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Infrared Study of the Formation and Stability of $La_2O_2CO_3$ during the Oxidative Coupling of Methane on La_2O_3

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The formation and stability of $La_2O_2CO_3$ under CO_2/He and the CH_4/O_2/He reaction mixture were investigated by infrared spectroscopy in the 650–750°C range. $La_2O_2CO_3$ is not stable under flowing He at 650°C. Bulk $La_2O_2CO_3$ is formed during the oxidative coupling of CH_4 at 650°C, although thermodynamic considerations predict that it cannot be generated from the gaseous CO_2 produced by the catalytic reaction. On this basis, it is suggested that the dioxymonocarbonate is formed via the surface deep oxidation of CH_4 and/or the reaction products. FTIR spectroscopy indicates that 15% of the starting catalyst La_2O_3 is transformed into $La_2O_2CO_3$ by the catalytic reaction at 650°C.

INTRODUCTION

Recent studies have shown that alkali, alkaline earth, and rare earth oxides such as La_2O_3 and Sm_2O_3 exhibit good performance in the catalytic oxidative coupling of methane (OCM) (*1–6*). The tendency of La_2O_3 to react with CO_2 is well documented. When La_2O_3 is exposed to dry CO_2 or to atmospheric air at room temperature, surface carbonates (*7*) or hydroxycarbonates (*8–10*) are formed respectively, whereas when CO_2 is chemisorbed at temperatures higher than 450°C, dioxymonocarbonates $La_2O_2CO_3$ are obtained (*11, 12*). The influence of carbonates and oxycarbonates on the catalytic performances has already been suggested for the OCM reaction (*13–15*). The incorporation of stable carbonates into rare earth oxides has been found to improve the C_2^+ selectivity (*14*) and interesting catalytic performances of $La_2O_2CO_3$ have been reported (*15*). Recently, Bernal *et al.* (*16*) claimed that $La_2O_2CO_3$ of hexagonal structure formed under the catalytic oxidative dehydrogenation of ethane is the active phase. However, the OCM reaction takes place at temperatures higher than those used in the oxidative dehydrogenation of C_2H_6, and the stability of this phase under the OCM conditions is thus questionable.

Recent studies in our laboratory have shown that the best performances of La_2O_3 in the OCM are observed in the 850–900°C range (*17*). At these temperatures, $La_2O_2CO_3$ is unstable (*9, 10*). However, the transformation of La_2O_3 into $La_2O_2CO_3$ in the 600–650°C range, is known to improve the selectivity in C_2^+ of the OCM at 750°C (*18, 19*). This result was confirmed by the recent catalytic study of Taylor and Schrader (*20*) who carried out the characterization of the catalysts by X-ray diffraction and infrared spectroscopy before the OCM reaction and after 2 h on stream. In their study, the catalyst was transferred in a dry box for KBr pelletization for postreaction characterization.

Up to now, there exists no infrared study performed with self-supported pellets located in an infrared cell acting as a reactor, which allows one to perform various treatments, the spectra being registered after quenching, without air pollution for the catalyst.

The aim of this paper is to determine the role played by the dioxymonocarbonate

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phases in the OCM reaction. To this purpose, we have characterized by infrared spectroscopy the catalyst phases produced during the OCM reaction in the 650–750°C range. We also have quantitatively estimated, from the infrared results, the amount of $La_2O_2CO_3$ formed during the OCM reaction. On the other hand, we have performed a kinetic study of the formation and stability of the dioxymonocarbonate phases (monoclinic and hexagonal, the hexagonal phase being the stable phase at high temperature (*11*)) under CO_2/He mixtures in the 500–650°C range. The infrared basis for the quantitative analysis for $La_2O_2CO_3$ phases in the kinetic study will be discussed in a subsequent paper.

EXPERIMENTAL

La_2O_3 was prepared by calcination at 800°C for 16 h of high purity $La(NO_3)_3 \cdot 5\ H_2O$, supplied by Rhône–Poulenc. Bulk dioxymonocarbonate may be obtained either from the decomposition of $La_2(C_2O_4)_3$ (*21*, *11*), $La(O_2CH_3)$ (*15*), $La_2(CO_3)_3 \cdot nH_2O$ (*22*) or by heating La_2O_3 in flowing CO_2 in the 500–750°C range (*16*, *20*). In this last procedure, the phase composition of $La_2O_2CO_3$ (monoclinic and hexagonal phases) depends strongly on the exposure time and temperature (*23*). Bernal *et al.* prepared the hexagonal phase by exposing La_2O_3 to flowing CO_2 at 500°C for 4 h (*16*), while Taylor and Schrader chose an isothermal heating at 700°C for 30 min (*20*). In this work, the hexagonal phase was prepared by exposing La_2O_3 to flowing CO_2 for 2 h at 650°C and its presence was confirmed by thermogravimetric and XRD measurements. This treatment gives rise to the hexagonal phase only.

For the infrared study, self-supported pellets were obtained by compressing 35 mg of La_2O_3 at $3\ t \cdot cm^{-2}$. The pellets were then mounted in a quartz holder within a classical quartz IR cell, allowing high-temperature flowing treatments (CO_2/He or the reaction mixtures). The catalytic apparatus consisted of a gas feed system, a reactor, and a chromatograph. The reactor was either a plug-flow microreactor or the IR cell itself. The OCM reaction was investigated using the cofeed mode at atmospheric pressure with a methane to oxygen ratio of 4, diluted by helium ($CH_4/O_2/He$ = 8/2/92). The total flow rate was 50 ml/min. The microreactor made of sintered alumina with an internal diameter of 3 mm was positioned vertically with the catalyst held between two quartz-wool plugs and heated by an external furnace whereas the IR cell made of a 300-mm-long quartz tube with a diameter of 30 mm was positioned horizontally in the furnace. The composition of the reaction products leaving the IR cell was determined by gas phase chromatography. The catalytic runs were performed at the steady state with the same disk (35 mg) located inside the quartz IR cell, in the 650–750°C range, and the results compared with those obtained with the isothermal plug-flow microreactor, using 5 mg of catalyst.

The conditions of formation and stability of the dioxymonocarbonate $La_2O_2CO_3$ were investigated in the 650–750°C range with CO_2/He mixtures of 0.66 and 5% (mol%) which corresponds to CO_2 partial pressures of 5 and 38 Torr, respectively. The 5% mixture corresponds to the partial pressure we used earlier for thermogravimetric experiments (*19*), while the 0.66% mixture is reasonably close the the CO_2 partial pressure observed in the OCM reaction.

The following experimental procedure was adopted: the sample was exposed to the CO_2/He mixture at a given temperature for various times. After rapid cooling to 25°C, the IR spectrum was recorded. In order to obtain a pure bulk $La_2O_2CO_3$ reference, the sample was exposed at the end of each experiment to flowing pure CO_2 at 650°C for 2 h to ensure complete conversion of the oxide. The ν_1 mode was selected to estimate the amount of $La_2O_2CO_3$ produced under a given CO_2/He mixture (or during the catalytic reaction), assuming that the surface of the ν_1 band is proportional to the molar ratio of $La_2O_2CO_3$. This nondegenerate mode, corresponding to the symmetric stretching vibration of the CO_3^{2-} ion (infrared inactive for the free ion) (*24*), was chosen because it gives rise to one band only for the polymorph of hexagonal structure (*11*). The percentage amount of $La_2O_2CO_2$ was determined by the ratio of the surface of the ν_1 band after CO_2/He (or OCM gases) and pure CO_2 treatments. This procedure (formation of a bulk oxycarbonate at the end of each experiment) gives the 100% level for the dioxymonocarbonate and avoids thus the need of a standardization curve giving the integrated intensity of ν_1 versus the pellet weight.

The spectra were registered at 25°C in the transmittance mode, using a FTIR Perkin–Elmer spectrophotometer M 1700 equipped with a KBr beamsplitter and a 3600 data station. The resolution was 4 cm^{-1}.

RESULTS

The Ln_2O_3 oxides are well known to undergo partial conversion to carbonate hydroxide (or hydroxycarbonate) when exposed to wet air (*8–10*). Figure 1a exhibits the IR spectrum of La_2O_3 after exposure to wet air at 25°C for 24 h. A small and sharp band at 3610 cm^{-1}, broad and intense bands at 1398 and 1481 cm^{-1}, and smaller ones at 1067, 850, 755, and 647 cm^{-1}, are observed. The sharp band at 3610 cm^{-1} and the band at 647 cm^{-1} are characteristic of stretching and bending OH vibrations of lanthanum hydroxide, respectively (*25*, *26*). Similar results (bands at 3600 and 640 cm^{-1} growing with the time of exposure to wet air) were reported by Bernal *et al.* (*8*, *9*). The intense bands at 1481 and 1398 cm^{-1} correspond to the ν_3 vibration of CO_3^{2-} groups (*24*). Table 1 shows the wavenumbers of CO_3^{2-} groups in lanthanum carbonates and hydroxycarbonates. La_2O_3 aged in air does not present the characteristic vibrations of the well-crystallized carbonate hydroxide (synthesized by hydrolysis of the carbonate) (*27*). The values observed for ν_1, ν_2, and ν_3 (spectrum 1a) are similar to those observed for an ill-crystallized carbonate. The broad band at 647 cm^{-1} corresponds to the overlap of the ν_4 of CO_3^{2-} and the δ_{OH} of the hydroxide phase. After treatment at 850°C with flowing He, the most intense bands characteristic of the ν_3 mode (1481 and 1398 cm^{-1}) and the band at 3610 cm^{-1} vanish (spectrum 1b), showing that those hydroxycarbonates species are decomposed. Nevertheless, bands at 620, 646, 755, 850, and around 950 cm^{-1} are still present. These bands may be accounted for by overtone and combination of La–O fundamental modes which appear at 242, 386, and 435 cm^{-1} (*28*). We suggest that the thickness of the wafer is responsible for the presence of these combination modes which do not appear when the sample is conditioned in KBr pellets (*20–23*).

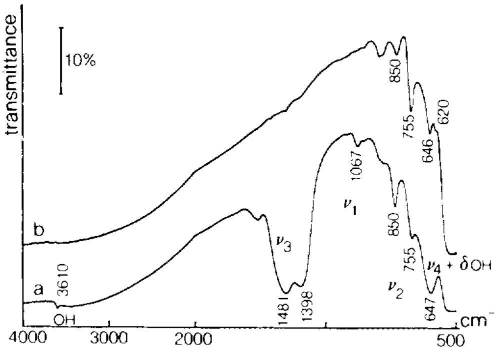

FIG. 1. IR spectrum of La_2O_3 (a) after exposure to wet air at 25°C for 24 h and then (b) after flowing He treatment at 850°C for 3 h.

In earlier thermogravimetric experiments using a 5 mol% CO_2/air mixture the dioxymonocarbonate was shown to be stable in the 600–820°C range (*19*). The XRD pattern of a sample exposed to a similar treatment up to 780°C revealed the presence of two types of $La_2O_2CO_3$, referred to as type Ia (monoclinic structure) and type II (hexagonal structure), the main phase corresponding to type II (*11*). The temperature values indicated above must be understood in terms of a relative scale of the stability range since they do not correspond to isothermal treatments.

TABLE 1

Infrared Absorption Wavenumbers (cm^{-1}) of Lanthanum Carbonates and Hydroxycarbonates

Materials	CO_3^{2}				OH	
	ν_3	ν_1	ν_2	ν_4	ν	δ
$La_2(CO_3)_3 \cdot xH_2O$[a]	1477 1385	1075	839 747	683	3420	
$La_2(CO_3)_3 \cdot xH_2O$[b]	1474 1384 1334	1075	850 746	678 652	3510 3358 3176	
$LaCO_3OH$[c]	1512 1435 1408	1074	872 849 777	727 706	3631 3618	590
La_2O_3 aged in air[d]	1481 1398	1067	850 755	647	3610	647

[a] Ill-crystallized carbonate supplied by Aldrich (KBr pellet).

[b] Well-crystallized carbonate supplied by Rhône–Poulenc (KBr pellet).

[c] From Ref. (25).

[d] This work.

Figure 2 exhibits the spectra registered at the beginning (spectrum 2b) and the end (spectrum 2c) of the treatment in a 5 mol% CO_2/He mixture at 650°C, which present similar features. Spectrum 2c shows three groups of bands around 1088, 856, and 750–670 cm^{-1}, whereas spectrum 2b reveals a splitting of these bands into several components. It has been shown that for the monoclinic polymorph, the nondegenerate ν_1 and ν_2 modes are split into three components, while the degenerate ν_3 and ν_4 modes experience threefold and sixfold splitting, respectively. The splitting of the nondegenerate ν_1 and ν_2 modes has been interpreted by the presence of nonequivalent carbonate groups (*11*). The spectra shown in Fig. 2 do not include the ν_3 band, which is too intense owing to the thickness of the pellet and whose transmittance is close to zero. However, experiments performed with thinner pellets reveal a splitting of this band into three components.

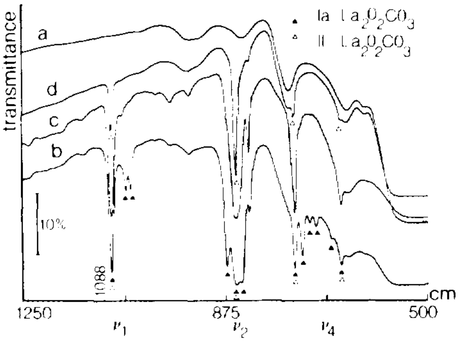

FIG. 2. IR spectrum of La_2O_3 (a) after He treatment at 850°C for 3 h, (b) after a 5 mol% CO_2/He treatment at 650°C for 30 min, and then (c) after 22 h; (d) After exposure to the reaction mixture for 45 h (▲, bands characterizing type-Ia $La_2O_2CO_3$; △, bands characterizing type-II $La_2O_2CO_3$).

The splitting observed for bands of spectrum 2b reveals therefore the presence of the monoclinic polymorph (type Ia), while spectrum 2c corresponds to the hexagonal polymorph (type II). For each mode, it is observed that the position of the band in spectrum 2c coincide with one of the split components in spectrum 2b (Fig. 2). This observation indicates that, after 30 min, types Ia and II are present, whereas after

TABLE 2

Solid Phases Identified by IR under CO_2/He Mixtures or during the Catalytic Reaction

Starting materials	Temperature (°C)	Reactant mixtures	Phases
La_2O_3	650	5%/CO_2/He	II $La_2O_2CO_3$ (96%)^a
		0.66%/CO_2/He	La_2O_3
		CH_4/O_2/He	II $La_2O_2CO_3$ (15%)^b + La_2O_3
	750	5%/CO_2/He	La_2O_3
		0.66%/CO_2/He	
		CH_4/O_2/He	
II $La_2O_2CO_3$	650	CH_4/O_2/He	II $La_2O_2CO_3^c$ + La_2O_3
		He	$La_2O_3^d$
	750	CH_4/O_2/He	$La_2O_3^e$
		He	

[a] Characterized after 22 h.
[b] Estimated after 2 and 45 h reaction.
[c] Characterized after 2 h reaction.
[d] Characterized after 6 h flowing He.
[e] Characterized after 1 h reaction.

22 h type II only is observed. This result is not surprising, since the monoclinic phase was shown to be less stable than the hexagonal one (*11*).

When the temperature is raised to 750°C, bands corresponding to $La_2O_2CO_3$ disappear and the spectrum corresponds to that of the starting material. Nevertheless, weak bands around 1485 and 1400 cm^{-1} characteristic of surface carbonates are also observed (not shown on Fig. 2).

With the 0.66 mol% CO_2/He mixture, the dioxymonocarbonate is not observed at 650°C. Surprisingly, this compound is produced when La_2O_3 is flushed with the catalytic mixture at 650°C although the CO_2 partial pressure produced is only 1 Torr (Fig. 2d). At the beginning of the experiment, bands characteristic of type Ia and II appear. After 30 min, type-II $La_2O_2CO_3$ increases at the expense of type Ia, which eventually disappears (not shown on Fig. 2). Beyond 2 h, the intensity of bands characteristic of type-II $La_2O_2CO_3$ remains constant. However, the comparison of spectra 2c and 2d shows that the amount of $La_2O_2CO_3$ obtained in the catalytic conditions is definitely lower than that formed with the 5% CO_2/He mixture. The presence of LaO overtones at 620, 648, and 755 cm^{-1} in spectrum 2d suggests that La_2O_3 partially transforms into $La_2O_2CO_3$.

The ν_1 mode at 1088 cm^{-1} was selected to estimate the amount of $La_2O_2CO_3$ produced when La_2O_3 was either exposed to a 5 mol% CO_2/He or used as the oxidative coupling catalyst at 650°C. After a 5 mol% CO_2/He treatment for 22 h at 650°C, the transformation of La_2O_3 into bulk $La_2O_2CO_3$ is almost complete (Table 2). The ν_1 band of type-II $La_2O_2CO_3$ is given in Fig. 3 after the catalytic reaction (a) and after a subsequent treatment in flowing pure CO_2 at 650°C duing 2 h (b). The amount of $La_2O_2CO_3$ produced in the OCM reaction and estimated from the ratio of the integrated intensities of ν_1, corresponds roughly in our conditions to 15% of the bulk compound. This amount decreases when the reaction is performed at 670°C and reaches zero at 750°C.

The stability of bulk dioxymonocarbonate was also investigated under flowing He

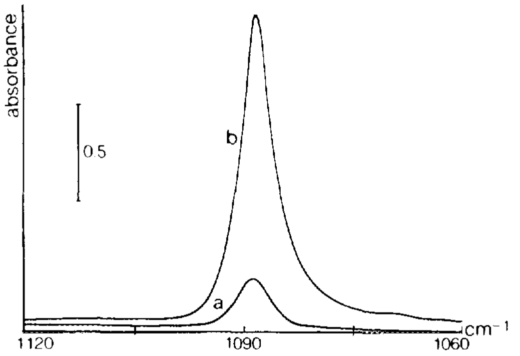

FIG. 3. ν_1 band of type-II $La_2O_2CO_3$ (a) obtained when La_2O_3 was exposed to the reaction mixture at 650°C for 45 h and (b) after a subsequent treatment in flowing CO_2 at 650°C for 2 h.

or the catalytic mixture. After a 6 h exposure to flowing He at 650°C, $La_2O_2CO_3$ was completely decomposed into La_2O_3. After exposure to the reaction mixture at 650°C, when both polymorphs are present, type Ia rapidly transformed into type II, then partially transformed into La_2O_3. At 750°C, type-II $La_2O_2CO_3$ rapidly decomposed into La_2O_3. Table 2 summarizes the different phases identified under CO_2/He or CH_4/O_2/He mixtures.

The catalytic results for the OCM reaction performed at 650°C with the pellet inside the IR cell or with the catalyst in the microreactor are listed in Table 3. With both samples, the selectivity values to coupled products C_2^+ and to carbon oxides CO_x are reasonably close, although the reactant feed passes through the catalyst bed in the microreactor and flows parallel to the pellet in the IR cell.

DISCUSSION: ORIGIN OF THE $La_2O_2CO_3$ PRODUCED DURING THE OCM REACTION

In contrast to the rare earth oxides beyond Pr_2O_3 in the Ln_2O_3 series, the high reactivity of La_2O_3 towards CO_2 is known to give rise to the reversible formation of $La_2O_2CO_3$, at temperatures above 450°C, according to the equilibrium (*11*, *12*)

$$La_2O_3 + CO_2 \leftrightarrow La_2O_2CO_3. \qquad (1)$$

The oxycarbonate is formed *via* the insertion of CO_2 molecules between the $(LaO)_2$ layers of La_2O_3, a process which requires a thermal activation (*29*).

It appears necessary to determine whether the oxycarbonate observed after the OCM at 650°C originates only from the gaseous CO_2 produced during the catalytic reaction. Thermodynamic considerations may clarify this question. The calculated solid–gaseous CO_2 equilibrium pressures estimated from the thermodynamic data established by Watanabe *et al.* (*30*) are listed in Table 4. When the CO_2 partial pressure

TABLE 3

Comparison of the Catalytic Performances for the OCM Reaction at 650°C over La_2O_3 in the Microreactor and the Infrared Cell

Starting materials	Conversion (%)		Total activity (mol h⁻¹ g⁻¹)	Selectivity (%)		
	CH_4	O_2		C_2^+	CO	CO_2
$La_2O_3^a$ microreactor	2	13	0.04	25.5	50.8	23.7
$La_2O_3^b$ pellet	4.9	18	0.014	28.9	36.4	36.8

Note. Catalytic conditions: $CH_4/O_2/He$ = 8/2/90 (mol %). Total flow rate = 50 ml · min⁻¹.

[a] m = 0.005 g.

[b] m = 0.035 g; S La_2O_3 = 1.4 m² · g⁻¹.

TABLE 4

Calculated CO_2 Equilibrium Pressures or Temperatures for the Formation of $La_2O_2CO_3$ (from Data in Ref. (*28*))

Temperature (°C)	600	**617**[a]	650	**716**[a]	750
Equilibrium pressure (Torr)	3.4	**5**	10.3	**38**	119.6
% CO_2 at 1 atm	0.45	**0.66**	1.35	**5**	15.7

[a] Boldface type corresponds to the 0.66 and the 5 mol% CO_2/He mixtures.

over La_2O_3 is higher than the equilibrium pressure, La_2O_3 may completely transform into $La_2O_2CO_3$. The higher the CO_2 partial pressure in comparison with the equilibrium pressure, the faster the rate of the transformation. Because our samples are studied in flowing conditions, the CO_2 partial pressure in CO_2/He mixtures is constant and, when higher than the equilibrium pressure, can lead to a complete transformation of the oxide into $La_2O_2CO_3$. The results concerning the phases obtained at 650 and 750°C using the 0.66 and 5 mol% CO_2/He mixtures (corresponding to 5 and 38 Torr, respectively) are consistent with the thermodynamic data. At 750°C, the CO_2 partial pressures in the two mixtures are lower than the equilibrium pressure (119.6 Torr) so that $La_2O_2CO_3$ cannot form. At 650°C, the dioxymonocarbonate is obtained only with the 5 mol% CO_2/He mixture, and not with the 0.66 mol% CO_2/He mixture. The incomplete (96%) conversion of the oxide into the oxycarbonate after 22 h may be due to a kinetic limitation (Table 2).

Turning to the catalytic results, the selectivity to CO_2 at 650°C (Table 3) corresponds to a CO_2 steady-state partial pressure of 1 Torr, which is not sufficient for the formation of $La_2O_2CO_3$. It therefore appears that the formation of $La_2O_2CO_3$ in these catalytic conditions does not proceed from gas-phase CO_2 adsorption, but arises more likely from the surface oxidation of CH_4 and/or the reaction products. It implies that the concentration of CO_2 produced on the surface is high enough to give rise to a large amount of $La_2O_2CO_3$ (15%). Moreover, the amount of $La_2O_2CO_3$ produced during the catalytic reaction at 650°C is constant in the 2–45 h reaction (Table 2). This result suggests that an equilibrium between the rates of formation and decomposition of $La_2O_2CO_3$ occurs according to the following scheme:

$$La_2O_3 + CH_4 + O_2 \xrightarrow{k_1} La_2O_2CO_3 \xrightarrow{k_2} La_2O_3 + CO_2.$$

In this scheme, the amount of $La_2O_2CO_3$ appears to depend on the k_1/k_2 ratio of the rate constant of formation and decomposition. Above 650°C, the rate constant of decomposition of $La_2O_2CO_3$, k_2, is believed to increase more rapidly than its rate of formation, k_1, which could explain the lower amount of $La_2O_2CO_3$ observed at 670°C. At 750°C, k_2 is assumed to be very high in comparison with k_1, leading to the disappearance of $La_2O_2CO_3$. In this view, in the 650–700°C range $La_2O_2CO_3$ appears to be an intermediate for the production of CO_2.

$La_2O_2CO_3$ used as a starting material, is observed to be unstable under flowing He at 650°C whereas it only partially decomposes into La_2O_3 under the reaction mixture (Table 2). The same result was found by Taylor and Schrader with this material (*20*). These authors have characterized by XRD and IR the different phases obtained after catalytic runs performed in the 600–800°C range on different starting materials such as $La_2(CO_3)_3$, type-II $La_2O_2CO_3$ and La_2O_3. They characterized their La_2O_3 catalyst after 2 hours on stream, at 600 and 800°C and not at intermediate temperatures. In our view, they could not observe the formation of the oxycarbonate because at 600°C the rate of formation of $La_2O_2CO_3$ is very low, whereas at 800°C the rate of decomposition of $La_2O_2CO_3$ prevails, and they identified only La_2O_3 phase. Using their catalytic results on La_2O_3, the calculated CO_2 partial pressure at 650°C is found to be 0.6 Torr, which is consistent with our observation (1 Torr). It confirms that the dioxymonocarbonate cannot be generated from only the gaseous CO_2 produced by the OCM reaction.

Whether the oxycarbonate participates as a catalytic intermediate in the OCM is still an open question. Our own recent results emphasize the role of the morphology of La_2O_3 in the catalytic performances for the OCM reaction, during which the oxycarbonate appears to act as a precursor for a particular catalyst morphology leading to improved selectivity to C_2^+ (*18, 31*).

CONCLUSION

This IR study shows that the dioxymonocarbonate phase which is not stable under flowing He at 650°C, is nevertheless generated during the catalytic reaction in the 650–670°C range. In agreement with previous results (*11*), type-II $La_2O_2CO_3$ (hexagonal phase) is far more stable at 650°C than type Ia (monoclinic phase). FTIR spectra indicate that a sizable fraction of the starting oxide catalyst is converted into $La_2O_2CO_3$ (15% at 650°C) and that this amount remains constant after the OCM reaction reaches the steady state.

Since the low CO_2 partial pressure in the reaction products rules out the formation of the oxycarbonate from the gaseous phase, a route involving the surface deep oxidation of methane and/or the reaction products is suggested. The amount of $La_2O_2CO_3$ is assumed to result from an equilibrium between its formation and decomposition rates, showing that at moderate reaction temperatures (<750°C), a part of the gaseous CO_2 is at least generated from the catalyst.

This study emphasizes the role of the catalyst, which can be considered much more than a simple sparkle that induces the dimerization of methane.

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