is found to be significant as shown in Figure 1. The selectivities over the catalysts in the $Ce_{1-x}Yb_xO_{3-0.5x}$ group first decreased and then increased with the Yb_2O_3 content, giving a minimum around $x = 0.05$. This tendency was reversed in the $SrCe_{1-x}Yb_xO_{3-0.5x}$, giving a maximum around $x = 0.10$. These results appear to have a clear correlation with the nature of their conductivity, *i.e.*, oxygen ion or proton mobility respectively. These mixed oxide systems are known to yield maximum conductances at several mol % of Yb_2O_3[7,8] *i.e.*, high oxygen ion conductance lowers the selectivity while high proton conductance enhances it. A similar tendency was also observed on other oxides with oxygen ion mobility *e.g.* ZrO_2–Yb_2O_3.

The cause of the correlation between the selectivity and ionic conduction species is yet to be clarified, but a qualitative picture may be drawn. The first oxidized intermediate from methane, *e.g.* a methyl radical on the catalyst surface, may be further oxidized to CO or CO_2 on the oxygen ion conductive catalysts if oxygen is supplied through the bulk, but this cannot occur in the proton conductive catalysts. In addition, if a hydrogen from a methane molecule is removed by transfer to other surface sites through the bulk and is oxidized there, the remaining half-oxidized species would have a chance to dimerize to C_2 compounds.

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