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A study of the oxidative coupling of methane over $SrO–La_2O_3/CaO$ catalysts by using CO_2 as a probe

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20%SrO–20%La_2O_3/CaO catalyst (SLC-2), prepared by impregnation, has shown 18% CH_4 conversion and 80% C_2-selectivity for the oxidative coupling of methane (OCM) at 1073–1103 K with $CH_4 : O_2$ molar ratio = 9 : 1 and total flow rate of 100 ml/min. Addition of SrO onto La_2O_3/CaO (LC) catalyst strengthens the surface basicity and leads to an increase in CH_4 conversion and C_2-selectivity. Meanwhile, the reaction temperature required to obtain the highest C_2-yield increases with increasing SrO content. The formation of carbonate on the catalyst surface is the main reason for the deactivation of LC and SLC catalysts. If the amount of CO_2 added into the feed is appropriate and the reaction temperature is high enough, there is no deactivation at all. In such case, the added CO_2 will suppress the formation of CO_2 produced via the OCM reaction, therefore, improves the C_2-selectivity. The FT-IR spectra of CO_2 adspecies recorded at different temperatures show that CO_2 interacts easily with the catalyst surface to form different carbonate adspecies. Unidentate carbonate is the main CO_2 adspecies formed on the catalyst surface. On the LC catalyst surface, the unidentate carbonate was first formed on Ca^{2+} cations at room temperature. If the temperature is higher than 473 K, it will form on La^{3+} cations. On the SLC catalyst surface, if the temperature is lower than 573 K, only the unidentate carbonate formed on Ca^{2+} cations could be observed. When the temperature is higher than 673 K, it will then form on Sr^{2+} cations. This suggests that the unidentate carbonate can migrate on the LC and SLC catalyst surface on one hand, and on the other hand, that the surface composition of SLC catalysts is dynamic in nature. On the basis of both the decomposition temperatures of the carbonate species, and the temperature dependence of the $\Delta\nu$ value which is the difference of symmetric and asymmetric stretching frequencies of surface carbonates, the in situ FT-IR technique offered two approaches to measure the surface basicity of the SLC catalyst. The results thus obtained are in good agreement with that of CO_2-TPD. The role of the surface basicity of the SLC catalyst is also discussed.

Keywords: oxidative coupling of methane (OCM); $SrO–La_2O_3/CaO$; basicity; CO_2-TPD; carbonates; in situ FT-IR; CO_2 adspecies

1. Introduction

The oxidative coupling of methane (OCM), after having been studied extensively by catalytic chemists in the world since 1982, is now a mature field. Recently, it

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was pointed out for the first time by Lunsford that it is possible to achieve 20% CH_4 conversion and 80% C_2-selectivity under 1 atm of undiluted reagent stream and operating in a co-feed mode [1]. The improvement of C_2-selectivity will still be the most crucial advancement in catalyst development in the near future. From the academic point of view, this is also a strong and serious challenge for catalytic chemists. OCM is the most complicated and difficult catalytic reaction ever studied. This reaction has many unique and distinct features such as: the co-existence of hetero- and homogeneous reactions [2,3]; the relatively high reaction temperature (usually above 973 K) and the hot spot temperature effect [4]; the co-existence of selective oxidation and total oxidation; different oxygen species which may be in dynamic equilibrium on the catalyst surface; basicity of the catalyst surface in most cases and poisoning by CO_2, an unavoidable by-product [5–14] and so on. To understand the OCM mechanism and to improve the reactivity and selectivity, the origin and effect of CO_2 are both key questions [1]. However, the effect of CO_2 is still debated. Many researchers thought that the basicity of the catalyst surface plays an important role in OCM. Bearns et al. reported that the C_2-selectivity over alkali earth metal oxides increased in the order BeO < MgO < CaO < BaO [6]. This is consistent with the order of their basicity. However, Campbell et al. found that hydrothermally treated La_2O_3 showed much higher activity and C_2-selectivity than CeO_2 [7–9]. Therefore, the activities of rare earth metal oxides are also parallel with their basicities.

The effect of carbonate formation on catalytic performance in OCM is recently an interesting subject. Yamashita et al. reported that there is a close relationship between the decomposition temperatures of carbonates and the catalytic activities [10]. The higher the decomposition temperature of the carbonate, the lower the reaction temperature required to reach a certain CH_4 conversion [10]. Korf et al. reported that addition of CO_2 into the feed resulted in a reversible deactivation of Li/MgO catalyst due to the formation of the corresponding carbonates [11]. They claimed that Li species usually exist on the surface in the form of its carbonate, and that the active sites result from the carbonate decomposition in O_2 atmosphere. Addition of CO_2 into the feed resulted in an increase in C_2-selectivity over MgO and Sm_2O_3/MgO catalysts [12]. Meanwhile, Aika et al. found that there is a decrease in C_2-selectivity over CaO supported alkaline earth metal oxide catalysts [13]. The authors also found that due to the reaction of CH_4 and CO_2, the addition of CO_2 into the feed over PbO–CaO and PbO–MgO catalysts resulted in an increase in C_2-yield [14].

In our previous study, we have shown that SrO additive greatly improves the catalytic performance of La_2O_3/CaO (LC) catalyst [15]. In this paper, we show that the SrO–La_2O_3/CaO (SLC) catalyst exhibits as high as 18% CH_4 conversion and 80% C_2-selectivity under 1 atm of undiluted reagents with $CH_4 : O_2$ molar ratio $= 9 : 1$ and total flow rate of 100 ml/min. Since the SLC catalyst mainly consists of alkaline earth metal oxides, the basicities and CO_2 adspecies are characterized by CO_2-TPD and in situ FT-IR technique. The effect of the addition of CO_2 in the feed on catalytic performance is investigated in this paper in order to gain an insight into the nature of the SrO promoter and the role of carbonates in the OCM-reaction.

2. Experimental

2.1. CATALYST PREPARATION AND BET SURFACE AREA MEASUREMENT

LC and SLC catalysts were prepared by impregnating CaO with a solution of Sr and La nitrates of desired ratios and left overnight. It was then dried and calcined at 1173 K for 2 h. The sample was ground, tableted, crushed and sieved to 40–60 mesh and stored in a desiccator before use. BET surface area measurement was performed on a Micromeritics ASAP-2000 instrument.

2.2. CATALYTIC EVALUATION

OCM was performed in a fixed-bed flow reactor system. A quartz reactor of 4 mm i.d. was used. The catalyst charge was usually 100 mg. To minimize the dead volume behind the catalyst bed and for placing a thermocouple, a tube was inserted upwards into the reactor. The total flow rate was 100 ml/min with $CH_4 : O_2$ molar ratio = 9 : 1 and the reaction was carried out at 1073 K under atmospheric pressure, unless otherwise specified. The effluent was analyzed on-line by GC with a TCD detector. CH_4 conversion and C_2-selectivity were calculated on the basis of carbon balance before and after reaction.

To study the influence of partial pressure of CO_2 in the feed, the reaction conditions were as follows: $T = 973–1103$ K; $F = 120$ ml/min; catalyst charge = 100 mg and $CH_4/O_2/CO_2/He = 90 : 10 : X : (20 - X)$ ml/min. In several cases, to amplify the effect of partial pressure of CO_2 in the feed, the total flow rate was 120 ml/min and the composition of the feed was adjusted to $CH_4/O_2/CO_2/He = 48 : 12 : X : (60 - X)$ ml/min.

2.3. X-RAY DIFFRACTION (XRD) MEASUREMENT

XRD measurements were performed on a Rigaku X-ray diffractometer using a Cu rotary target at room temperature. The operating conditions were 40 kV and 100 mA at a scanning rate of 8°/min.

2.4. CO_2-TPD

CO_2-TPD experiments were carried out in a quartz U-shape reactor. CO_2 with a purity of 99.95% was used and the desorbed CO_2 was detected by TCD. The catalyst charge was 200–500 mg. It was first pretreated in O_2 stream (30 ml/min) at

1073 K for 1 h, then flushed with He for 1 h. After the pretreatment, the temperature of the reactor was adjusted to the desired adsorption temperature under a flow of helium. Then CO_2 was introduced into the U-shape reactor and maintained for 5 min. After the CO_2 adsorption, the sample was cooled down to room temperature in He stream. When the baseline of the integrator was stable, the TPD run was promptly started at a heating rate of 8 K/min from room temperature to 1073 K. The desorption peak area was calibrated by decomposition of high purity $CaCO_3$. To confirm the desorbed species, several cases of CO_2-TPD were performed in a flow reactor system equipped with a multichannel mass spectrometer. The procedure used was the same as above. The data were collected, recorded and processed by an IBM computer system interfaced with the multichannel mass spectrometer.

2.5. CO_2 ADSPECIES OVER $SrO–La_2O_3/CaO$ CHARACTERIZED BY IN SITU FT-IR TECHNIQUE

In situ FT-IR measurements were carried out using a specially designed IR cell with NaCl windows. The cell can be heated up to 1073 K, and connected to a vacuum system for sample evacuation or adsorption study at variable pressures. The sample, pressed into a self-supporting wafer, was pretreated by calcining with O_2 at 1073 K for 2 h, followed by evacuation at 1073 K until its surface adspecies were almost completely removed. After the pretreatment, the sample was cooled down to room temperature under vacuum, and the background spectrum was recorded. CO_2 with a purity of 99.95% was then introduced into the IR cell and the sample was heated stepwise. The FT-IR spectra after CO_2 adsorption were recorded by a Bio-Rad FTS-7 infrared spectrometer with a resolution of 4 cm^{-1} and 16 scans. All the results presented in the text are in the form of subtracted spectra.

3. Results

3.1. CATALYTIC PERFORMANCE OF SLC CATALYSTS

Table 1 lists the catalyst codes and their BET surface areas. The surface area of CaO decreased strongly after impregnation with a solution of Sr and La nitrates and calcination at 1173 K for 2 h.

Table 2 lists the results of catalytic performance in OCM over $SrO–La_2O_3$/CaO catalysts. The results show that CH_4 conversion, C_2-selectivity, C_2-yield and the ratio of $C_2^=/C_2$ increase with increasing amount of SrO. The SLC-2 catalyst shows good results with 18% CH_4 conversion and 80% C_2-selectivity. These results are very close to the data recently summarized by Lunsford [1].

Both the CH_4 conversion and C_2-selectivity over SLC-2 catalyst were lower than that of LC catalyst if the reaction was performed at 973 K. However, the for-

Table 1
Catalyst codes and their BET surface areas

Catalyst[a]	Catalyst composition (%)			Surf. area (BET) (m^2/g)
	CaO	La$_2$O$_3$	SrO	
LC	80	20	0	13.3
SLC-1	75	20	5	7.7
SLC-2	60	20	20	4.8
CaO	100	0	0	19.7
La$_2$O$_3$	0	100	0	3.7
SrO	0	0	100	5.7

[a] CaO, La$_2$O$_3$ and SrO were prepared by calcining CaO, La(NO$_3$)$_3$ and Sr(NO$_3$)$_2$ respectively at 1173 K for 2 h.

mer exhibited the highest catalytic performance at 1073–1103 K. This implies that the SLC-2 catalyst requires a higher reaction temperature to activate and/or produce their active sites than LC catalyst in OCM.

3.2. CO$_2$-TPD

CO$_2$-TPD was performed at different temperatures of initial exposure of the sample to CO$_2$, ranging from room temperature to 873 K. Fig. 1 shows the profiles of CO$_2$-TPD for various catalysts obtained at room temperature. The profiles obtained at higher temperatures also follow the same dependence on SrO content in

Table 2
Catalytic performance of LC and SLC catalysts at various reaction temperatures

Catalyst	Temp. (K)	X_{CH_4} (%)	S_{C_2} (%)	Y_{C_2} (%)	C_2H_4/C_2H_6
LC	973	12.5	59.7	7.5	0.29
	1023	14.7	67.2	9.9	0.46
	1073	14.8	67.4	10.0	0.54
	1103	15.0	66.7	10.0	0.57
SLC-1	973	10.4	55.2	5.8	0.21
	1023	15.6	73.3	11.4	0.45
	1073	16.8	77.3	12.9	0.62
	1103	16.5	77.1	12.7	0.64
SLC-2	973	6.4	49.2	3.1	0.10
	1023	11.6	69.5	8.1	0.29
	1073	18.5	78.4	14.2	0.63
	1103	17.9	79.5	14.2	0.73

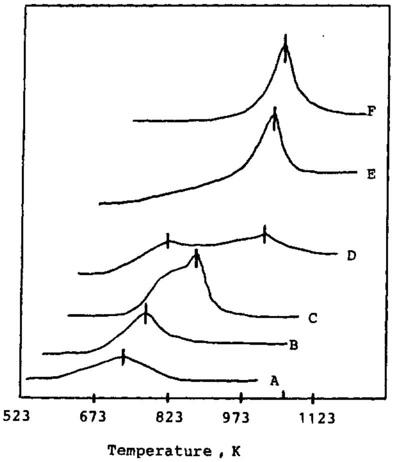


Fig. 1. The profiles of CO$_2$-TPD for various catalysts obtained at room temperature. (A) La$_2$O$_3$; (B) LC; (C) CaOX(1/4); (D) SLC-1; (E) SLC-2; (F) SrO.

the catalyst. The CO$_2$ adsorption capacity of various catalysts is listed in table 3. For comparison, these data are given on the basis of both catalyst weight and surface area. In most of the TPD profiles, desorption of CO$_2$ occurred in the temperature range of 673–1123 K, which can be divided into two parts: low temperature range of 673–973 K and high temperature range of 973–1123 K. In the case of La$_2$O$_3$, CaO and LC catalysts, CO$_2$ desorption only takes place at the low temperature range and in the case of SrO and SLC-2 catalysts, it takes place at the high temperature range. While in the case of SLC-1, it takes place partly in the low temperature range and partly in the high temperature range. The higher the SrO content, the more CO$_2$ desorbed at the high temperature range. This is thus evidence that the addition of SrO onto LC increases the basic strength of the catalyst surface. According to the temperature of CO$_2$ desorption at peak maximum, the order of basic strength of the catalysts studied is as follows:

$$\mathrm{SrO; SLC\text{-}2 > SLC\text{-}1 > CaO > LC > La_2O_3}.$$

The amount of CO$_2$ desorbed at low temperature is relatively large for the SLC-1 catalyst as shown in table 3. This implies that the addition of a little amount of SrO promotes the CO$_2$ adsorption capacity of CaO in the catalyst. A large amount of

Table 3
CO$_2$ adsorption capacity of various catalysts at room temperature

	Catalyst					
	CaO	La$_2$O$_3$	SrO	LC	SLC-1	SLC-2
μmol/g	74	16.2	22.4	9.4	15.8	10.7
μmol/m^2	3.8	4.4	4.0	0.7	2.0	2.2

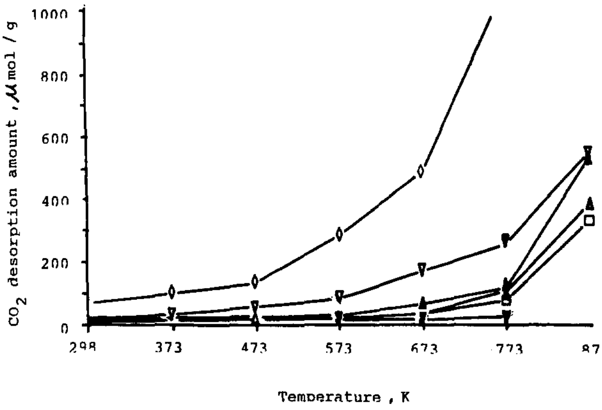


Fig. 2. The dependence of CO_2 adsorption capacity on the temperatures of initial exposure of various catalysts to CO_2. (◇) CaO, (▽) La_2O_3, (▼) SrO, (▲) LC, (△) SLC-1, (□) SLC-2.

SrO will inhibit the CO_2 adsorption capacity of CaO since most of its surface will be covered. Therefore, we do not detect any CO_2 desorbed at the low temperature range.

Fig. 2 shows the dependence of CO_2 adsorption capacity on the temperature of initial exposure of various catalysts to CO_2. Both CaO and LC catalysts are more sensitive to the exposure temperature as we can see from the figure. If the exposure temperature is higher than 573 K, the adsorption capacity will increase sharply with increasing exposure temperature. XRD analysis showed that high temperature of exposure of the sample to CO_2 will lead to the formation of bulk carbonates (table 4). If the adsorption is performed at lower temperatures, the profiles of CO_2-TPD will correspond to the decomposition of surface carbonates. Since the temperature of CO_2 desorption is much lower than the decomposition temperature of bulk carbonate, it is obvious that decomposition of the surface carbonates formed during CO_2 adsorption is much easier than that of bulk carbonates.

3.3. EFFECT OF THE PARTIAL PRESSURE OF CO_2 IN THE FEED ON THE CATALYTIC PERFORMANCE OF SLC CATALYSTS

Fig. 3 shows that the CH_4 conversion, the C_2-selectivity and the ratio of $C_2^=/C_2$ decrease remarkably with increasing CO_2 partial pressure in the feed over LC cat-

Table 4
XRD results of LC and SLC catalysts after CO_2 chemisorption at 673 K for 0.5 h

Catalyst	Main phases in bulk phase
LC	CaO $CaCO_3$ La_2O_3
SLC-1	CaO $CaCO_3$ La_2O_3 SrO
SLC-2	CaO $CaCO_3$ La_2O_3 SrO $SrCO_3$

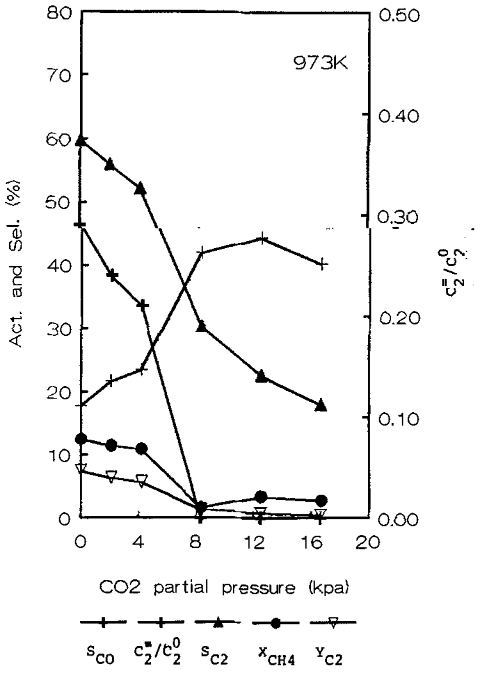


Fig. 3. Effect of partial pressure of CO$_2$ in the feed on the catalytic performance of LC catalyst at 973 K (reaction condition: $F = 120$ ml/min; catalyst charge $= 100$ mg and CH$_4$/O$_2$/CO$_2$/He $= 90 : 10 : X : (20 - X)$ ml/min).

alyst at 973 K. At 1073 K, the effect of CO$_2$ partial pressure in the feed on the catalytic performance over the SLC-1 catalyst is more severe than over the LC catalyst, as we can see from fig. 4. For the SLC-2 catalyst with higher SrO loading, the effect of CO$_2$ partial pressure is severe even at 1103 K as shown in fig. 5. It seems that the poisoning effect of CO$_2$ on SLC catalysts strongly depends on the reaction temperature and the SrO content in the catalyst.

To amplify the effect of CO$_2$ partial pressure on SLC catalysts, the feed composition was adjusted to CH$_4$/O$_2$/CO$_2$/He $= 48 : 12 : X : (60 - X)$. Fig. 6 shows the results obtained at 1073 K. The C$_2$-yield slightly increases with increasing partial pressure of CO$_2$ for the LC catalyst. Meanwhile, there is a special value of CO$_2$ partial pressure in the feed for SLC-1 and SLC-2 catalysts. At that CO$_2$ partial pressure, the C$_2$-yield sharply decreased. The higher the SrO content in SLC catalysts, the smaller the special value of CO$_2$ partial pressure in the feed. It is also interesting to note that the CO-selectivity increases remarkably with increasing partial pressure of CO$_2$ (see fig. 5).

3.4. CHARACTERIZATION OF CO$_2$ ADSPECIES BY USING IN SITU FT-IR

Fig. 7 shows the background spectra of the samples studied after pretreating and evacuating at 1073 K. There are still some adspecies remained on the surface

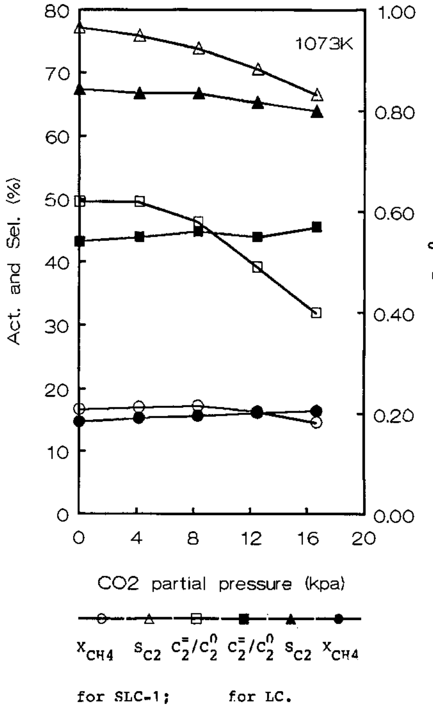


Fig. 4. Effect of partial pressure of CO$_2$ in the feed on the catalytic performance of LC and SLC-1 catalysts at 1073 K (reaction condition: $F = 120$ ml/min; catalyst charge $= 100$ mg and CH$_4$/O$_2$/CO$_2$/He $= 90 : 10 : X : (20 - X)$ ml/min).

after severe pretreatment and evacuation. Fig. 8 shows the FT-IR spectra of CO$_2$ (1 kPa) adsorbed on CaO surface at different temperatures. CO$_2$ easily forms various adspecies on the CaO surface [16]. It seems clear that (1) the main bands at 1469 and 1405 cm^{-1} which appear at room temperature can be assigned to symmetric and asymmetric stretching vibration modes of unidentate carbonate species (I) (see scheme 1) coordinated to calcium ions; (2) the band at 1630 cm^{-1} comes from the interaction between CO$_2$ and the hydroxyls of the CaO surface (III); (3) the band at 1781 cm^{-1} can be assigned to bridged carbonate species (IV); in addition, the band at 2330–2500 cm^{-1} comes from gaseous CO$_2$ (V). The intensity of the bands concerned lead us to the conclusion that CO$_2$ interacts with CaO surface at room temperature forming mainly unidentate carbonate adspecies. With increasing temperature under vacuum, the band at 1469 cm^{-1} shifts to lower frequency and the intensity of the bands at 1630 and 1781 cm^{-1} decreased. When the catalyst was heated up to 773 K, the latter two bands disappeared while the bands corresponding to the unidentate carbonate at 1469 and 1405 cm^{-1} overlapped to give a single peak at 1459 cm^{-1}. This indicates that decomposition begins at 773 K for uni-

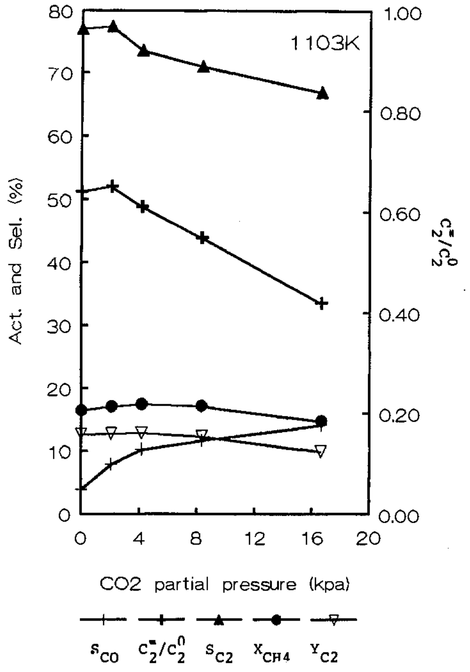


Fig. 5. Effect of partial pressure of CO$_2$ in the feed on the catalytic performance of SLC-2 catalyst (reaction condition: $F = 120$ ml/min; catalyst charge = 100 mg and CO$_2$/He = 90 : 10 : X : $(20 - X)$ ml/min).

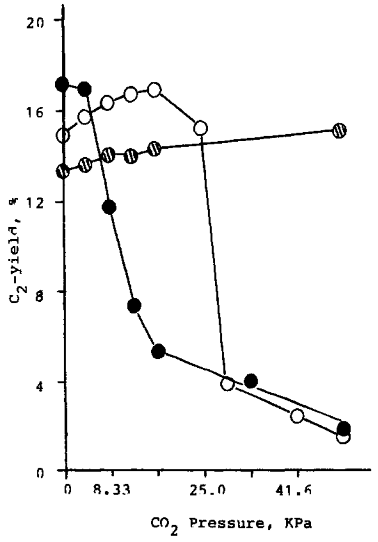


Fig. 6. Effect of high partial pressure of CO$_2$ in the feed on the C$_2$-yield of various catalysts. (◍) LC; (○) SLC-1; (●) SLC-2 (reaction condition: $F = 120$ ml/min; catalyst charge = 100 mg and CH$_4$/O$_2$/CO$_2$/He = 48 : 12 : X : $(60 - X)$ ml/min).

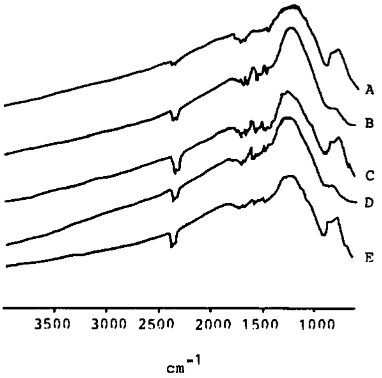


Fig. 7. The background spectra of the samples after pretreating and evacuating at 1073 K. (A) CaO; (B) La_2O_3; (C) SrO; (D) LC; (E) SLC-2. Spectra were recorded at 1023 K.

dentate carbonate species. When the temperature was increased to 923 K, the unidentate carbonate decomposed totally.

For La_2O_3 and SrO catalysts, the interaction between CO_2 and the catalyst surface is almost the same as that in the case of CaO. Only small differences are observed in terms of frequency and the thermal stabilities of adspecies formed. Table 5 summarizes the results.

The FT-IR spectra for the interaction between CO_2 and the surface of the LC

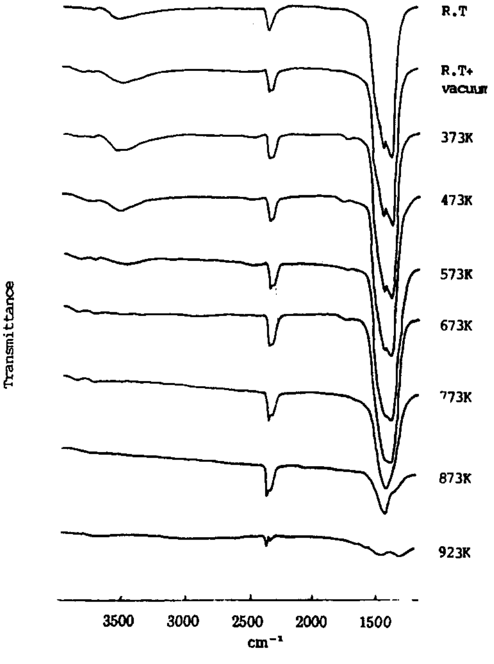
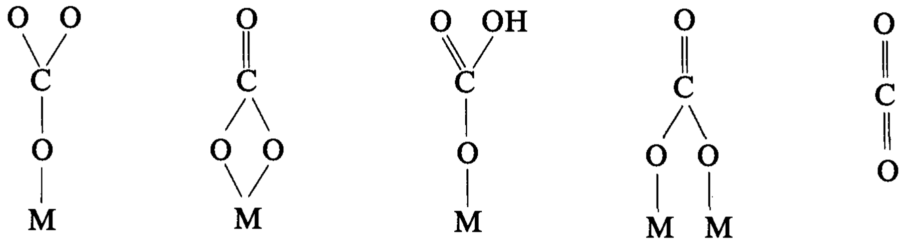


Fig. 8. The FT-IR spectra of CO_2 (10 Torr) adsorbed on CaO surface at different temperatures.



I unidentate carbonate;

II bidentate carbonate;

III bicarbonate;

IV bridging carbonate;

V gasesous CO$_2$

Scheme 1.

Table 5
CO$_2$ adspecies on various catalysts (cm^{-1})

	Unidentate carbonate I		Bidentate carbonate II	Bicarbonate III		Bridging carbonate IV	Gaseous CO$_2$ V
CaO							
r.t.	1469	1405		1630	1781	2367	2340
773 K	1459	–		–	–	2366	2340
923 K	–	–		–	–	2366	2337
La$_2$O$_3$							
r.t.	1495	1389	1565	1630			2349
373 K	1478	1399	1565	–		2364	2339
673 K	1461	1400	–	–		2364	2341
773 K	–	–	–	–		2367	2336
SrO							
r.t.	1452	1356	1514	1640		1771	2352
773 K	1442	–	–	–		2364	2339
923 K	1456	–	–	–	–	2363	2332
LC							
r.t.	1470	1407	1567			2368	
473 K	1499	1412	1567			2370	2333
573 K	1499	1413	–			2370	2333
773 K	–	–	–			2368	2333
SLC-2							
r.t.	1467	1404				2368	
473 K	1464	1411				2365	
573 K	1455	1411				2368	2334
773 K	1462	–				2370	2332

catalyst are similar to that of CaO at low temperatures as we can see from table 5. Therefore, for LC catalyst, CO_2 initially reacts with the CaO surface to form carbonate adspecies (at 1470 and 1407 cm^{-1}, compared with CaO at 1469 and 1405 cm^{-1} for unidentate carbonate). The CO_2 adspecies will migrate onto lanthanum cations at 473 K (at 1499 and 1412 cm^{-1}, compared with La_2O_3 at 1478 and 1399 cm^{-1}). The carbonate species thus formed will decompose completely under vacuum when the temperature is further increased to 773 K. The decomposition temperature of carbonate species on LC catalyst is lower than that of CaO catalyst. This is mainly due to the formation of surface unidentate carbonate species coordinated to lanthanum ions on LC catalyst. This is in agreement with the results obtained from CO_2-TPD experiments.

The FT-IR spectra of CO_2 adspecies on the surface of SLC catalyst also followed the same trend as mentioned in the case of the LC catalyst. At room temperature, only carbonate species coordinated to calcium cations with bands at 1467 and 1404 cm^{-1} could be observed. When the temperature was increased to 673 K, these bands changed gradually into a sharp band centered at 1463 cm^{-1} and a shoulder at 1409 cm^{-1}. Further increase in temperature up to 873 K shifted the band at 1463 cm^{-1} toward lower frequency, and the shoulder at 1409 cm^{-1} disappeared. The band at 1453 cm^{-1} arises from unidentate carbonate species coordinated to strontium cations. When the temperature was increased to 973 K, all the carbonate species decomposed. Therefore, for SLC catalyst, CO_2 reacts initially with the CaO surface at room temperature to form $CaCO_3$. Part of the CO_2 adspecies then migrates and forms $La_2O_2CO_3$. At 673 K, both surface $CaCO_3$ and $La_2O_2CO_3$ disappeared, and surface carbonate $SrCO_3$ was formed. When the temperature was further increased to 973 K surface $SrCO_3$ species decomposed.

3.5. CHARACTERIZATION OF THE BASICITY BY USING IN SITU FT-IR TECHNIQUE

It is well known that $\Delta\nu$, which is the difference of the symmetric and asymmetric stretching frequencies of surface carbonate, decreases if the partial electric charge on the lattice oxygen increases [16,17]. The smaller the value of $\Delta\nu$, the stronger the electron donating ability of the catalyst surface. Therefore, the magnitude of $\Delta\nu$ is directly related to the Lewis basicity of the catalyst surface. Fig. 9 shows the temperature dependence of $\Delta\nu$ for various catalysts. It is clear from fig. 9 that $\Delta\nu$ of SrO decreases at the fastest rate with increasing temperature. This implies that the density of the partial electric charge on the lattice oxygen of SrO is the highest among the catalysts tested. In other words, the basic strength of the SrO surface is the strongest. Since $\Delta\nu$ decreases with increasing temperature, this means that higher temperature is in favor of increasing the electric density on lattice oxygen, and therefore, the surface basicity. The catalytic performance of SLC catalyst is thus greatly improved.

The dependence of $\Delta\nu$ on temperature is quite unique for La_2O_3 and LC catalysts, since they do not follow the same trend as that for SrO and CaO catalysts.

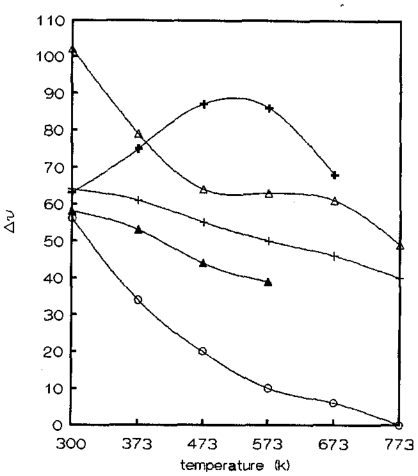


Fig. 9. The dependence of $\Delta\nu$ of various catalysts on temperature. (+) CaO; (△) La_2O_3; (○) SrO; (+) LC; (▲) SLC-2.

This also gives us a clue that the mechanism and nature of oxidative coupling reaction of methane over La_2O_3 and LC catalysts may follow a different line.

4. Discussion

4.1. CHARACTERIZATION OF THE BASICITY OF $SrO–La_2O_3/CaO$ CATALYSTS

From the temperatures of the CO_2 desorption peak in TPD, the ordering of the basic strengths of various oxides concerned are as follows:

$$SrO; SLC\text{-}2 > SLC\text{-}1 > CaO > La_2O_3; LC\,. \qquad (1)$$

CO_2-TPD shows that the SLC-2 catalyst has the strongest basic sites and is mainly due to the addition of SrO oxide. Meanwhile, the LC catalyst has the weakest basic sites and is mainly due to La_2O_3 partially covering the surface of CaO.

In situ FT-IR study of CO_2 adspecies offers us two approaches to measure the relative basic strengths of the catalyst surface. We may estimate the basic strengths either from the thermal stability of the surface carbonate formed or from the dependence of $\Delta\nu$ on temperature. From the in situ FT-IR study on the thermal stability of surface carbonates, the basic strengths of various oxides concerned are in the following order:

$$SrO; SLC\text{-}2 > La_2O_3; LC > CaO\,. \qquad (2)$$

While from the dependence of $\Delta\nu$ on temperature, we have obtained the order of basic strengths of various oxides concerned as follows:

$$SrO; SLC\text{-}2 > CaO\,. \tag{3}$$

Comparing the above-mentioned three ordering sequences, the basic strengths of SrO and SLC-2 catalysts are higher than that of the CaO catalyst. There are some contradictory results for La_2O_3, LC and CaO. This implies that the three methods are only applicable fully for the oxides with cations belonging to the same group in the periodic table. Sr and Ca belong to the same group, so all the three methods are applicable. La is not belonging to the same group as Ca, therefore, these methods do not apply fully to their oxides.

4.2. THE POSITIVE AND NEGATIVE FUNCTIONS OF THE BASICITY OF SrO–La_2O_3/CaO CATALYSTS FOR OCM

The reactivity increases in the order SLC-2 > SLC-1 > LC. This suggests that the stronger basic sites on SLC-2 and SLC-1 catalysts extract more readily a hydrogen atom from CH_4 thereby producing methyl radicals, and thus increasing the catalytic activity and C_2-selectivity. The addition of SrO onto LC catalyst results in an increase in the catalytic activity due mainly to the increase in the surface basicity. This is the positive function of basicity of SLC catalysts in OCM.

The effect of CO_2 partial pressure in the feed on the catalytic performance over LC and SLC catalysts reveals that the reaction temperature and the CO_2 partial pressure are two important factors. The CH_4 conversion and C_2-selectivity decrease remarkably at 973 K with increasing CO_2 partial pressure. Meanwhile, the CH_4 conversion and C_2-selectivity at 1073 K remained unchanged with an initial increase in CO_2 partial pressure. At higher partial pressure of CO_2, they decrease gradually. For the SLC-2 catalyst, addition of a small amount of CO_2 into the feed resulted in a significant decrease in CH_4 conversion and C_2-selectivity.

The effect of CO_2 described above can be explained as follows: during the reaction $CaCO_3$ on the surface of CaO may be in equilibrium with CO_2 in the gas phase:

$$CaO + CO_2 \rightleftharpoons CaCO_3 \tag{4}$$

Addition of CO_2 into the feed at 973 K will cause the formation of surface carbonates which are inactive in the OCM reaction. Consequently, this results in a decrease in catalytic activity and C_2-selectivity for LC and SLC catalysts. Although the decomposition temperature of bulk $CaCO_3$ is 1171 K, freshly formed surface carbonates, such as $CaCO_3$ and $La_2O_2CO_3$, may decompose at 1073 K, as we pointed out above. Therefore, addition of a small amount of CO_2 has no effect on the catalytic activity and C_2-selectivity of the LC catalyst at 1073 K.

For the SLC catalyst, when CO_2 was added into the feed at 973 K, surface SrO may react easily with CO_2 to produce $SrCO_3$. The decomposition temperature of bulk $SrCO_3$ is 1613 K which is much higher than the reaction temperature of 973 K.

Therefore, with increasing CO_2 partial pressure, the catalytic activity and C_2-selectivity decrease greatly. According to the following equilibrium:

$$SrO + CO_2 \rightleftharpoons SrCO_3 \qquad (5)$$

the poisoning effect of CO_2 in the feed on the catalyst will also strongly depend on the reaction temperature and CO_2 concentration. In OCM, the temperature at the top of the catalyst bed can be much higher than the measured one due to the hot spot temperature effect. Therefore, $SrCO_3$ once formed in that region, can decompose partly. The higher the CO_2 partial pressure in the feed, the less of $SrCO_3$ will decompose. The catalytic activity and C_2-selectivity of SLC catalyst will obviously decrease. Meanwhile, $SrCO_3$ will form on the other part of the catalyst bed, and there the hot spot temperature effect will be much smaller and the CO_2 concentration will be much higher than at the top of the catalyst bed. That is why for SLC catalyst, a relatively high reaction temperature is required as compared with LC catalyst.

For the SLC-2 catalyst, even if 1103 K is used for OCM reaction, a small amount of CO_2 will give rise to a significant decrease in catalytic activity and C_2-selectivity. This is because the catalyst surface is mainly covered by SrO and therefore, formed inactive $SrCO_3$ easily. On the other hand, the reaction between CH_4 and CO_2 to produce CO may be possible via the following reaction:

$$CH_4 + 3CO_2 \rightleftharpoons CO + 2H_2O \qquad \Delta G = -45\ \mathrm{kJ/mol}\ (\mathrm{at}\ 1073\ \mathrm{K}) \qquad (6)$$

The reaction is thermodynamically favorable. Therefore, the increase in CO-selectivity with increasing CO_2 partial pressure in the feed can be well explained.

5. Conclusions

(1) The addition of SrO into the LC catalyst results in an increase in catalytic activity and C_2-selectivity. The SLC-2 catalyst shows good results with 18% CH_4 conversion and 80% C_2-selectivity, very close to the data recently summarized by Lunsford [1]. This is mainly due to the better surface basicity of the SLC-2 catalyst as revealed by CO_2-TPD and in situ FT-IR characterization of CO_2 adspecies. This indicates that the surface basicity of SLC catalyst plays an important role in OCM reaction.

(2) CO_2-TPD and in situ FT-IR characterization of CO_2 adspecies are effective methods for measuring the surface basicity of CaO, SrO, and SLC-2, but not for La_2O_3 and LC.

(3) When CO_2 is introduced into the feed at low reaction temperature, the catalytic activity and C_2-selectivity decrease over CaO, LC, and SLC catalysts mainly due to the formation of the surface carbonates. At high reaction temperature, CO_2 addition in the feed has almost no effect on the catalytic activity and C_2-selectivity over CaO and LC catalyst. For SLC-2 catalyst, having higher SrO load-

ing, a more serious effect of CO_2 on its catalytic performance can be observed. This is mainly due to the formation of inactive surface $SrCO_3$.

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