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The Oxidative Coupling of Methane over $BaCO_3$/LaOBr—Catalysts of High Ethylene Yield

C. T. Au,[1] H. He, S. Y. Lai, and C. F. Ng

Chemistry Department and Centre for Surface Analysis and Research, Hong Kong Baptist University, Kowloon Tong, Hong Kong

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Tetragonal LaOBr is a better catalyst than La_2O_3 for the oxidative coupling of methane (OCM), whereas $BaCO_3$ is a good promoter for LaOBr. With contact time equal to 0.2 g s ml^{-1} and a $CH_4 : O_2 : N_2$ ratio of 1 : 1 : 12, a C_2 yield of 26.3% with a C_2H_4/C_2H_6 ratio of 4.3 could be achieved over the 50 mol% $BaCO_3$/LaOBr catalyst at 800°C. When the $CH_4 : O_2 : N_2$ ratio was 0.5 : 1 : 12 and the contact time was 0.6 g s ml^{-1}, the C_2 yield became 18.9% and C_2H_4 was the sole C_2 product. Fixing the $CH_4 : O_2 : N_2$ ratio to 2.6 : 1 : 12 and contact time to 0.6 g s ml^{-1}, the C_2H_4/C_2H_6 ratios over the LaOF, LaOBr, and 30 mol% $BaCO_3$/LaOBr catalysts were, respectively, 1.6, 3.3, and 11.3 at 800°C. Generally speaking, the performance of $BaCO_3$/LaOBr catalysts may be considered quite competitive, especially from the point of view of high ethylene production from methane. Detail XRD investigations reveal that new phases such as La_2O_3, $La(OH)_3$, and $Ba_3Br_4CO_3$ were generated in the $BaCO_3$/LaOBr catalysts. *In situ* Raman studies showed that the LaOBr and 10 mol% $BaCO_3$/LaOBr catalysts were capable of forming O_2^{2-} and O_2^{n-} ($1 < n < 2$) species during OCM reaction, while LaOF could form O_2^{n-} and O_2^{-} species. We suggest that for a mixed catalyst like $BaCO_3$/LaOBr, nonstochiometric behavior is expected and defects such as O^- centers and trapped electrons which would bring about the generation of surface dioxygen species could be present within the constituent structures or at the interfaces. We suggest that the direct interaction of CH_4 with O_2^{2-} is an efficient way of producing carbene, and the coupling of carbene, rather than methyl radical, could be the major step for C_2H_4 generation over these highly C_2H_4 selective $BaCO_3$/LaOBr catalysts.

INTRODUCTION

Since the work of Keller and Bhasin (1), considerable progress has been made in the understanding of the OCM reaction. Various aspects have been investigated and a large number of compounds have been tested as catalysts or promoters (2). However, questions regarding the nature of active sites, the role of oxygen species, the effect of CO_2, and the factors that control product selectivity still remain.

Halogen has been used as promoter for OCM catalysts. Burch and co-workers (3, 4) carried out a series of studies on the effect of chlorine over various catalysts. They found that pulse injection of gaseous chlorinated compounds over MnO_2-based catalysts and lithium-doped MgO and Sm_2O_3 catalysts markedly increased the C_2 selectivity. They also investigated OCM reaction over Sm_2O_3, SmOCl, and $SmCl_3$ and claimed that the chlorine-containing catalysts were especially effective in ethylene production.

Ueda and co-workers (5–7) have reported a C_2H_4/C_2H_6 ratio of 30 over layered bismuth oxychloride catalysts. Moffat and co-workers (8, 9) investigated OCM reaction over La_2O_3, CeO_2, Pr_6O_{11}, and Sm_2O_3. They found that the addition of a small amount of tetrachloromethane to the reactant stream could improve the catalytic activity of these catalysts and attributed the improvement to oxychloride formation. Khan and Ruckenstein (10) found that the BiOCl/Li_2CO_3/MgO catalyst was active and selective. Neither BiOCl nor Li_2CO_3/MgO was very effective, but BiOCl/Li_2CO_3/MgO gave 18% CH_4 conversion, 83% C_2 selectivity, and a C_2H_4/C_2H_6 ratio of 2.9. Lunsford *et al.* (11) reported that at temperature as low as 625°C, a CH_4 conversion of 29% and a C_{2+} selectivity of 60% could be obtained over Li^+–MgO–Cl^- catalysts.

With other halides, fluoride and bromide were also tested as promoters or catalysts. Otsuka *et al.* (12) carried out OCM reaction with NiO catalysts promoted by LiF, LiCl, and LiBr. The NiO–LiBr catalyst gave a CH_4 conversion of 35% and a C_2 selectivity of 46%, with a C_2H_4/C_2H_6 ratio equal to 15. Loading alkaline earth halides (F^-, Cl^-, and Br^-) on CaO and MgO, Fujimoto *et al.* (13) observed that the ability of the oxides in decomposing methane diminished, resulting in the suppression of methane deep oxidation. Zhou *et al.* (14) developed a series of fluoro-oxide catalysts which were active at 650°C. They suggested that O^{2-}–F^- exchange between lattices might produce O^- ions and anion vacancies which can activate O_2 and influence the selectivity of OCM reaction.

La_2O_3 has been studied as a catalyst for OCM reaction. During OCM reaction over La_2O_3, Van *et al.* (15) observed $La_2O_2CO_3$ formation. Becker *et al.* (16) also detected the existence of $La_2O_2CO_3$ after 24 h of OCM reaction over a La_2O_3/CaO catalyst by XRD. We observed previously

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[1] To whom correspondence should be addressed.

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the existence of hexagonal $La_2O_2CO_3$ inside the 10 mol% $BaBr_2/La_2O_3$ catalyst after OCM reaction (17) and it was suggested that the catalytic activity might be ascribed to the defect sites inside the crystal frame of $La_2O_2CO_3$ generated by the decomposition of $La_2O_2CO_3$. Recently, we have studied the modification of LaOBr catalyst by $BaCO_3$. In this paper, the performance as well as the characterization of the $BaCO_3$/LaOBr catalysts are reported.

EXPERIMENTAL

The chemicals (purity >99.9%) used in the preparation of the catalysts were products of Johnson Matthey & Co. Ltd. LaOBr was prepared by heating a ground mixture of La_2O_3 and $LaBr_3$ in 1 : 1 molar ratio in air in a furnace at 800°C for 6 h. The $BaCO_3$/LaOBr catalysts were prepared by mixing LaOBr powder with the right proportion of $BaCO_3$ in the form of aqueous suspension. After water evaporation, the mixture was ground and dried overnight in an oven at 110°C and pressed into small pellets before being calcined at 800°C for 6 h. The pellets were then crushed and sieved to a grain size of 40–60 mesh. Standard sample of $La_2O_2CO_2$ was prepared by heating La_2O_3 in CO_2 (ca. 1 atm) at 800°C for 24 h, followed by cooling in CO_2 to room temperature.

The O_2 (99.7%), CH_4 (99.9%), C_2H_6 (99.0%), and N_2 (99.99%) gases were from Hong Kong Oxygen Ltd., while the $^{18}O_2$ (98%) and CD_4 (99%) isotopes were purchased through the Hong Kong Special Gas Ltd. The gases were used without further purification.

Catalytic interactions were studied at 750 and 800°C using a laboratory scale fixed-bed reactor system operating under atmospheric pressure (18). The reactors were constructed of fused quartz. A thermocouple was placed in direct contact with the catalyst for accurate temperature measurement. Catalyst (0.5 g) was placed in the reactor and treated with a mixture of O_2 and N_2 (flow rate, 50 ml min^{-1}) at 750°C for 2 h before reaction. Products were analyzed, usually 60 min after temperature stabilization, by on-line gas chromatography (Shimadzu GC-8APT). A Porapak Q column was used to separate CH_4, CO_2, C_2H_4, and C_2H_6. A 5A molecular sieve column was used (in parallel) to separate N_2, O_2, CH_4, and CO.

Phase composition of catalysts was determined by X-ray diffraction (D-MAX, Rigaku), whereas X-ray photoelectron spectroscopy (Leybold Heraeus-Shenyang SKL-12) was used to characterize the catalyst surface. *In situ* Raman experiments were performed in Xiamen University, People's Republic of China, using the Raman spectrometer SPEX Ramalog-6. Thermogravimetric studies were performed on a Satatam TA-92 system under an atmosphere of argon. The catalysts (ca. 0.05 g) were heated with a rate of ca. 5°C min^{-1}.

The isotope exchange experiments were performed at atmospheric pressure at 750 and 800°C, using a pulse reaction system (similar to the one described previously (19) with pulse size of 1.12 μmol. Catalyst (0.2 g) was placed in a quartz reactor and treated first with pure O_2 (1 h) and then N_2 (1/2 h) (flow rate, 50 ml min^{-1}) at 750°C before the isotope exchange experiments. The effluent from the reactor was directed to a HP G1800A GCD system. Temperature programmed desorption experiments were performed on the HP G1800A GCD system as well.

RESULTS AND DISCUSSION

Catalytic Activities

For comparison purposes, the catalytic activities of La_2O_3 and LaOBr were also studied. The results are summarized in Table 1. The catalytic performance decreases in the order of $BaCO_3/LaOBr > LaOBr > La_2O_3$, showing that $BaCO_3$ is a promoter for LaOBr catalyst. Thus OCM reactions

TABLE 1

Catalytic Performance at 750 and 800°C

Catalysts	Temp. (°C)	CH_4 conv. (%)	Selectivity (%)				C_2H_4/ C_2H_6	C_2 yield (%)	Rate of CH_4 react. (10^{-3} mol g^{-1} h^{-1})	Rate of CH_4 react. (10^{-3} mol m^{-2} h^{-1})	Surface area (m^2 g^{-1})
			CO_x	C_2H_4	C_2H_6	C_2					
Blank	750	0.9	37.4	8.6	54.0	62.6	0.2	0.6	—	—	—
Blank	800	5.0	41.3	21.5	37.2	58.7	0.6	2.9	—	—	—
La_2O_3	750	24.1	71.9	15.0	13.1	28.1	1.2	6.8	10.7	1.6	6.6
La_2O_3	800	25.2	67.3	20.4	12.3	32.7	1.7	8.2	11.3	1.7	6.6
LaOBr	750	40.7	72.1	20.2	7.7	27.9	2.6	11.3	18.1	0.7	27.7
LaOBr	800	42.7	67.8	24.7	7.5	32.2	3.3	13.7	19.1	0.7	27.7
30 mol% $BaCO_3$/LaOBr	750	29.1	53.2	42.2	4.6	46.8	9.2	13.6	13.0	1.7	7.7
30 mol% $BaCO_3$/LaOBr	800	39.7	55.2	43.1	3.8	46.9	11.3	18.6	17.7	2.3	7.7

Note. $CH_4 : O_2 : N_2$ ratio, 2.6 : 1 : 12. The total flow rate was 50 ml min^{-1}. Contact time, 0.6 g s ml^{-1}. The weight of catalyst was 0.5 g. The $BaCO_3$ loading was 30 mol%.

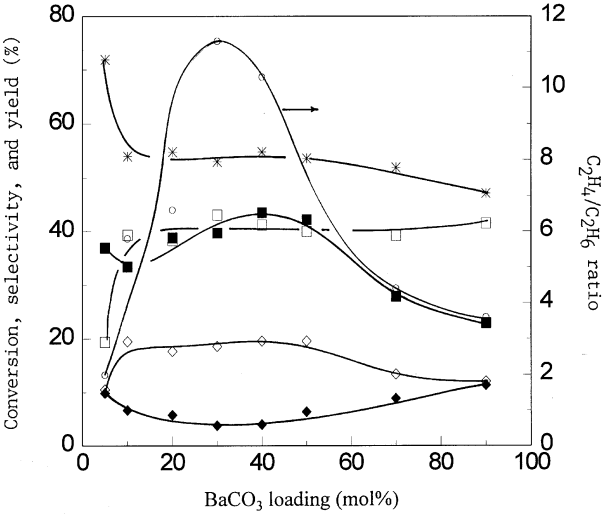

FIG. 1. The catalytic performance of $BaCO_3$/LaOBr catalysts at 800°C as related to $BaCO_3$ loading. The contact time was 0.6 g s ml^{-1} and the $CH_4:O_2:N_2$ ratio was 2.6 : 1 : 12. (■) CH_4 conversion, (□) C_2H_4 selectivity, (◆) C_2H_6 selectivity, (∗) CO_x selectivity, (◇) C_2 yield, (○) C_2H_4/C_2H_6 ratio.

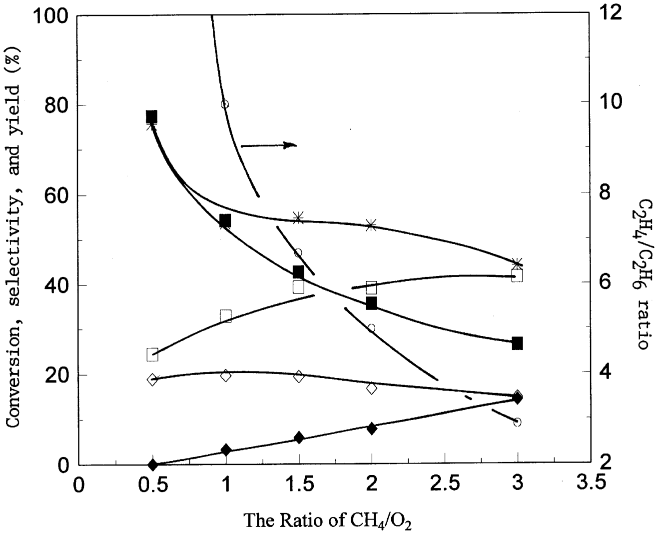

FIG. 2. The catalytic performance of a 50 mol% $BaCO_3$/LaOBr catalyst at 800°C as related to the ratio of CH_4/O_2 (contact time = 0.6 g s ml^{-1}). (■) CH_4 conversion, (□) C_2H_4 selectivity, (◆) C_2H_6 selectivity, (∗) CO_x selectivity, (◇) C_2 yield, (○) C_2H_4/C_2H_6 ratio.

on $BaCO_3$/LaOBr catalysts were carried out over a wide range of catalyst compositions, temperature, CH_4/O_2, ratio and contact time. Figure 1 shows the conversion, selectivity, and C_2 yield over a wide range of $BaCO_3$ loading (800°C, $CH_4:O_2:N_2$ ratio of 2.6 : 1 : 12, and contact time of 0.6 g s ml^{-1}). While CH_4 conversion reached a shallow maximum near 40 mol% of $BaCO_3$ loading, the C_2 selectivity (and C_2 yield) did not vary significantly in the range of 10–50 mol%. Subsequently, most of the kinetic data were obtained over the 30 and 50 mol% $BaCO_3$/LaOBr catalysts.

Figure 2 shows the catalytic performance of a 50 mol% $BaCO_3$/LaOBr catalyst at various CH_4/O_2 ratios. The general behavior of high CH_4 conversion at low CH_4/O_2 ratio was also observed for this catalyst. The CO_x selectivity decreased rather sharply below a ratio of one. However, the more pre-eminent result was that the C_2H_4 selectivity was constantly much higher than that for C_2H_6 over a wide range of CH_4/O_2 ratio and most strikingly still, at CH_4/O_2 of 0.5, the observed C_2H_4/C_2H_6 ratio was found to be infinite (i.e., C_2H_6 not detectable). Thus it is obvious that $BaCO_3$/LaOBr catalyst is highly selective for ethylene formation.

The performance of a 50 mol% $BaCO_3$/LaOBr over different contact time (τ) is shown in Fig. 3. While the increase in CO_x selectivity with reference to contact time was expected, the observed maximum of CH_4 conversion at $\tau = 0.6$ g s ml^{-1} may deserve a little explanation. Presumably the catalyst was already working in the region of high oxygen conversion so that a longer contact time might actually lead to competition for oxygen for deep oxidation, resulting in net decline in CH_4 conversion. Anyhow, apart from $\tau = 0.6$ g s ml^{-1} appearing to be an optimum contact time and therefore being adopted for most of the kinetic measurements, it should be noted that at $\tau = 0.2$ g s ml^{-1}, the values of CH_4 conversion, C_2 selectivity, C_2 yield, and C_2H_4/C_2H_6 ratio were respectively 54%, 49%, 26.3%, and 4.3.

Table 2 summarizes the activity data of some catalysts with high C_2H_4/C_2H_6 ratio in OCM reaction. Thomas *et al.* (20) reported C_2H_4/C_2H_6 ratios of 34 and 25.1, respectively, over $NaCa_2Bi_3O_4Cl_6$ and $LiCa_2Bi_3O_4Cl_6$ at 720°C. They demonstrated that ethylene formation could be enhanced by using catalysts which contained chlorine.

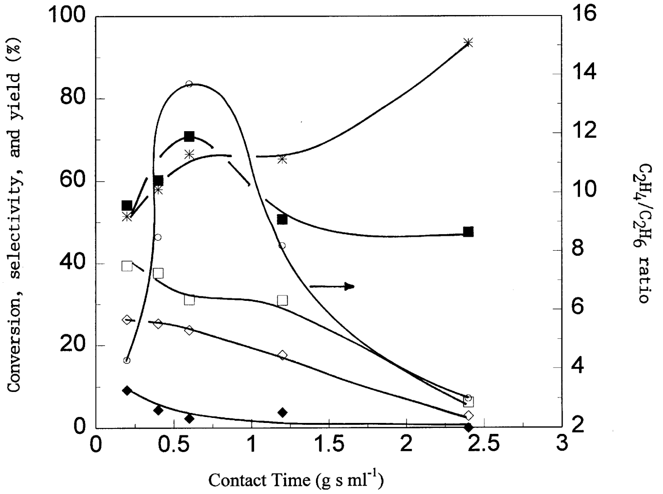

FIG. 3. The catalytic performance of a 50 mol% $BaCO_3$/LaOBr catalyst at 800°C as related to contact time. Reactant feed $CH_4:O_2:N_2$ (1 : 1 : 12). (■), CH_4 conversion, (□) C_2H_4 selectivity, (◆) C_2H_6 selectivity, (∗) CO_x selectivity, (◇) C_2 yield, (○) C_2H_4/C_2H_6 ratio.

TABLE 2

A Comparison of Catalysts with High C_2H_4/C_2H_6 Ratio in OCM Reaction

Catalyst	$CH_4:O_2:$dil.	Contact time (g s ml^{-1})	T (°C)	CH_4 conversion (%)	C_2 selectivity (%)	C_2 yield (%)	C_2H_4/ C_2H_6	Ref.
$NaCa_2Bi_3O_4Cl_6$	2 : 1 : 7	1.7	720	33.8	43.2	14.6	34	20
$LiCa_2Bi_3O_4Cl_6$	2 : 1 : 7	1.7	720	41.7	46.5	19.4	25.1	20
SmOCl	2 : 1 : 3.7	0.005	750	44.5	39.1	17.4	11.6	3, 4
Sm_2O_3/MgO	1 : 0.3 : 0	0.02	750	?	?	?	15	3, 4
NiO/LiBr	2 : 1 : 37	0.65	750	35.0	46.0	16.1	15	12
LiCl/MgO	2 : 1 : 62	1.3	750	46	62.8	29	20	21
LiCl/MgO	1 : 1 : 9	?	650	31.0	53.5	16.6	11	11
50 mol% $BaCO_3$/LaOBr	0.5 : 1 : 12	0.6	800	77.3	24.5	18.9	∞	This work
	0.5 : 1 : 12	0.4	800	59.5	32.2	19.2	14.3	This work
	0.5 : 1 : 12	0.2	800	45.0	44.0	18.8	4.4	This work
	1 : 1 : 12	0.6	800	67.8	33.0	23.7	12.9	This work
	1 : 1 : 12	0.2	800	54.0	48.6	26.3	4.3	This work
30 mol% $BaCO_3$/LaOBr	2.6 : 1 : 12	0.6	800	39.7	46.9	18.6	11.3	This work

The participation of chlorine was also suggested by Chan *et al.* (21) to be the reason for the high C_2H_4/C_2H_6 ratios observed over the LiCl/MgO catalysts. Lunsford *et al.* (11) found that when a small amount of HCl was introduced into the OCM reaction, a C_2 yield of 16.6% with a C_2H_4/C_2H_6 ratio of 11 was obtained over the LiCl/MgO catalyst. They claimed that homogeneous reactions in the gas phase were responsible for the high C_2H_4/C_2H_6 ratio. Burch *et al.* (3, 4) reported C_2H_4/C_2H_6 ratios of 11 and 15 over SmOCl and $SmCl_3$/MgO catalysts, respectively. They suggested that chlorine interaction with O^{2-} in the catalysts would result in the formation of new O^- sites capable of activating the weaker C–H bond in ethane more effectively that the stronger C–H bond in methane. From Table 2, one can see that the 30 and 50 mol% $BaCO_3$/LaOBr catalysts were capable of giving high C_2H_4/C_2H_6 ratios in OCM reaction. With such performance—(CH_4 conversion + C_2 selectivity) > 100, reasonable high C_2 yield and C_2H_4/C_2H_6 ratio, and high thermal stability—$BaCO_3$/LaOBr might be considered to be a competitive OCM catalyst particularly from the point of view of high ethylene production (noting that most of the existing high ethylene selectivity catalysts contain thermally unstable lithium; see Table 2 for comparison).

Catalyst Composition and Structure

XRD investigation revealed that the LaOBr prepared was tetragonal. When $BaCO_3$ was loaded on LaOBr, reaction occurred between these two phases during catalyst preparation, resulting in the formation of orthorhombic $Ba_3Br_4CO_3$, monoclinic $BaBr_2 \cdot 2H_2O$, hexagonal La_2O_3, and hexagonal $La(OH)_3$. From Fig. 4a, one can see that as the loading of $BaCO_3$ increased from 5 to 40 mol%, the amount of LaOBr in the prepared catalysts decreased and crystal phase of compounds such as La_2O_3, $La(OH)_3$, and $Ba_3Br_4CO_3$ were detected. From 40 to 100 mol%, the amount of La_2O_3 and $La(OH)_3$ decreased together with the upcoming of hexagonal $BaCO_3$. At 5, 40, and 50 mol% of $BaCO_3$ loadings, trace amount (not showed in the figure) of monoclinic $BaBr_2 \cdot 2H_2O$ was detected.

After OCM reaction at 800°C, hexagonal $La_2O_2CO_3$ was observed inside the 10 to 30 mol% $BaCO_3$/LaOBr catalysts. At 40 mol% loading, LaOBr could barely be detected and the dominant compounds were La_2O_3 and $La(OH)_3$. $Ba_3Br_4CO_3$ was present when $BaCO_3$ loading was above 5 mol%. Between 30 and 90 mol%, $BaBr_2 \cdot 2H_2O$ was present. $BaCO_3$ was detected only at a loading as high as 90 mol% (Fig. 4b).

When a 40 mol% $BaCO_3$/LaOBr catalyst was subjected to thermogravimetric analysis after OCM reaction, weight loss occurred at ca. 362, 504, and 761°C. The loss at 362 and 504°C were likely to be a result of $La(OH)_3$ dehydration (22):

$$2La(OH)_3 \xrightarrow{362^\circ C} La_2O_3 \cdot H_2O + 2H_2O$$

$$La_2O_3 \cdot H_2O \xrightarrow{504^\circ C} La_2O_3 + H_2O.$$

The standard $La_2O_2CO_3$ prepared in our laboratory decomposed at ca. 790°C. The observed weight loss at 761°C might be considered to be due to the decomposition of $La_2O_2CO_3$ generated during OCM reaction. Based on the weight loss at 761°C, the amount of $La_2O_2CO_3$ generated was estimated to be about 5.1 wt%. When a 10 mol% $BaCO_3$/LaOBr catalyst was examined, the amount of $La_2O_2CO_3$ was found to be 17.0 wt% (Table 3). The results are consistent with the XRD data, which showed that more $La_2O_2CO_3$ was generated during OCM reaction in the 10

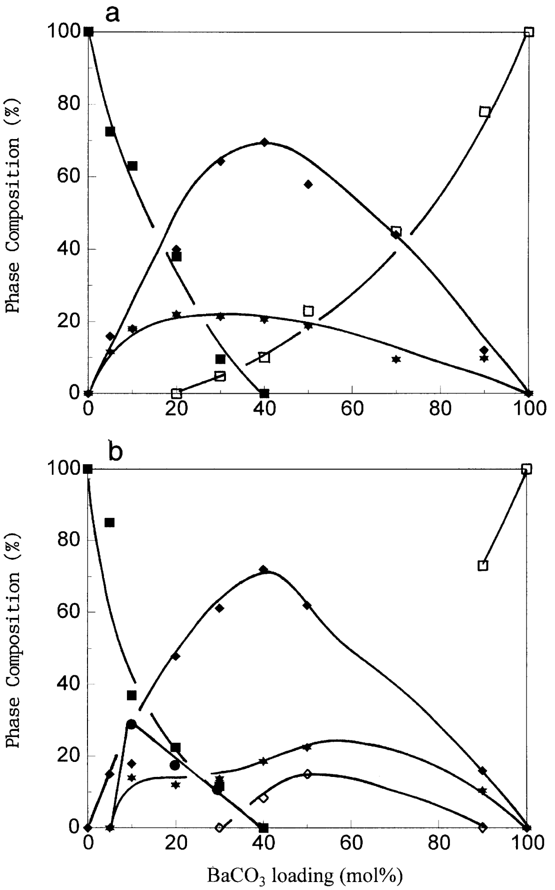

FIG. 4. Phase composition of the $BaCO_3$/LaOBr catalysts as related to $BaCO_3$ loading (a) before and (b) after OCM reaction. (■) LaOBr, (◆) $La_2O_3 + La(OH)_3$, (●) $La_2O_2CO_3$, (⋆) $Ba_3Br_4CO_3$, (□) $BaCO_3$, (◇) $BaBr_2 \cdot 2H_2O$.

mol% $BaCO_3$/LaOBr catalyst than in the 40 mol% one (Fig. 4b).

Referring back to Fig. 1, the CH_4 conversion, C_2 yield, and C_2H_4 selectivity are quite constant over a $BaCO_3$ composition range of 10–50 mol%. Compared with the XRD results (Fig. 4b), the only crystal structures which were found to exist over this whole range are $La_2O_3 + La(OH)_3$ and $Ba_3Br_4CO_3$. The former appears unlikely to be the active phase on two counts. One, $La_2O_3 + La(OH)_3$ have not been found to exhibit high C_2H_4 selectivity; two, the rather constant CH_4 conversion, C_2H_4 selectivity, and C_2 yield is more difficult to be reconciled with the great variation in the amount of $La_2O_3 + La(OH)_3$ over the 10–50 mol% $BaCO_3$ composition range. Therefore, $Ba_3Br_4CO_3$ appears to be the only candidate for the active phase.

XPS spectra of the catalysts before and after OCM reaction showed La $3d_{5/2}$ peak at 834.3 eV binding energy, accompanied by a staellite peak at 838.1 eV. The Ba $3d_{5/2}$ peak was at 780.2 eV while the Br 3d peak was at 68.7 eV. After OCM reaction, C 1s signals at 284.4 and 288.1 eV which could be assigned, respectively, to CH_x ($x = 0$–3) and surface carbonate (23) were recorded. O 1s peak profile showed two main components at 530.0 and 531.5 eV. The former was due to surface oxide O^{2-}, while the latter could be attributed to the presence of surface OH^- and/or CO_3^{2-} (23).

TABLE 3

TGA Results of Catalysts after OCM Reaction

Catalysts	T (°C)	ΔW (mg)	P (%)
$La_2O_2CO_3$	785	−5.1	NA
10 mol% $BaCO_3$/LaOBr	719	−0.91	17.0
40 mol% $BaCO_3$/LaOBr	740	−0.3	5.1

Note. T, temperature at which $La_2O_2CO_3$ decomposed; ΔW, weight loss of sample at T; P, percentage of $La_2O_2CO_3$ produced in the OCM reaction.

Based on the XPS peak areas and the atomic sensitivity factors of the elements, the elemental compositions on the surface of $BaCO_3$/LaOBr catalysts were calculated (Table 4). Generally speaking, with the increase in $BaCO_3$ loading, the surface composition of barium increased while that of lanthanum decreased, signifying the accumulation of Ba^{2+} on the surface of the catalysts with high $BaCO_3$ loading. For the 20 mol% and 40 mol% $BaCO_3$/LaOBr catalysts, the surface composition of barium increased by 89 and 35%, respectively, after OCM reaction; for the 70 mol% $BaCO_3$/LaOBr catalyst, there was a decrease of 21%, possibly due to sintering of surface barium compound(s). There was no marked change in surface composition of oxygen, bromine, and carbon during OCM reaction but a clear decrease in lanthanum composition due to accumulation of surface species.

Surface Oxygen Species

Using $^{18}O_2$, we performed $^{18}O/^{16}O$ isotope exchange experiments over LaOBr, as well as over the 10 and 30 mol% $BaCO_3$/LaOBr catalysts (Fig. 5). The catalysts were first

TABLE 4

Surface Elemental Composition of the Catalysts before (BR) and after (AR) OCM Reaction, Based on the XPS Data

$BaCO_3$/LaOBr catalysts $BaCO_3$ loading (mol%)	Ba (%)	Br (%)	La (%)	O (%)	C (%)
10 (BR)	3.4	12.9	6.9	35.0	40.0
10 (AR)	3.1	10.5	4.3	38.0	44.0
20 (BR)	3.5	16.2	7.5	36.8	35.9
20 (AR)	6.6	13.8	3.9	42.0	33.7
40 (BR)	6.2	13.2	5.3	40.2	35.0
40 (AR)	8.4	10.9	3.2	38.8	38.6
70 (BR)	9.8	11.2	3.8	44.3	30.9
70 (AR)	7.6	7.0	3.6	40.7	41.0

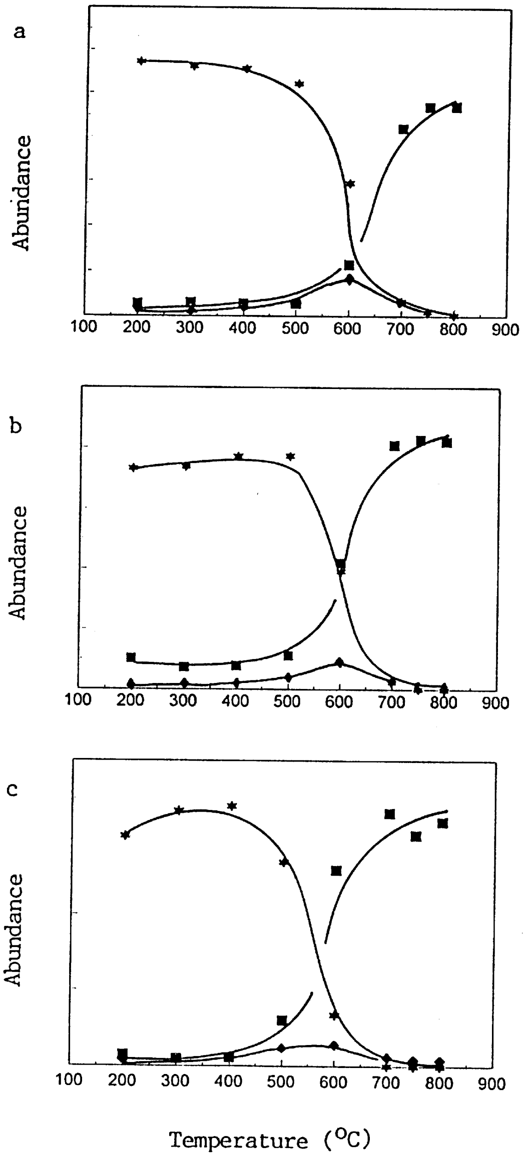

FIG. 5. $^{18}O/^{16}O$ isotope exchange over (a) LaOBr, (b) 10 mol% $BaCO_3$/LaOBr, and (c) 30 mol% $BaCO_3$/LaOBr catalysts. (■) $^{16}O_2$, (⋆) $^{18}O_2$, (◆) $^{18}O^{16}O$.

treated in a flow of $^{16}O_2$ at 750°C for 1 h and then purged with N_2 for 30 min at the same temperature before cooling to the desired temperature for $^{18}O_2$ pulsing. Below 400 °C, no isotope exchange occurred and only $^{18}O_2$ was detected by mass spectrometry. From 400 to 700°C, $^{18}O^{16}O$ was detected together with $^{16}O_2$. Above 700°C, only $^{16}O_2$ was detected. The results suggest that interchange between gaseous and surface oxygen of the catalysts becomes feasible above 400°C. However, the "active exchange" temperature appears to be lowered as the content of $BaCO_3$ increases. Above 700°C, lattice oxygen was heavily involved in such exchange. The data also indicate the existence of dioxygen species on the surface of the catalysts.

When the 20 and 50 mol% $BaCO_3$/LaOBr catalysts which were heated at 800°C (1 h) and then cooled to 25°C in a flow of oxygen (50 ml min^{-1}, ca. 1 atm) were subjected to temperature programmed desorption (TPD), oxygen desorption peaks were observed at 458 and 475°C, respectively. The oxygen desorption peak of LaOBr under similar treatment was at 443°C. It is generally believed that molecular oxygen is first adsorbed and then converted to oxygen species such as O^- and O_2^{2-} before its actual involvement in oxidation processes. In order to characterize the dioxygen species on the catalysts, we performed a number of *in situ* Raman experiments. Before discussing these results, it may be helpful to recall that Eysel and Thym (24) suggested that the vibrational frequency for surface peroxides (O_2^{2-}) lied in the region of 730–950 cm^{-1}, while Valentine (25) suggested that perturbed intermediate oxygen species O_2^{n-} ($1 < n < 2$) should give rise to bands in the 900–1100 cm^{-1} region. Furthermore, since Bösch and Kanzig reported that NaO_2 showed a band at 1164 cm^{-1} (26) and the vibrational frequency for neutral O_2 was known to be around 1550 cm^{-1} (27), the observed Raman bands in the region 1384–1452 cm^{-1} might be ascribed to $O_2^{\delta-}$ ($0 < \delta < 1$), species intermediate between O_2^- and neutral O_2 (28).

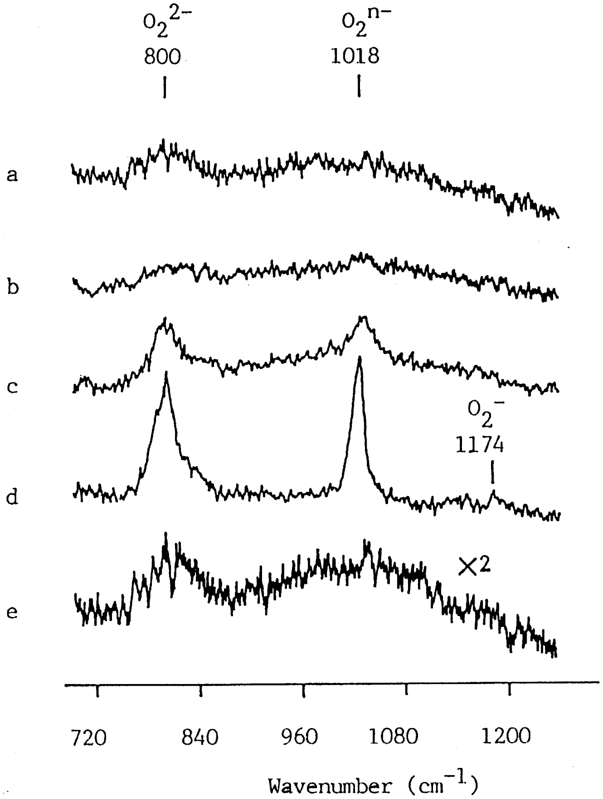

FIG. 6. Raman spectra obtained when a LaOBr catalyst was under (a) O_2 at 700°C, (b) O_2 at 500°C, (c) O_2 at 300°C, (d) O_2 at 100°C, and (e) $CH_4:O_2$ (2.6 : 1) at 700°C.

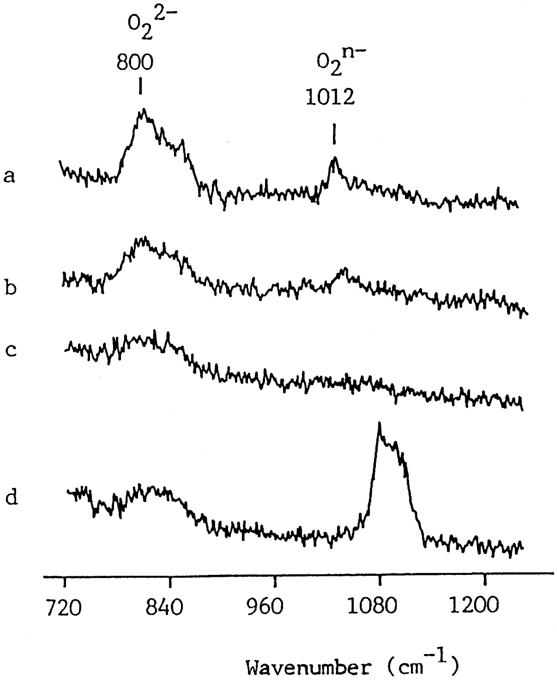

FIG. 7. Raman spectra obtained when a 10 mol% BaCO$_3$/LaOBr catalyst was under (a) O_2 at 100°C, (b) O_2 at 300°C, (c) O_2 at 650°C, and (d) $CH_4:O_2$ (2.6 : 1) at 650°C.

Figure 6 shows the Raman spectra of LaOBr under different atmospheres and temperatures. In the presence of oxygen (ca. 1 atm), two Raman bands at ca. 800 and 1032 cm^{-1} were observed at 700 and 500°C (spectra (a) and (b)). These two bands intensified significantly when the temperature was lowered to 300°C (spectrum (c)). By cooling to 100°C, they evolved into two intense, distinct bands at 800 and 1018 cm^{-1}, while a very small band at 1174 cm^{-1} appeared (spectrum (d)). These bands can be assigned to O_2^{2-}, O_2^{n-} ($1 < n < 2$), and O_2^-, respectively. Comparing spectrums (a) and (e), the spectrum obtained under CH_4/O_2 (2.6/1) mixture at 700°C looks very similar to the one under oxygen only; i.e., two bands at 800 and 1032 cm^{-1} were observed (notice the sensitivity scales of the two spectra differ by a factor of two).

Figure 7 shows the Raman spectra of 10 mol% BaCO$_3$/LaOBr catalyst under different atmospheres and temperatures. Under oxygen atmosphere only, at 100°C, three bands, viz. around 800, 1012, and 1056 cm^{-1} were observed. Similar to the case of LaOBr, the latter two bands decreased in intensity at higher temperatures and eventually disappeared at 650°C, while the first band, though also diminished, did persist even at 650°C. However, there is clear a distinction between the two cases. First, the 800 cm^{-1} band in the barium containing catalyst apparently consisted of two unresolved peaks, one slightly taller and sharper, centered at 800 cm^{-1} and the other broader, at around 845 cm^{-1}. Second, relatively speaking, the degree of diminishing due to raising temperature was significantly less than that of the LaOBr catalyst, and the 800 cm^{-1} peak was the part which accounted for most of the diminution. This appears to suggest that of the two O_2^{2-} species in the BaCO$_3$/LaOBr catalyst, the one with higher frequency (845 cm^{-1}) was thermally more stable than the one with frequency identical to that found in the LaOBr case. When the BaCO$_3$/LaOBr catalyst was under $CH_4:O_2$ (2.6 : 1) at 650°C, only the O_2^{2-} species at 845 cm^{-1} and an intense peak at 1056 cm^{-1} were observed (spectrum (d)). The latter could be assigned to CO_3^{2-} symmetric stretch mode arising from BaCO$_3$ (17). Together with results shown in Fig. 8 (spectra (a)–(c)), the thermally stable O_2^{2-} species found only for BaCO$_3$/LaOBr catalyst might well be responsible for its catalytic behavior toward OCM.

The LaOF catalyst which gave a C_2H_4/C_2H_6 ratio of 1.6 in OCM reaction at 800°C was chosen for comparison. Under an atmosphere of oxygen at 100°C, this catalyst gave strong Raman bands at 998, 1050, 1074, 1100, 1132, and 1148 cm^{-1} (Fig. 8). They are suggested to be due to O_2^{n-} and O_2^- species. No band at 800 cm^{-1} corresponding to O_2^{2-} was observed. Under CH_4/O_2 (2.6/1) at 700°C, only a small band at 988 cm^{-1} was detected. Based on the Raman results, we conclude that the LaOBr and 10 mol% BaCO$_3$/LaOBr catalysts are more capable of forming O_2^{2-} species than LaOF.

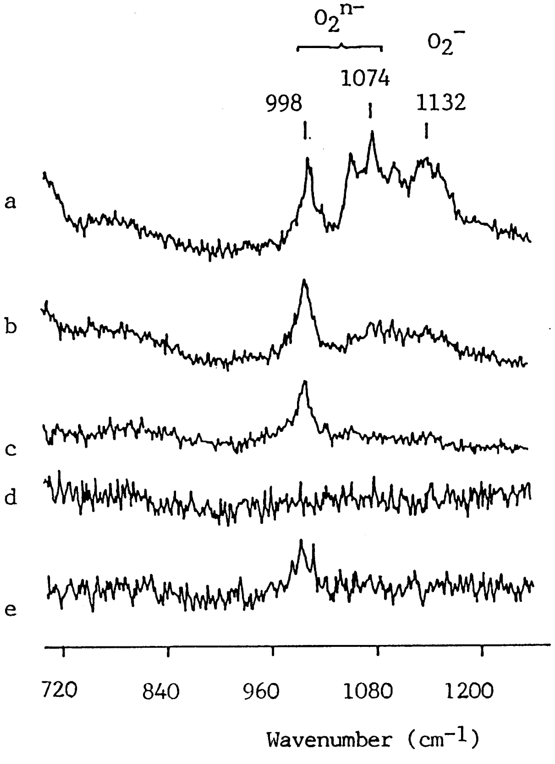

FIG. 8. Raman spectra obtained when a LaOF catalyst was under (a) O_2 at 100°C, (b) O_2 at 300°C, (c) O_2 at 500°C, (d) O_2 at 700°C, and (e) $CH_4:O_2$ (2.6 : 1) at 700°C.

TABLE 5

CD_4/CH_4 Isotope Exchange over LaOF, LaOBr, and $BaCO_3$/LaOBr Catalysts

Catalysts	Temp. (°C)	$X(CD_4)$ (%)	$X(CH_4)$ (%)	Isotope distribution after reaction (%)					C_2H_4/C_2H_6[a]
				CD_4	CD_3H	CD_2H_2	CDH_3	CH_4	
LaOF	750	11.5	11.4	67.7	3.1	1.4	2.3	25.5	1.0
	800	17.5	17.2	57.6	6.3	1.0	6.4	28.7	1.6
LaOBr	750	14.0	4.4	55.9	4.2	1.0	2.6	36.3	2.6
	800	14.7	14.2	52.9	6.2	3.5	4.4	33.0	3.3
10 mol% $BaCO_3$/LaOBr	750	27.5	12.3	59.1	2.9	3.1	1.9	33.0	4.2
	800	28.1	15.1	55.0	5.3	5.4	1.5	33.1	5.9
30 mol% $BaCO_3$/LaOBr	750	22.3	26.6	64.7	0.4	3.5	0.4	31.0	9.2
	800	25.7	23.5	58.0	2.3	8.1	0.3	58.0	11.3

Note. $CH_4 : CD_4$ ratio, 1 : 1.4.

[a] Data obtained in OCM reaction with conditions identical to that in Table 1.

Based on the XRD results, we know that reaction occurred between the $BaCO_3$ and LaOBr phases during preparation of the $BaCO_3$/LaOBr catalysts. From 5 to 30 mol% $BaCO_3$ loading, $BaCO_3$ phase was converted to orthorhombic $Ba_3Br_4CO_3$ and monoclinic $BaBr_2 \cdot H_2O$, while a certain amount of LaOBr was converted to hexagonal La_2O_3 and hexagonal $La(OH)_3$. We propose that during preparation of $BaCO_3$/LaOBr catalysts, it is possible to form O^- centers and trapped electrons in the catalysts. For example, in the crystal frame of La_2O_3, if one Br^- ion (radius, 1.95 Å) remains to occupy an O^{2-}(radius, 1.4 Å) lattice point, one anion vacancy which can trap an electron is generated. Also if one O^- substitutes one Br^- inside the lattice of crystal LaOBr, O^{2-} may lose an electron to form O^-. Likewise, in the case of $Ba_3Br_4CO_3$, it is possible to have bromine ion vacancies that can trap electrons which subsequently give rise to O^- centers.

Islam *et al.* (29) performed computer simulation on the {011} surface of La_2O_3 and suggested that O^- species can couple to form peroxide O_2^{2-} inside the La_2O_3 lattice. That trapped electrons can combine with molecular oxygen to form partially reduced oxygen species had been suggested by Ito *et al.* (30) and Wang *et al.* (31). In the presence of O_2 trapped electrons could combine with O_2 to O_2^- and O_2^{2-}, while O^- centers could combine with O_2 to from O_3^-. A good example is the observation of Steinberg (32) who reported the EPR signals of trapped electrons over partially reduced CeO/SiO_2 and their combination with molecular oxygen to form O_2^-. For a mixed catalyst like $BaCO_3$/LaOBr which comprises of several compounds with numerous interfaces, nonstochiometric behavior can almost be considered to be a norm. Defects such as O^- centers and trapped electrons could be present within a constituent structure or at the interface. In short, the detection of oxygen species such as O_2^{2-}, O_2^{n-}, O_2^-, and $O_2^{\delta-}$ over LaOBr and $BaCO_3$/LaOBr by *in situ* Raman spectrometry bears out this expectation.

Since inside the $BaCO_3$/LaOBr catalysts, La_2O_3, LaOBr, as well as $Ba_3Br_4CO_3$ are prone to exhibit vacancies that can trap electrons, the O_2^{2-} species responsible for the catalytic behavior need not be generated from the $Ba_3Br_4CO_3$ phase “proper”; it may also be generated from LaOBr and/or La_2O_3 phase near their interfaces with $Ba_3Br_4CO_3$. At present, our data are not sufficient to pin down which of these sources is predominant. Additional work on $Ba_3Br_4CO_3$ may be useful to resolve this issue.

C_2H_4 Formation through Carbene

The $BaCO_3$/LaOBr catalysts have a distinct ability in producing C_2 hydrocarbons with high C_2H_4/C_2H_6 ratio (Table 1 and Fig. 1). From Fig. 2, one can see that with the increase in CH_4/O_2 ratio, there was reduction in CO_x selectivity and consequently increase in total C_2 selectivity. Both C_2H_4 and C_2H_6 selectivities increased but the former remained constantly higher than the latter. The most striking result is that at 0.5 CH_4/O_2 ratio, C_2H_4 was the sole C_2 product. As the CH_4/O_2 ratio increased from 0.5 to 3, the C_2H_4/C_2H_6 ratio decreased from infinity to 2.9. The increase of contact time would cause CO_x selectivity to increase and C_2 selectivities to fall (Fig. 3). Compared with the C_2H_6 selectivity, C_2H_4 selectivity was always on the high side. At a contact time of 0.2 g s ml^{-1}, a C_2 yield of 26.3% could be obtained over the 50 mol% $BaCO_3$/LaOBr catalyst with a C_2H_4/C_2H_6 ratio of 4.3.

In order to understand the cause of high C_2H_4/C_2H_6 ratios in OCM reaction over the $BaCO_3$/LaOBr catalysts, we carried out CD_4/CH_4 isotope exchange experiments over LaOF, LaOBr, and the 10 and 30 mol% $BaCO_3$/LaOBr catalysts at 750 and 800°C (Table 5). For these catalysts, the products included CD_3H, CD_2H_2, and CH_3D. No ethane or ethylene was observed. No reaction was observed in the absence of the catalysts. We found that the generation of CD_2H_2 increased in the order of LaOF < LaOBr < 10

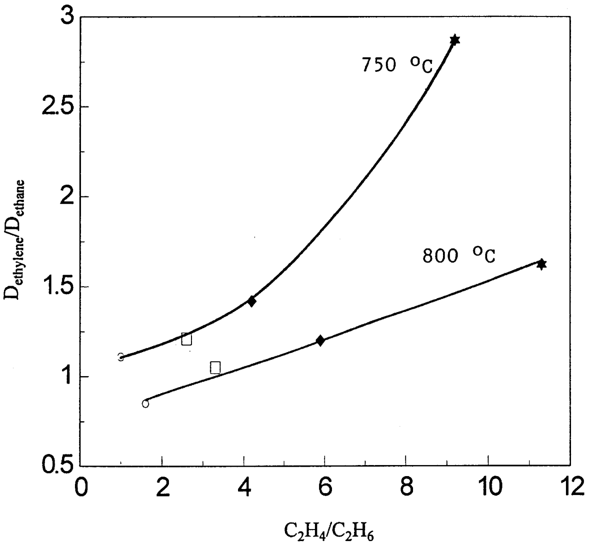

FIG. 9. The plotting of the ratios of deuterium distribution in ethene and ethane ($D_{ethylene}/D_{ethane}$) versus the C_2H_4/C_2H_6 ratios obtained over LaOF (○), LaOBr (□), 10 mol% $BaCO_3$/LaOBr (◆), and 30 mol% $BaCO_3$/LaOBr (⋆) at 750 and 800°C.

mol% $BaCO_3$/LaOBr $<$ 30 mol% $BaCO_3$/LaOBr and the generation of CD_3H and CH_3D behaved in the reversed order. The CD_2H_2 distributions are parallel to the ratios of C_2H_4/C_2H_6 observed over these catalysts. Could carbene be generated in OCM reaction and take part in the production of C_2H_4 over the $BaCO_3$/LaOBr catalysts? To answer this question, we used a 1 : 1 mixture of CH_4/CD_4 instead of CH_4 in OCM reaction and analyze the deuterium distribution in ethane and ethylene. The idea is that if methyl radicals are the intermediates, one could expect to see the same deuterium distribution in ethane and ethylene since all ethylene comes from ethane. If both methyl radicals and carbenes are generated, the distribution of deuterium in ethylene is expected to be higher since it now has two additional pathways, viz., $:CH_2 + :CD_2 \rightarrow CH_2CD_2$ and $:CD_2 + :CD_2 \rightarrow CD_2CD_2$. Figure 9 shows the results of such reaction over the LaOF, LaOBr, 10 mol% $BaCO_3$/LaOBr, and 30 mol% $BaCO_3$/LaOBr catalysts at 750 and 800°C. It is apparent that over catalysts that would give high C_2H_4/C_2H_6 ratios, the deuterium distribution in ethylene is higher than that in ethane. For the two $BaCO_3$/LaOBr catalysts studied, the distribution of deuterium in ethylene is distinguishably higher than that in ethane, implying that the carbene was abundant over the catalysts. Consequently, the chance of producing C_2H_4 by $:CH_2$ coupling over the $BaCO_3$/LaOBr catalysts improves. The results could be related to the amount of O_2^{2-} species detected at 650 or 700°C under CH_4/O_2 in the *in situ* Raman investigations (Figs. 6–8); no O_2^{2-} species was detected in the LaOF case but a O_2^{2-} species of moderate thermal stability was observed over LaOBr and a O_2^{2-} species of high thermal stability was observed over the 10 mol% $BaCO_3$/LaOBr catalyst. It is possible that the existence of O_2^{2-} has a link with the relatively high C_2H_4/C_2H_6 ratios recorded over the LaOBr and $BaCO_3$/LaOBr catalysts. Noting that Hutchings *et al.* (33) suggested that O^- and O_2^{2-} might be responsible for the abstraction of hydrogen atoms from methane molecules, we propose that in our case the formation of C_2H_4 might be principally through the coupling of $:CH_2$:

$$CH_4 + O_2^{2-} \rightarrow :CH_2 + 2OH^-$$

$$2:CH_2 \rightarrow C_2H_4.$$

While other workers (Lin *et al.* (34), Martin *et al.* (35), Nelson (36), and Hutchings *et al.* (33) also suggested carbene as intermediate for the formation of C_2H_4, the results of this work appear to provide additional evidence for a major carbene mechanism.

CONCLUSION

The $BaCO_3$/LaOBr catalysts had good catalytic performance for OCM reaction. Two sets of outstanding performance results are as follows: a C_2 yield of ca. 26.3% with a C_2H_4/C_2H_6 ratio of 4.3 and a C_2 yield of 18.9% with a C_2H_4/C_2H_6 ratio of infinity could be obtained at 800°C over the 50 mol% $BaCO_3$/LaOBr catalyst. Thus, one advantage of the $BaCO_3$/LaoBr catalysts is that they can produce C_2 hydrocarbons with high C_2H_4/C_2H_6 ratios. XRD investigations reveal the generation of new phases such as $La(OH)_3$, La_2O_3, and $Ba_3Br_4CO_3$ inside the $BaCO_3$/LaOBr catalysts. *In situ* Raman studies revealed the presence of O_2^{2-} species during OCM reaction over the LaOBr and 10 mol% $BaCO_3$/LaOBr catalysts. We conclude that defects such as O^- centers and trapped electrons were created in the catalysts. The coupling of O^- species and the interaction of O_2 with trapped electrons would result in the presence of dioxygen species which are responsible for the catalytic behavior of the catalysts. We propose that carbene was produced over the $BaCO_3$/LaOBr catalysts and that the coupling of carbene, rather than methyl radical, could be the major step for C_2H_4 generation over the $BaCO_3$/LaOBr catalysts.

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REFERENCES

1. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73**, 9 (1982).
2. Maitra, A. M., *Appl. Catal. A* **104**, 11 (1993).
3. Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **46**, 69 (1989).

4. Burch, R., Chalker, S., and Loader, P., *in* "New Frontiers in Catalysis," (L. Guczi, Ed.), 1992.
5. Ueda, W., and Thomas, J. M., *J. Chem. Soc. Chem. Commun.* 1148 (1988).
6. Ueda, W., Isozaki, T., Morikawa, Y., and Thomas, J. M., *Chem. Lett.* 2103 (1989).
7. Ueda, W., Thomas, J. M., Philips, M. J., and Ternan, M., "Proceedings, 9th International Conference on Catalysis, Calgary 1988" (M. J. Philips and M. Ternan, Eds.). Chem. Institute of Canada, Ottawa, 1988.
8. Sugiyama, S., Matsumura, Y., and Moffat, J. B., *J. Catal.* **139**, 338 (1993).
9. Voyatzis, R., and Moffat, J. B., *J. Catal.* **142**, 45 (1993).
10. Khan, A. Z., and Ruckenstein, E., *Catal. Lett.* **13**, 95 (1992).
11. Lunsford, J. H., Hinson, P. G., Rosynek, M. P., Shi, C., Xu, M., and Yang, X., *J. Catal.* **147**, 301 (1994).
12. Otsuka, K., Hatano, M., and Komatsu, T., *Stud. Surf. Sci. Catal.* **36**, 383 (1988).
13. Fujimoto, K., Hashimoto, S., Asami, K., Omata, K., and Tominaga, H., *Appl. Catal.* **50**, 223 (1989).
14. Zhou, X. P., Zhang, W. D., Wan, H. L., and Tsai, K. R., *Catal. Lett.* **23**, 113 (1993).
15. Van, T. L., Che, M., Kermarec, M., Louis, C., and Tatibouet, J. M., *Catal. Lett.* **6**, 395 (1990).
16. Becker, S., and Baerns, M., *J. Catal.* **128**, 512 (1991).
17. Au, C. T., He, H., Lai, S. Y., and Ng, C. F., *J. Catal.* **159**, 280 (1996).
18. Au, C. T., Zhang, Y. Q., Ng, C. F., and Wan, H. L., *Catal. Lett.* **23**, 37 (1994).
19. Au, C. T., Hu, Y. H., and Wan, H. L., *Catal. Lett.* **27**, 199 (1994).
20. Thomas, J. M., Ueda, W., Williams, J., and Harris, K. D. M., *Faraday Discuss. Chem. Soc.* **87**, 33 (1989).
21. Chan, T. K., and Smith, K. J., *Appl. Catal.* **60**, 13 (1990).
22. Rau, R. C., and Glover, W. J., Jr., *J. Am. Ceram. Soc.* **47**, 382 (1964).
23. Au, C. T., Li, X. C., Tang, J., and Roberts, M. W., *J. Catal.* **106**, 538 (1987).
24. Eysel, H. H., and Thym, S., *Anorg. Allg. Chem.* **411**(2), 97 (1975).
25. Valentine, J. S., *Chem. Rev.* **73**, 237 (1973).
26. Bösch, M., and Kanzig, W., *Helv. Phys. Acta.* **48**, 743 (1975).
27. Smith, P., *J. Phys. Chem.* **60**, 1471 (1956).
28. Zhou, X. P., Chao, Z. S., Wang, S. J., Wan, H. L., and Tsai, K. R., *Chem. Res. Chin. Univ.* **11**(1), 84 (1995).
29. Islam, M. S., and Ilett, D. J., *J. Phys. Chem.* **98**, 9637 (1994).
30. Ito, T., Watanabe, M., Kogo, K., and Tokuda, T., *Z. Phys. Chem.* **124**, 83 (1981).
31. Wang, J. X., and Lunsford, J. H., *J. Phys. Chem.* **90**, 5883 (1986).
32. Steinberg, M., *Isr. J. Chem.* **8**, 877 (1970).
33. Hutchings, G. J., and Woodhouse, J. R., *J. Chem. Soc. Faraday Trans. 1* **85**(8), 2507 (1989).
34. Lin, C., Campbell, K. D., Wang, J., and Lunsford, J. H., *J. Phys. Chem.* **90**, 534
35. Martin, G., and Mirodators, C., *J. Chem. Soc. Chem. Commun.*, 1393 (1987).
36. Nelson, P. E., Lakey, C. A., and Cant, N. W., *J. Phys. Chem.* **92**, 6176 (1988).