Oxidative coupling of methane over LaF_3/La_2O_3 catalysts

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We studied the oxidative coupling of methane over the LaF_3/La_2O_3 (50 : 50) catalyst. The catalyst was found active even at 873 K. At 1023 K, the C_2 yield was 12.7% at 26.0% CH_4 conversion and 49.1% C_2 selectivity. It was found to be stable and had a lifetime not less than 50 h at 1023 K. The catalyst was effective in C_2H_6 conversion to C_2H_4. XRD results indicated that the catalyst was mainly rhombohedral LaOF. It is suggested that the catalyst has ample stoichiometric defects and generates active oxygen sites suitable for methane dehydrogenation.

Keywords: Oxidative coupling of methane; LaF_3; La_2O_3; rhombohedral LaOF

1. Introduction

The earth is rich in natural gas and rare-earths. The utilization of these resources is of economic and commercial interest. It is our aim to utilize the rare-earth compounds as catalysts to convert methane to value added products such as ethene [1].

The first methane coupling over a rare-earth oxide was reported by Fung and Yeh who used ThO_2/SiO_2 as catalyst [2]. Later on, Otsuka et al. investigated the catalytic process over various rare-earth metals and Sm_2O_3 was thought to be the most active compound [3]. It has been reported that the promotion of Sm_2O_3 and La_2O_3 with alkali or alkaline earth metals could improve the C_2 selectivity [4–14] and the use of chloride as promoter could further enhance the utility of the catalyst [4].

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It is generally accepted that the oxidative coupling of methane on catalysts involves the dehydrogenation of methane molecule at an active surface oxygen site, the coupling of two methyl radicals to produce an ethane molecule and subsequent oxidative dehydrogenation of ethane to ethene [3,6,15–19].

In this paper, we report the results of LaF_3/La_2O_3 catalysts in the methane oxidative coupling process.

2. Experimental

Catalysts were prepared by grinding the appropriate amounts of LaF_3 (Fluka, 99.9%) and La_2O_3 (Fluka, 99.98%) in a mortar. A suitable amount of distilled water was added to turn the powder into paste. The paste was dried overnight in an oven at 383 K and pressed into small pellets before being calcinated at 1073–1173 K for 6 h. The pellets were then crushed and sieved to a grain size of 20–40 mesh before use.

Unless mentioned otherwise, the reactions were performed in a fixed-bed quartz reactor at atmospheric pressure with reaction temperature 1023 K, $N_2 : CH_4 : O_2 = 12.0 : 2.6 : 1.0$, weight of catalyst of 500 mg and a gas flowrate of 50 ml/min.

A Shimadzu GC-8A gas chromatograph using a thermal conductivity detector (MS 5A and Porapek Q as columns) was employed to analyse the gaseous products. The specific surface area of the catalysts was measured by the BET process using the flow adsorption method with N_2 as the adsorbate and helium as the carrier gas. Phase composition of the catalysts was determined with X-ray diffraction (RU-200B, D/MAX-B, RIGAKU), while X-ray photoelectron spectroscopy (Leybold Heraeus-Shenyang SKL-12) was used to characterize the catalyst surfaces.

At 1023 K, the blank reactor was found to have a CH_4 conversion of 1.0% and a C_2 selectivity of 68.2%, giving a C_2 yield of 0.7%.

3. Results and discussion

Fig. 1 shows the effect of composition on the catalytic activity and selectivity of LaF_3/La_2O_3 catalysts. The 25 : 75 and 50 : 50 catalysts gave a C_2 yield of 12.7%. One can easily see that there was a sudden change in performance when the LaF_3 content was above 50 mol%. There were large declines in CH_4 conversion rate and certain enhancement in total C_2 selectivity. The net results were poor CH_4 and O_2 conversions and poor C_2 yield. A carbon balance of $100 \pm 1\%$ was obtained for every run over the catalysts. Beside the C_2's, the side products were CO_2, CO (detected only when below 15 mol% LaF_3) and H_2O, no higher hydrocarbons were observed.

According to the LaF_3 composition, the performance of catalysts can be divided into three stages: LaF_3 content below 15 mol%, from 15 to 50 mol% and above

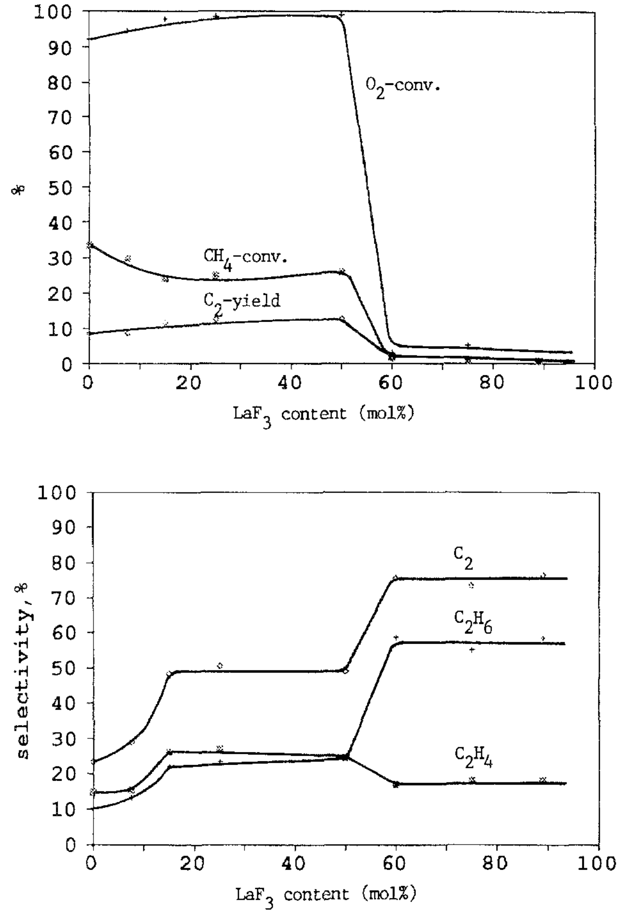


Fig. 1. Effect of LaF_3 content in LaF_3/La_2O_3. $T = 1023$ K, $CH_4 : O_2 = 2.6 : 1.0$, $W/F = 0.6$ g s/ml.

50 mol%. Between 0 and 15 mol%, CH_4 conversion dropped by 27.5% (from 33.4 to 24.2%) and C_2 selectivity increased by 88.3% (from 25.7 to 48.4%). Between 15 and 50 mol%, both CH_4 conversion and C_2 selectivity stayed roughly at 25 and 49% respectively, mainly due to the exhaustion of oxygen. When the LaF_3 content had exceeded 50 mol%, there was a sudden drop (from 26.0 to 1.9%) in CH_4 conversion and a large increase (from 49.1 to 75.6%) in C_2 selectivity. As a result, the C_2 yield increased steadily from 8.6 to 12.7% as the LaF_3 content was raised from 0 to 50 mol% and suffered a sudden drop (from 12.7 to 1.5%) mainly due to the large decrease in CH_4 conversion when the LaF_3 content was above 50 mol%. Other observations worth mentioning are the decline of O_2 conversion (from 99.1 to about 3.1%) and the decrease in C_2H_4/C_2H_6 ratio (from 1.0 to 0.3) when the LaF_3 content was increased from 50 to 60 mol%.

The measurement of the specific area of the catalysts (fig. 2) shows that there

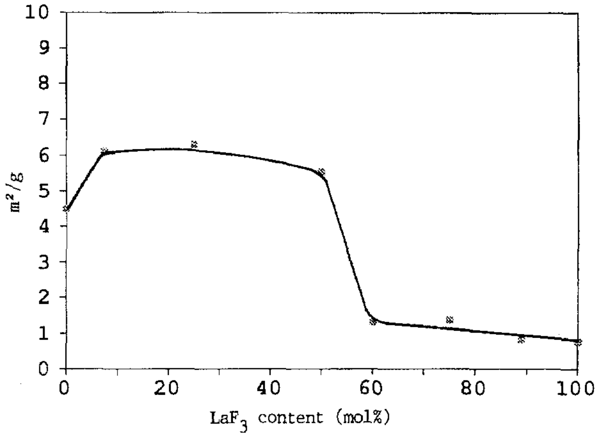


Fig. 2. The specific surface area of LaF_3/La_2O_3.

was a 25% increase at low LaF_3 content and at 76% decrease (from about 5.5 to 1.3 m^2/g) when the LaF_3 content was above 50 mol%. XRD data reveal that for "pure" La_2O_3, there existed La_2O_3 and $La(OH)_3$ crystals before calcination. After calcination, $La(OH)_3$ lines disappeared due to dehydration. As the content of LaF_3 increased, the presence of LaOF phase was observed (fig. 3). Hence LaOF was generated according to the chemical equation

$$LaF_3 + La_2O_3 \rightarrow 3LaOF\,.$$

It is well known that LaOF exists in rhombohedral form at low LaF_3 content and is changed to tetragonal when the LaF_3 content is above 50 mol%. In our case, at 75 mol%, cubic LaF_2 crystal was found. For a 50 : 50 LaF_3/La_2O_3 mixture, only rhombohedral LaOF was detected by XRD before and after the reaction, suggesting this active catalyst is essentially rhombohedral LaOF. Apparently, rhombohedral LaOF was favoured in the fluorine deficient stage while tetragonal LaOF was formed in the fluorine rich stage. The initial increase in specific surface area is due to rhombohedral LaOF formation and the sintering of tetragonal LaOF and cubic LaF_2 could be the reason for a large decrease in specific surface area.

The unit cells of rhombohedral and tetragonal LaOF are shown in fig. 4 (after Wells [20]). It should be noted that in the rhombohedral case, each La^{3+} ion has a F^- and an O^{2-} ion as its nearest neighbour while in the tetragonal case, F^- and O^{2-} ions exist in alternate layers, resulting in some La^{3+} ion having either O^{2-} or F^- ions in its closest vicinity. We suggest that the $[La^{3+}F^-O^{2-}]$ entities are active sites for methane oxidative dehydrogenation. The loss of these entities in tetragonal LaOF resulted in the drop of CH_4 conversion. The excess F atoms occupying the midpoints of the edges of the outer tetragon would likely impart an unfavourable steric influence on the active sites, if there is any.

Fig. 5 shows the XPS spectra of the LaF_3/La_2O_3 catalysts with different LaF_3

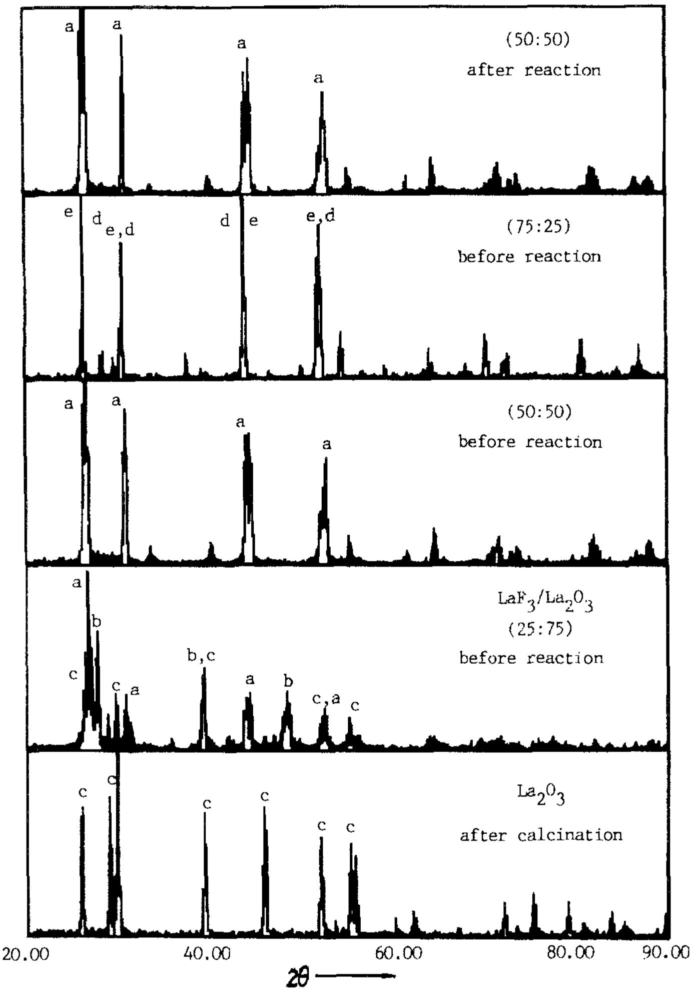
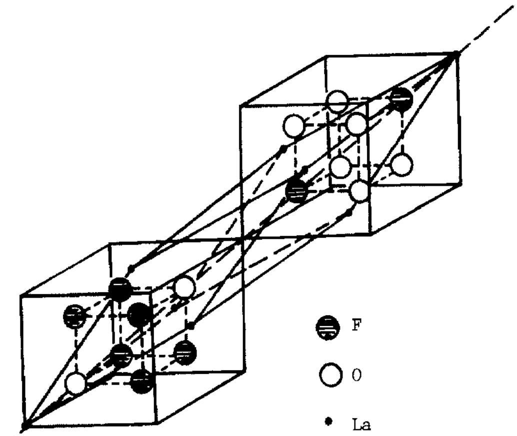


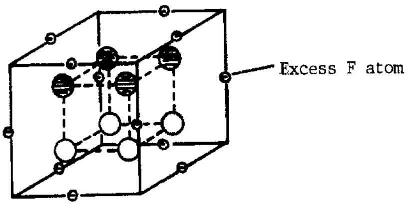
Fig. 3. XRD spectra of LaF_3/La_2O_3 catalysts. (a) Rhombohedral LaOF, (b) $La(OH)_3$, (c) La_2O_3, (d) tetragonal LaOF, (e) cubic LaF_2.

contents. As expected, the F 1s signal at 684.9 eV binding energy increased in intensity as the LaF_3 content in the catalysts increased. The La $3d_{5/2}$ signal of pure La_2O_3 is at 834.9 eV with a satellite peak at 838.7 eV. As the LaF_3 content increased, the 834.9 eV peak shifted to higher binding energy, indicating the increase of fluoride ions in the vicinity of the lanthanum ions. At 75 mol% LaF_3 content, it was at 836.1 eV. The La $3d_{5/2}$ peak for pure LaF_3 was at 837.3 eV and was without any satellite peak.

It is clear that the existence of rhombohedral LaOF or tetragonal LaOF/cubic LaF_2 can enhance the C_2 selectivity but decrease the CH_4 conversion. There was near an order of magnitude reduction in CH_4 (93%) and O_2 (97%) conversions between 50 and 60 mol% LaF_3 content and such an amount could not be accounted



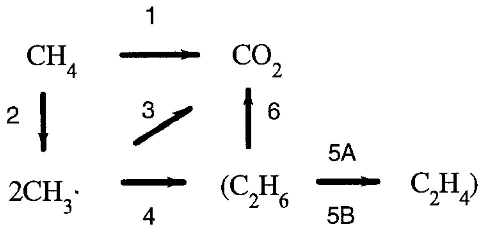
(a) rhombohedral



(b) tetragonal

Fig. 4. Structures of the two forms of LaOF. (After Wells [20], lines were added to show the rhombohedral unit cell and the position of the lanthanum ions.)

for solely by the three quarter decrease in specific surface area. However, the increase in C_2 selectivity can be explained by the drop of specific surface area. According to the heterogeneous–homogeneous reaction scheme, for example, one that was referred to by Lin et al. [21] and Iwamatsu et al. [22]:



heterogeneous steps: 1, 2, 3, 5A, 6
homogeneous steps: 4, 5B.

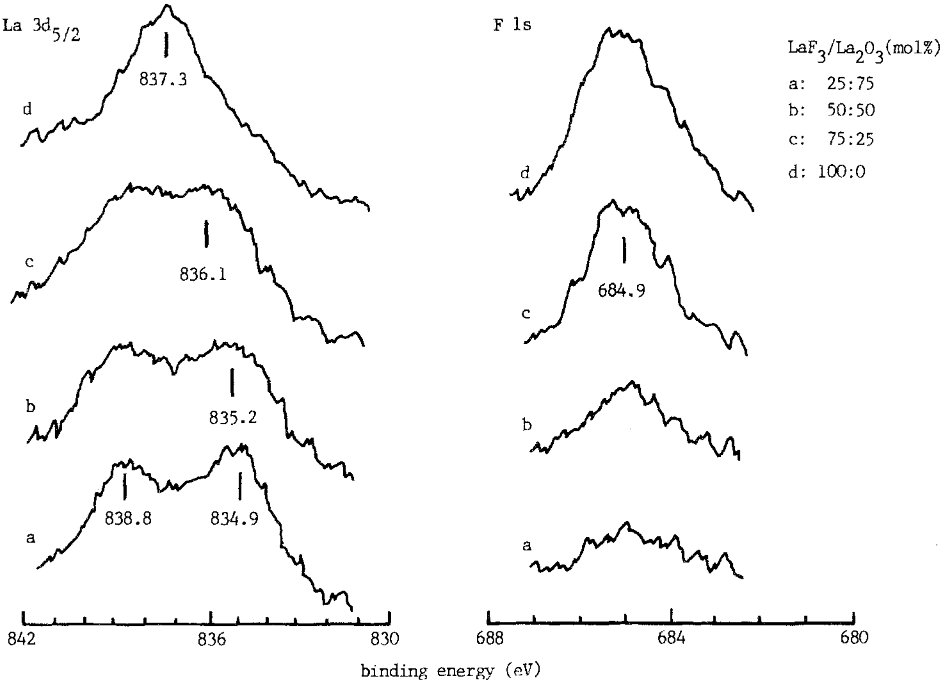


Fig. 5. XPS spectra of LaF_3/La_2O_3 catalysts.

The diminution in specific surface area will make the heterogeneous steps unfavourable and relatively speaking, enhance the homogeneous formation of C_2H_6. Hence as the specific surface area gets smaller, we see a reduction in CH_4 and O_2 conversion (steps 1 and 2 retarded) and an increase in C_2 selectivity (step 4 enhanced while steps 3, 5A and 6 retarded). The reduction in C_2H_4 selectivity indicates that step 5 is more heterogeneous than homogeneous in nature over the LaF_3/La_2O_3 catalysts.

The LaF_3/La_2O_3 (50 : 50) catalyst was chosen to perform experiments to find out the effect of temperature on the reactivity. At 1023 K, this catalyst has a life time not less than 50 h as shown in fig. 6.

The effect of the reaction temperature is shown in fig. 7. One can see that at 873 K, the O_2 conversion was over 95% and this is why CH_4 conversion did not change much above 873 K. The highest C_2 yield of about 13% occurred at temperature ranging from 1023 to 1073 K and the highest C_2 selectivity occurred at about 1073 K. From 823 to 1073 K, there was a gradual increase in C_2 selectivity and the increase in temperature favoured the formation of C_2H_4. Beyond 1073 K, C_2H_4 selectivity declined. As for the C_2H_6 selectivity, it went through a maximum at 973 K, and started to decline; presumably partly due to dehydrogenation to C_2H_4 and partly due to complete oxidation. An increase in the C_2 selectivity with temperature was observed before in the oxidative coupling of methane over La_2O_3 by

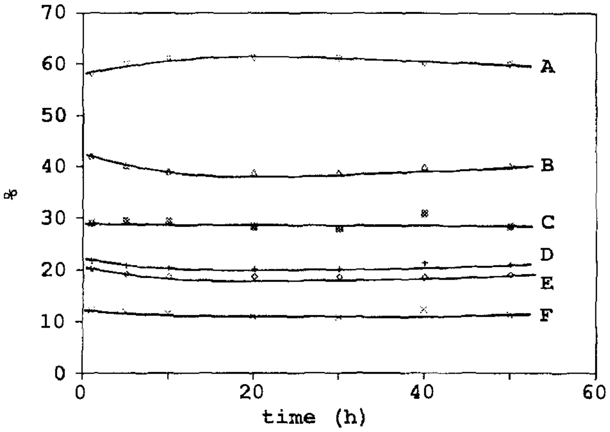


Fig. 6. Life testing on LaF_3/La_2O_3. (A) CO_2 selectivity, (B) C_2 selectivity, (C) CH_4 conversion, (D) C_2H_4 selectivity, (E) C_2H_6 selectivity, (F) C_2 yield. Reaction conditions: $T = 1023$ K, $CH_4 : O_2 = 2.6 : 1.0$, $W/F = 0.6$ g s/ml.

Lin et al. [17]. They pointed out that the formation of methyl peroxy radicals (CH_3OO) rendered the complete oxidation of surface methyl radicals unfavourable at higher temperatures.

In view of the high activity at relatively low temperature and the effective conversion of C_2H_6 to C_2H_4, the catalyst probably possesses sites which are abundant and active for the generation of $CH_3\cdot$ and $C_2H_5\cdot$ from CH_4 and C_2H_6 respectively. Since the rhombohedral structure existed when the LaF_3 content was less than 50 mol%, it is reasonable to expect that La and F vacancies in the LaOF lattice exist due to deficiency of LaF_3. Such vacancies can trap holes and electrons, leading to the generation of active oxygen species:

O_s^{2-} [h] O_s^- +[e]
$La^{3+}\ F_s^- \rightarrow La^{3+}\ F_s^-$
normal lattice

O_s^{2-} [h] O_s^- +[e]
$La^{3+}[e] \rightarrow La^{3+}[e]$
$\downarrow \frac{1}{2}O_2$

O_s^{2-}
$La^{3+}O_s^-$

[h]: hole
s: surface species

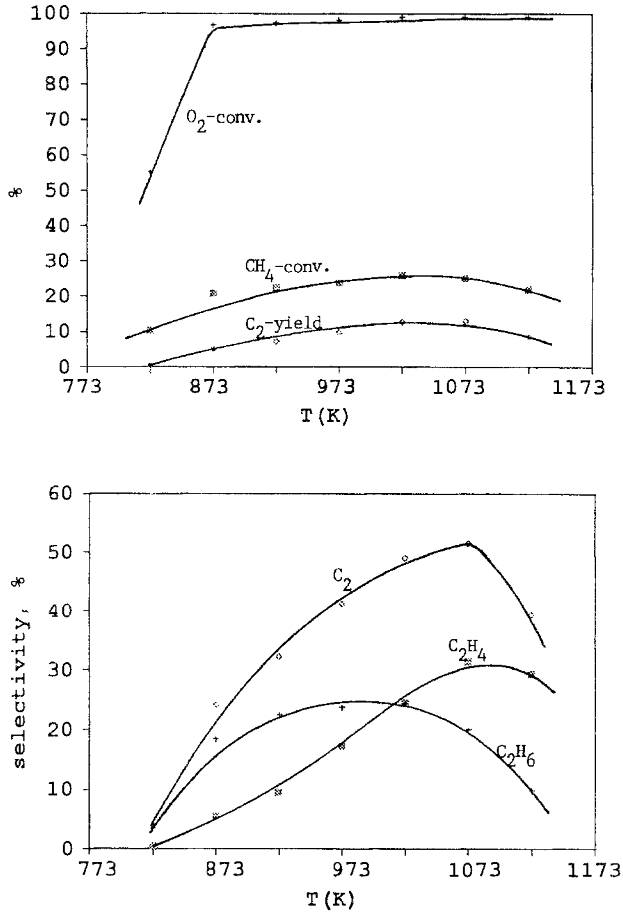


Fig. 7. Effect of temperature on performance of LaF_3/La_2O_3 (50 : 50) catalyst. $CH_4 : O_2 = 2.6 : 1.0$, $W/F = 0.6$ g s/ml, carbon balance = $100 \pm 1\%$.

A possible candidate, O_s^-, which was first proposed by Ito et al. [23] as the active species for methane oxidative coupling, may be formed by an O_s^{2-} attracting a hole from the lattice. In the absence of concrete experimental evidence, further speculation is not warranted; suffice it to say that a LaF_3 deficient LaOF compound has the potential of exhibiting a variety of active sites. The characterization of these active sites by suitable physico-chemical methods will be our next phase of work.

4. Conclusion

The LaF_3/La_2O_3 (50 : 50) catalyst was found to be essentially rhombohedral

LaOF and was active in the conversion of CH_4 and C_2H_6. We suggest that there are stoichiometric defects in the LaOF lattice, suitable for the generation of active oxygen species for the dehydrogenation of methane and ethene.

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