ELSEVIER

Catalysis Today 30 (1996) 59–65

CATALYSIS TODAY

The performance and structure of rare earth oxides modified by strontium fluoride for methane oxidative coupling

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Abstract

Strontium fluoride promoted rare earth (La, Nd, Sm, Eu, Gd, Dy, and Y) oxides were more selective than the corresponding unpromoted rare earth oxides for the methane oxidative coupling to ethane and ethene. The XRD results indicated that the partial anionic or cationic exchanges and interaction between the oxide and fluoride phases took place in most of the catalysts studied in this paper, leading to the formation of new oxyfluoride phases. The possible formation of anionic vacancies in the lattice as the result of ionic exchange and interaction between the phases will be favorable to the activation of molecular oxygen and the improvement of catalytic performance.

Keywords: Methane oxidative coupling; Rare-earth oxide; Strontium fluoride; Ionic exchange; Anionic vacancy

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1. Introduction

Methane oxidative coupling (MOC) to C_{2+} hydrocarbons has been a much investigated area in recent decade. A large number of catalysts has been found to be active and selective for the formation of ethane and ethene. Among these catalysts, the rare earth oxides (REO), especially Sm_2O_3 and La_2O_3, have been extensively studied as MOC catalysts due to their high catalytic activities and selectivities as well as satisfactory thermal stabilities [1–4]. In order to further improve the catalytic performance of REO catalysts for MOC reaction, some promoters, usually alkali-metal or alkaline earth-metal oxides, have been added to the REO catalyst systems [5,6]. However, these alkali-metal or alkaline earth-metal oxides doped catalysts usually exhibit strongly basic property, and are easily poisoned by the CO_2 generated during the reaction, so that a higher reaction temperature is required to maintain an adequate level of activity. Besides the promotional effect of metal oxides mentioned above, the benefits of addition of chlorinated compounds to the MOC reaction have also been reported by many research groups [7–10]. Recently, Lunsford et al. [9,10] reported a Cl^- promoted Li^+–MgO catalyst which showed good catalytic performance for both MOC and ODE (oxidative dehydrogenation of ethane). In contrast to the unpromoted Li^+–MgO system, alkane conversions over the Li^+–MgO–Cl^- catalysts with a Cl/Li

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0920-5861/96/$32.00
SSDI 0920-5861(95)00328-2

ratio of 0.9 were almost unaffected by CO_2, since the presence of Cl^- ions at an appropriate level modified the catalyst so that it no longer functioned as a strongly basic oxide catalyst and would therefore not be easily poisoned by CO_2. In addition to chlorinated compounds, We have recently found that metal fluorides also showed significant promotional effects on the oxide catalysts for the MOC and oxidative dehydrogenation of light alkanes (C_2H_6 and C_3H_8) reactions [11–13]. The beneficial effects resulting from addition of fluorides to oxides include (i) possible formation of lattice defects, such as anionic vacancies, which are requisite for the adsorption and activation of O_2 over the catalysts with stable cationic valencies, (ii) modification of the basicity of metal oxides, and (iii) isolation of the surface active oxygen species. In this work, the catalytic property of a series of SrF_2 promoted Ln_2O_3 catalysts with Ln = La, Nd, Sm, Gd, Eu, Dy and Y will be reported. Attention will be focused on the correlations between catalytic properties and the bulk composition and structure of the catalysts.

2. Experimental

The SrF_2 promoted catalysts were prepared by grinding different mole ratios of rare earth oxides (La_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Eu_2O_3, Dy_2O_3 and Y_2O_3, purity > 99.5%) with SrF_2 into fine powder. The mixture was then mixed with certain amount of deionized water to form a paste, followed successively by drying at 120°C for 4 h and calcining at 900°C (850°C for SrF_2/Sm_2O_3) for 6 h. The resulting solid was crushed and sieved to 40–60 mesh particles. The pure rare earth oxides and SrF_2 used for the catalytic performance evaluation were also treated with the similar procedures as described above. Unless indicated elsewhere, the reagents used in the preparation were of analytical grade.

The catalytic reactions were carried out in a fixed bed quartz reactor (5.0 mm inside diameter) under the conditions of GHSV = 20000 h^{-1} and $CH_4/O_2 = 3$ (mole ratio). Methane (99.99%) and oxygen (99.5%) were used without further purification. In each experimental run, 0.20 ml of catalyst was used, and the

Table 1
Catalytic performance of the SrF_2/Ln_2O_3 catalysts for the oxidative coupling of methane

Catalyst (mole ratio)	Temperature (°C)	Conversion (%)		Selectivity (%)					C_2 Yield (%)
		CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_2	
Blank experiment	750	no activity							
SrF_2	750	0.7	2.4	0.0	46.0	0.0	54.0	54.0	0.4
La_2O_3	750	29.8	100	10.2	52.0	20.0	15.8	35.8	10.7
	700	29.4	100	10.5	52.3	21.5	15.7	37.2	10.9
SrF_2/La_2O_3 (1:4)	700	34.2	98.1	6.4	36.3	36.1	21.2	57.3	19.6
SrF_2/La_2O_3 (1:1)	750	35.6	99.2	10.6	34.3	31.4	23.7	55.1	19.6
Nd_2O_3	750	27.2	99.1	7.2	53.5	20.1	19.2	39.3	10.7
SrF_2/Nd_2O_3 (1:1)	750	34.3	98.9	4.0	38.9	33.1	24.0	57.1	19.6
Sm_2O_3	800	26.3	99.2	8.9	52.3	21.6	17.2	38.8	10.2
SrF_2/Sm_2O_3 (1:1)	800	34.0	99.5	3.9	40.3	33.1	22.7	55.8	19.0
Eu_2O_3	750	26.3	98.4	13.8	53.1	21.8	11.3	33.1	8.7
SrF_2/Eu_2O_3 (1:1)	750	33.1	99.0	6.7	40.4	31.9	21.0	52.9	17.5
Gd_2O_3	750	29.5	99.7	17.5	49.0	20.1	13.4	33.5	9.9
SrF_2/Gd_2O_3 (1:1)	750	34.4	99.5	5.9	39.5	32.0	22.6	54.6	18.8
Dy_2O_3	750	31.3	99.5	12.4	45.0	25.0	17.6	42.6	13.3
SrF_2/Dy_2O_3 (1:1)	750	32.6	96.3	8.5	40.0	32.0	19.5	51.5	16.8
Y_2O_3	750	27.2	98.3	16.9	50.2	20.1	12.8	32.9	9.0
SrF_2/Y_2O_3 (2:1)	750	33.6	94.4	8.3	35.1	34.1	22.5	56.6	19.0

Feed: $CH_4/O_2 = 3:1$, no inert gas for dilution, GHSV = 20000 h^{-1}. The data were obtained after 30 min on stream.

gaseous effluent was analyzed at room temperature by an on-line Shang Fen 102GD gas-chromatograph equipped with thermal conductivity detector, with 5A molecular sieve column for O_2 and CO, and GDX 502 column for CH_4, C_2H_4, C_2H_6 and CO_2. The conversion of methane (C_{methane}) and selectivities of the products (S_i) were calculated from the equations: $C_{\text{methane}} = (\Sigma A_i \times F_i)/[\Sigma\ (A_i \times F_i) + A_{\text{methane}} \times F_{\text{methane}}]$ and $S_i = (A_i \times F_i)/\Sigma(A_i \times F_i)$, respectively, where A = peak area of carbon-containing species and F = correction factor of response and carbon number.

The XRD measurements were carried out at room temperature on a Rigaku Rotaflex D/Max-C system with Cu $K\alpha(\lambda = 1.5406$ Å) radiation. The samples were loaded on a sample holder with depth of 1 mm. XRD patterns were recorded in the range of $2\theta = 20$–70°.

3. Results and discussion

3.1. Catalytic performance evaluation

The catalytic performances of a series of SrF_2 promoted rare earth sesquioxide catalysts with different SrF_2/Ln_2O_3 mole ratios were evaluated and the results were summarized in Table 1. The blank reactor was found to have no activity for the reaction between CH_4 and O_2 at 750°C. For pure rare earth oxides, such as La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3 Gd_2O_3 and Y_2O_3 catalysts, 26–31% of CH_4 conversions with 30–43% of C_2 selectivities were obtained. When a certain amount of SrF_2, which had almost no activity for MOC reaction, was added to the oxide catalysts, CO_x ($CO + CO_2$) selectivities decreased significantly, while C_2 selectivities and yields were apparently improved under the same conditions, indicating that the addition of SrF_2 plays a significant promoting role for the MOC reaction with these REO as catalysts. Maximum C_2 yield of 19.6% was observed over SrF_2/La_2O_3 (1:4) and SrF_2/Nd_2O_3 (1:1) catalyst, respectively, which was about 9% higher than those over pure La_2O_3 and Nd_2O_3 under the same conditions. Comparatively, the promotional effect of SrF_2 on Dy_2O_3 was rather unpronounced, and similar results were also observed on the SrF_2 modified Ho_2O_3, Er_2O_3, Tm_2O_3 and Yb_2O_3 catalysts. This phenomenon may have resulted from the interaction between SrF_2 and Ln_2O_3 of which Ln = Dy, Ho, Er, Tm and Yb were relatively weak as compared with the other SrF_2 modified rare earth sesquioxide catalysts studied in this paper. It has been known that the conductivities of rare earth sesquioxides decrease with increasing atomic number (except for Y_2O_3), i.e. La_2O_3, $Nd_2O_3 > Sm_2O_3 > Eu_2O_3 > Gd_2O_3 > Dy_2O_3$ [14], suggesting that the mobilities of lattice

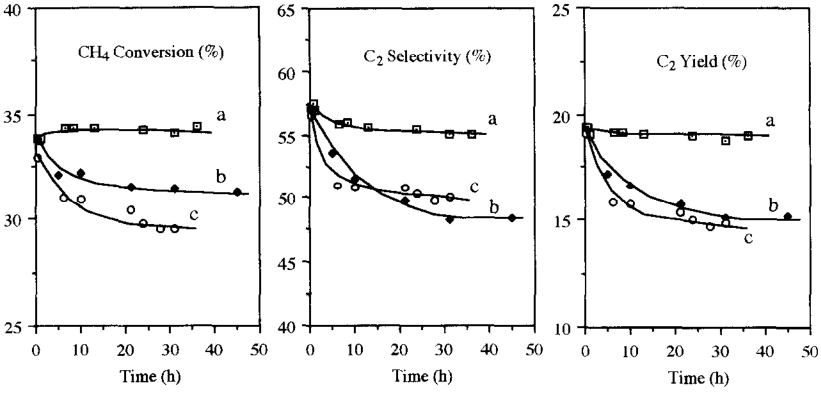

Fig. 1. Effect of time on stream over (a) SrF_2/La_2O_3 (1:4) at 700°C, (b) SrF_2/Nd_2O_3 (1:1) at 750°C, (c) SrF_2/Y_2O_3 (2:1) at 750°C under the conditions of $CH_4:O_2 = 3:1$ (no dilution gas) and GHSV = 20000 h^{-1}.

oxygen may also decrease in this order. For those rare earth oxides with higher mobility of lattice oxygen, the anionic exchange between oxides and fluoride might be easier, which will be favorable to promote the interaction between the oxide and fluoride phases. From the data in Table 1, it is interesting to see that the decrease in C_2 yields of SrF_2/Ln_2O_3 catalysts follows the same order as the decrease in the conductivities of rare earth sesquioxides. In the next section, more discussion concerned with ionic exchange between rare earth sesquioxides and SrF_2 will be presented. As can be seen from Table 1, on both promoted and unpromoted REO catalysts, oxygen was almost completely consumed ($\geqslant 95\%$) in the reactions carried out at 750°C or higher, which suggested that the results showed in Table 1 were obtained under an oxygen-limited condition.

The stability of the catalytic performance of the SrF_2 promoted Ln_2O_3 catalysts varied with the rare earth elements. The results in Fig. 1 shows the catalytic performance of three SrF_2 promoted catalysts with respect to time on stream. The SrF_2/La_2O_3 (1:4) catalyst was characterized by a little increase in CH_4 conversion and decrease in C_2 selectivity at the early period of reaction, as a result, the C_2 yield remained almost constant within a period of 36 h on stream. However, CH_4 conversion and C_2 selectivity over SrF_2/Nd_2O_3 (1:1) catalyst gradually decreased over a period of 30 h on stream, leading to the decrease of C_2 yield from 19.6% to 15.2%. After that, both CH_4 conversion and C_2 selectivity remained almost unchanged in the following 15 h. The decrease of catalytic performance was also observed over the SrF_2/Y_2O_3 (2:1) catalyst during a period of 31 h on stream. The loss of F^- from the catalysts as HF during the reactions appears not to be the only reason for the decrease in catalytic performance of the catalysts, because there is no a corresponding relation between the relative loss amounts of F^- from catalysts and the variations of catalytic performances.

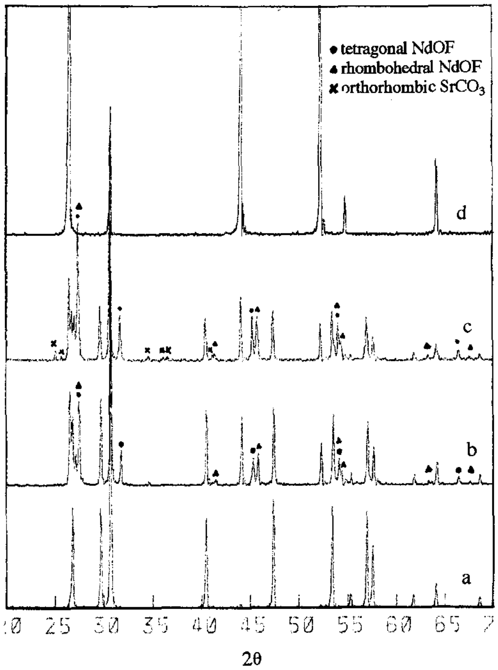

Fig. 2. ZX-ray powder patterns of (a) Nd_2O_3, (b) fresh SrF_2/Nd_2O_3 (1:1), (c) used SrF_2/Nd_2O_3 (1:1), (d) SrF_2 samples.

3.2. Structure characterization

The XRD measurements indicated that new phases such as tetragonal and rhombohedral NdOF were formed in the fresh SrF_2/Nd_2O_3 sample (Fig. 2), suggesting that, during the process of the catalyst preparation, part of the F^- ($r = 1.33$ Å) in SrF_2 and O^{2-} ($r = 1.32$ Å) in Nd_2O_3 were substituted by O^{2-} and F^-, respectively. Partial ionic exchange between SrF_2 and La_2O_3 phases and formation of the lanthanum oxyfluorides, such as tetragonal LaOF, may also happen in SrF_2/La_2O_3 system. Unfortunately, the diffraction lines of tetragonal LaOF [d = 3.35(100), 2.90(25), 2.06(60), 2.05(33), 1.76(22) and 1.75(44)] were overlapped with the characteristic diffraction lines of SrF_2 [d = 3.352(100), 2.900(25), 2.0508(80), 1.7486(52)] which made it difficult to identify the LaOF phase from a SrF_2/La_2O_3 catalyst. However, the formation of rhombohedral LaOF and LaF_3 have been detected by XRD in a similar $10\%BaF_2/La_2O_3$ catalyst [15]. For the

Table 2
The results of XRD analysis of the fresh SrF_2/Ln_2O_3 catalysts

Catalyst	Composition and structure [a]
SrF_2/La_2O_3 (1:4)	cubic SrF_2(w); hexagonal La_2O_3(s)
SrF_2/La_2O_3 (1:1)	cubic SrF_2(s); hexagonal La_2O_3(vs)
SrF_2/Sm_2O_3 (1:1)	cubic Sm_2O_3 (vs); cubic SrF_2(s); monoclinic Sm_2O_3(s)
SrF_2/Eu_2O_3 (1:1)	cubic Eu_2O_3(s); cubic SrF_2(m)
SrF_2/Gd_2O_3 (1:1)	cubic Gd_2O_3(s); cubic SrF_2(m)
SrF_2/Dy_2O_3 (1:1)	cubic Dy_2O_3(s); cubic SrF_2(m)
SrF_2/Y_2O_3 (2:1)	cubic Y_2O_3(vs); cubic SrF_2(s)

[a] vs — very strong, s — strong, m — medium, w — weak.

other samples, XRD only detected cubic SrF_2 and rare earth sesquioxide phases, such as hexagonal La_2O_3, cubic and monoclinic Sm_2O_3, cubic Eu_2O_3, cubic Gd_2O_3, cubic Dy_2O_3, and cubic Y_2O_3 (Table 2). Another interesting result from Table 2 was that the content of cubic Sm_2O_3 in the SrF_2/Sm_2O_3 (1:2) catalyst was a little more than that of monoclinic phase, while the pure Sm_2O_3 contained almost equal amounts of both phases, suggesting that cubic SrF_2 may play a certain role in stabilizing the cubic Sm_2O_3 at high temperature.

When the SrF_2/Ln_2O_3 catalysts were exposed to CH_4/O_2 (3:1) at 750°C for about 1.5 h, orthorhombic $SrCO_3$ resulting from the reaction between SrO and CO_2 (by-product of MOC reaction) was detected in the SrF_2/Nd_2O_3 (1:1) (Fig. 2) and SrF_2/La_2O_3 (1:4) catalysts (Table 3). This result provides further experimental evidence for the anionic or cationic exchanges between SrF_2 and the Ln_2O_3 phases. Besides, XRD also detected the formation of rhombohedral SmOF and YOF phases in the used SrF_2/Sm_2O_3 (1:1) and SrF_2/Y_2O_3 (2:1) catalysts, respectively (Table 3), which indicated that the exchange between F^- and O^{2-} was more favorable under the conditions of MOC reaction, and H_2O generated in the reaction might play a certain role in promoting such exchange. These results were also in line with the observation that the NdOF content in a used SrF_2/Nd_2O_3 (1:1) catalyst was higher than that in the fresh (Fig. 2). Based on these results, it is reasonable to suggest that the anionic exchange between oxide and fluoride phases also happened more or less in a fresh SrF_2/Sm_2O_3 (1:1) or SrF_2/Y_2O_3 (2:1) catalyst, but the content of SmOF or YOF is probably too low to be detected by XRD. No formation of new phase was detected in the used SrF_2/Eu_2O_3 (1:1) catalyst.

Table 3
The results of XRD analysis of the SrF_2/Ln_2O_3 catalysts after reacting about 1.5 h at 750°C

Catalyst	Composition and structure [a]
SrF_2/La_2O_3 (1:4)	cubic SrF_2 (w); hexagonal La_2O_3 (s) orthorhombic $SrCO_3$ (w)
SrF_2/Sm_2O_3 (1:1)	cubic Sm_2O_3 (s); cubic SrF_2(s); monoclinic Sm_2O_3 (vs); rhombohedral SmOF(w)
SrF_2/Eu_2O_3 (1:1)	cubic Eu_2O_3 (s); cubic SrF_2 (m)
SrF_2/Y_2O_3 (2:1)	cubic Y_2O_3 (vs); cubic SrF_2 (s); rhombohedral YOF (w)

[a] vs — very strong, s — strong, m — medium, w — weak.

It has been generally accepted that one of the essential conditions for a compound with stable cationic valency to be a good MOC catalyst is the presence and the mobility of the anionic vacancies in the lattice, so as to adsorb and activate O_2 during the reaction [16]. According to the literature, the structure of cubic Ln_2O_3 compounds is closely similar to that of the fluorite but with 1/4 intrinsic oxygen vacancies [17]. The structure of hexagonal Ln_2O_3 can be described by slabs of OLn_4 tetrahedrons linked by three of their edges and forming a complex group cation $(LnO)_n^{n+}$ separated by ionic oxygens O^{2-}. The monoclinic structure is very similar to hexagonal, but the tetrahedrons are distorted [17]. 'Genetic' vacancies also exist in the hexagonal structure of Ln_2O_3 and monoclinic structure of Sm_2O_3. However, their concentrations are lower (ca. 17% of vacant positions in the oxygen sublattice) than those of cubic phase [18]. The tetragonal NdOF can be expressed by the formula LnO_xF_{3-2x} $(0.7 < x \leqslant 1)$ [19,20], whose structure is closely similar to that of the fluorite. The excess of F^- ions can be accommodated in a fluorite-like structure and occupy some of the interstitial position as Frenkel defect [20]. The rhombohedral oxyfluorides are found to be of a single phase, which chemical composition is sharply defined and corresponds exactly to LnOF [19]. This structure is also a slightly distorted CaF_2-type structure. Taking into consideration the fact that many compounds with fluorite-type structure, such as alkaline earth halides, ZrO_2, etc. have anion Frenkel defects and anionic vacancies [21], it is reasonable to postulate that the similar anionic vacancies might also exist in the oxyfluoride compounds with fluorite-like structure. On the other hand, the ionic exchange between the oxide and fluoride phases of a SrF_2/Ln_2O_3 catalyst may also lead to the formation of anionic vacancies and other lattice defects such as F-center or O^- species in order to maintain electroneutrality. The presence of anionic vacancies and F-center in the above catalyst will be favorable to the adsorption and activation of O_2 under the reaction condition.

4. Conclusions

Based on the above results, it can be concluded that the extent of F^- and O^{2-} exchange in the SrF_2/Ln_2O_3 catalysts are in the order Nd, La > Sm, Y > Gd, Eu, Dy. For those rare earth oxides with higher mobility of lattice oxygen, the interaction between oxides and fluoride will take place easily, which will be favorable to the formation of new oxyfluoride compounds and lattice defects including anionic vacancies, F-centers and O^- in the catalysts. The existence of anionic vacancies and the possible formation of F-centers of the oxyfluoride compounds will be favorable to the adsorption and activation of molecular oxygen under the MOC condition. The adsorption and activation of oxygen on the catalyst surface have been supported by the in situ FTIR spectroscopic observation of O_2^- adspecies with characteristic vibration frequency near 1113 cm^{-1} on the O_2-adsorbed SrF_2/Nd_2O_3 (1:1) and SrF_2/La_2O_3 (1:4) catalysts at 700°C and 650°C, respectively [13,22]. On the other hand, the dispersion of F^- on the surface of the catalysts will also be helpful to the isolation of the surface 'active oxygen' centers and the improvement of the C_2 selectivity. Therefore, the highest C_2 yield was obtained over SrF_2 promoted Nd_2O_3 and La_2O_3 catalysts among these catalysts, whereas, due to the weak interaction between SrF_2 and Dy_2O_3, the promoting effect of SrF_2 was not apparent for MOC reaction over SrF_2/Dy_2O_3 (1:1) catalyst.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China.

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