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# The enhancement effects of $BaX_2$ (X = F, Cl, Br) on $SnO_2$ -based catalysts for the oxidative coupling of methane (OCM)

Rong Xi<sup>1</sup>, Junwei Xu<sup>1</sup>, Yan Zhang, Zhixuan Zhang, Xianglan Xu, Xiuzhong Fang, Xiang Wang\*

Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, College of Chemistry, Nanchang University, Nanchang, 330031, PR China

#### ARTICLE INFO

#### ABSTRACT

Keywords: Oxidative coupling of methane SnO<sub>2</sub>-based catalysts Barium halide promoters BaSnO<sub>3</sub> O<sub>2</sub>-and O<sub>2</sub><sup>2-</sup>active sites In this study, the promotional effects of different barium halides (BaF<sub>2</sub>, BaCl<sub>2</sub> and BaBr<sub>2</sub>) on SnO<sub>2</sub> for OCM reaction have been investigated. It is observed that the addition of all the barium halides can improve the reaction performance of SnO<sub>2</sub>, following the sequence of BaBr<sub>2</sub> > BaCl<sub>2</sub> > BaF<sub>2</sub>. Raman and XRD results have substantiated that adding barium halides to SnO<sub>2</sub> can increase the amount of surface vacancies/defects, hence creating more abundant surface OCM reactive oxygen sites by anion substitution. At the same time, the amount of the moderate basic sites contributing to OCM reaction is also improved. During OCM reaction, the amount of the OCM reactive oxygen species as well as the moderate basic sites can be further increased. As proved by *In situ* Raman and XPS results, on BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 and BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1, O<sub>2</sub><sup>-</sup> is the OCM reactive oxygen sites. In contrast, on BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1, O<sub>2</sub><sup>-2</sup> anions are reported to be favourable for the direct formation of C<sub>2</sub>H<sub>4</sub> through carbene mechanism, which explains the high ethylene selectivity on BaBr<sub>2</sub>-modified catalyst. The amount and properties of the surface active oxygen species and basic sites are of great importance for OCM reaction, and their concerted interaction determines the reaction performance of BaX<sub>2</sub>/SnO<sub>2</sub> catalysts. BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 contains the apporiate amount of both types of active sites, hence displaying the best OCM performance among all the catalysts.

#### 1. Introduction

Methane accounts for more than 95 % of natural gas, and it also occupies a relatively high proportion in shale gas [1,2]. Over the past three decades, numerous studies have investigated direct or indirect conversion of methane to value-added products including n-paraffins, ethylene, hydrogen, methanol and dimethyl ether [1,2]. The indirect conversion ways include dry reforming, steam reforming and partial oxidation of methane, which first convert methane into syngas, and then use syngas to produce more valuable products via Fischer-Tropsch reaction. The direct conversion ways include non-oxidative methane conversion into aromatics and oxidative coupling of methane into C<sub>2</sub> hydrocarbons, which have not yet been industrialized due to the lack of highly efficient catalysts [3,4]. Oxidative coupling of methane into C<sub>2</sub> hydrocarbons has aroused great interest because of the attractive prospect to transform directly inexpensive methane into ethylene, a critical platform product in petrochemical industry. The process generally includes the activation of CH4 on the catalyst surface active sites to generate CH3 radicals, followed by gas-phase coupling of CH3 radicals to form  $C_2H_6$ , which is then converted into  $C_2H_4$  via dehydrogenation [2,5,6].

Up to now, the most frequently studied catalyst systems are based on Li/MgO and Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>. Li/MgO exhibits good initial reaction performance, but suffers from an inherent instability due to the vaporization of Li<sup>+</sup> cation, which is believed to be a structure modifier of the catalyst [7,8]. In contrast, Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> exhibits not only better reaction performance, but also long-term stability, which is regarded as the catalyst with the highest potential for industrial application [9–11]. Whereas, over this catalyst, only 25–27% C<sub>2</sub> product yield can be obtained at a high temperature  $\sim 850$  °C [9–11]. Furthermore, the nature of the active sites in Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> have not yet been understood very clearly due to the complex of the catalyst [12]. Therefore, there is still strong incentive to seek for improved catalysts that can be operated at relatively lower temperature with enough C<sub>2</sub> yield to industrialize this important reaction.

Since Keller and Bhasin first reported their work on OCM in early 1980s [13], more than 1800 catalysts used for this reaction have been explored and reported [14]. By analyzing a large amount of literature

\* Corresponding author.

<sup>1</sup> These authors contributed equally.

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E-mail address: xwang23@ncu.edu.cn (X. Wang).



Fig. 1. XRD patterns of the catalysts, (a) fresh, (b) spent.

data, Takahashi et al. concluded that three kinds of materials are favorable for constructing OCM catalysts with considerable C<sub>2</sub> yield, which include alkaline earth metals, lanthanide metals and IIIA, VA, via and VIIA group metals [14]. In the early stage, alkaline earth metal oxides modified by alkali metals and some other un-modified or modified metal oxides have been adopted as typical catalysts to investigate the mechanism of OCM reaction. It was found that C2 selectivity is intimately related to the basicity of the catalysts, thus basic metal oxides are regarded as appropriate catalysts for the reaction [3,15]. On the other hand, pure or composite lanthanide oxides possessing surface or bulk oxygen vacancies are reported to be beneficial to generate reactive oxygen species for OCM reaction [16,17]. For instances, La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> have been investigated for the reaction, which display certain selectivity to C2 products [16,17]. Moreover, on composite lanthanide oxides such as ABO3 perovskites or A2B2O7 pyrochlores, abundant oxygen vacancies are present, which can induce the generation of a large amount of surface active oxygen sites favorable for OCM reaction [18–20]. It was formerly reported that using alkali metal and alkali earth metal halides as catalyst promoter can improve the C2 selectivity because the halogen anions have a negative effect on methane deep oxidation [21-23].

On the basis of the above details, it can be seen that a good OCM catalyst requires usually high thermal stability, suitable basicity to activate  $CH_4$  molecules, and certain amount of oxygen vacancies to generate selective oxygen species for the target product formation. Moreover, the addition of halogen anions to some catalysts can obviously improve the  $C_2$  selectivity and yield by avoiding methane deep oxidation.

As an *n*-type semiconductor with a high melting point at 1630 °C, SnO<sub>2</sub> has been reported to be a very good oxidation catalyst due to its abundant oxygen vacancies and reducible lattice oxygen species [24,25]. But SnO<sub>2</sub> related catalysts have been rarely used for OCM reaction except that several publications are reported to adopt SnO<sub>2</sub> as a catalyst additive [26,27]. When using different alkali metal oxides to modify SnO<sub>2</sub> for OCM reaction, our group has found that a Li-modified catalyst with a Sn/Li molar ratio of 5:5 exhibits the best reaction performance, which depicts much better low temperature reaction performance than Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> due to the synergistic effects of the abundant electrophilic oxygen species and moderate basic sites [25]. Chou et al. have investigated the mechanism of OCM reaction over LiCl/SnO<sub>2</sub>, and found that adding Cl<sup>-</sup> anions can improve its reaction performance due to the formation of higher concentration of surface anion vacancies, more rapid oxygen mobility and improved redox ability of Sn [28].

Inspired by these work, with the objective to develop more efficient catalysts, and to investigate the influence of alkaline earth metal halides and halogen anions on the reaction performance of SnO<sub>2</sub>, BaF<sub>2</sub>, BaCl<sub>2</sub> and BaBr<sub>2</sub> have been employed to modify SnO<sub>2</sub> to prepare catalysts for OCM reaction. It is revealed that in comparison with pure SnO<sub>2</sub>, all of

the modified catalysts exhibit significantly improved performance for the reaction, due to the concerted interaction between the surface basic sites, electrophilic oxygen species and halogen anions. A catalyst with a BaBr<sub>2</sub>:SnO<sub>2</sub> molar ratio of 1:1 displays the best promotional effects among all of the catalysts, on which the highest C<sub>2</sub> product yield of 18.0 % can be obtained, also with a high C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio of 4/1. By using different characterization means, the relationship between the reaction performance and the structure of the catalysts has been elucidated in depth.

#### 2. Experimental

#### 2.1. Catalyst synthesis

A series of SnO<sub>2</sub>-based catalysts modified by BaX<sub>2</sub> (X = F, Cl, Br) with a BaX<sub>2</sub>: SnO<sub>2</sub> molar ratio of 1:1 were synthesized with a physical mixing method, using BaF<sub>2</sub> (99.8 %), BaCl<sub>2</sub>.2H<sub>2</sub>O (99.99 %), BaBr<sub>2</sub>.2H<sub>2</sub>O (99.8 %) and CVD-SnO<sub>2</sub> as the precursors. In detail, the mixture of BaX<sub>2</sub> and SnO<sub>2</sub> was moistened with a certain amount of deionized water and ground in a mortar until it became a hard paste. After drying at 120 °C overnight, the paste was ground into powder, and then calcined in air at 800 °C for 4 h.

#### 2.2. Catalyst characterization and reaction performance evaluation

OCM reaction has been used to evaluate the performance of the catalysts. The bulk and surface properties of the catalysts have also been explored by different means. The equipment models, operation conditions, experimental procedures and parameters are listed in detail in the supporting information.

#### 3. Result and discussion

#### 3.1. XRD and N2-BET measurement of the catalysts

XRD techniques have been employed to identify the phase compositions of the fresh and spent catalysts, with the patterns displayed in Fig. 1. For comparative study, the individual fresh and spent barium halides were also analyzed, with the patterns exhibited in Fig. S1. Compared to fresh barium halides, the spent ones exhibit no crystalline phase change, indicating that they are stable during OCM process.

For all the fresh  $BaX_2/SnO_2$  catalysts, tetragonal rutile  $SnO_2$  and the corresponding barium halide diffraction peaks can be observed separately, testifying that no solid phase reaction between  $SnO_2$  and barium halides was taken place during the high temperature calcination process. Compared to the fresh catalysts, after OCM reaction, while the  $BaF_2:SnO_2 = 1:1$  and  $BaCl_2:SnO_2 = 1:1$  samples exhibit no any detectable change, a new  $BaSnO_3$  phase was detected for  $BaBr_2:SnO_2 = 1:1$ , as indicated by the intensive diffraction peaks at 30.6, 43.8 and 54.4°.

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#### Table 1

Specific surface areas, lattice parameters and Raman quantification results of the fresh and spent catalysts.

Samples	Surface area (m <sup>2</sup> g <sup>-1</sup> )		Lattice parameter <sup>a</sup> $\alpha = \beta = \gamma = 90^{\circ}, a =$	Lattice parameter <sup>a</sup> $\alpha = \beta = \gamma = 90^{\circ}, a = b \neq c (Å)$				A <sub>1</sub> /A <sub>1g</sub>	
	Fresh	Spent	Fresh		Spent		Fresh	Spent	
SnO <sub>2</sub>	30	28	a = b = 4.735	c = 3.178	a = b = 4.733	c=3.176	0	0	
$BaF_2:SnO_2 = 1:1$	9	7	a = b = 4.740	c = 3.177	a = b = 4.739	c=3.175	0.06	0.10	
$BaCl_2:SnO_2 = 1:1$	7	5	a = b = 4.765	c = 3.186	a = b = 4.806	c=3.204	0.08	0.20	
$BaBr_2:SnO_2 = 1:1$	4	3	a = b = 4.782	c = 3.193	-	-	0.17	-	

<sup>a</sup> Calculated using the Scherrer equation.

The initial BaBr<sub>2</sub> and SnO<sub>2</sub> phases can hardly be observed, indicating that solid phase reaction occurred between SnO<sub>2</sub> and BaBr<sub>2</sub> during the high temperature OCM process. To verify the formation of BaSnO<sub>3</sub>, a pure BaSnO<sub>3</sub> sample was also prepared intentionally by the same method described in the experimental section, but using Ba(NO<sub>3</sub>)<sub>2</sub> and SnO<sub>2</sub> as the precursors. XRD results in Fig. S1 (c) have proved that BaSnO<sub>3</sub> phase has indeed formed in BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalysts.

Compared with pure  $SnO_2$ , the 2 $\theta$  diffraction peaks of the  $SnO_2$ phase in the fresh BaX<sub>2</sub>/SnO<sub>2</sub> catalysts shift more or less to lower angles, which accompany the increase of the side lengths of the unit cell in the order of  $BaF_2 < BaCl_2 < BaBr_2$ , as listed in Table 1. This indicates that the addition of barium halides has enlarged the unit cell volume of SnO<sub>2</sub> phase in the modified samples, especially for BaCl<sub>2</sub> and BaBr<sub>2</sub> modified catalysts. This enlargement effect of SnO<sub>2</sub> cell may be a result of anion substitutions. It is known that Sn<sup>4+</sup> in SnO<sub>2</sub> lattice is 6-fold coordinated with a radius of 0.69 Å, and the 6-fold coordinated Ba2 has a radius of 1.35 Å. Therefore, it is impossible for  $Ba^{2+}$  to substitute  $Sn^{4+}$  in  $SnO_2$  lattice to form a solid solution structure [24,25]. Whereas, the radius of  $O^{2-}$  in SnO<sub>2</sub> lattice is 1.40 Å, and the radius of F-, Cl- and Br- is 1.33, 1.81 and 1.96 Å, respectively, in the range to be able to replace partially the lattice  $O^{2-}$ . Therefore, It is rational to propose that during the calcination process, a certain amount of O<sup>2-</sup> anions in the SnO<sub>2</sub> lattice could be replaced by the X- anions with larger radii, hence expanding the SnO<sub>2</sub> cell volume and side lengths [23]. As a side effect, surface vacancies could be formed to maintain electric neutrality, which is beneficial to generate surface mobile oxygen sites. For  $BaCl_2:SnO_2 = 1:1$  catalyst, Its side lengths of  $SnO_2$  phase become evidently bigger after OCM reaction, indicating that the anion substitution continued during the reaction process [23].

The specific surface areas of the catalysts were analyzed with  $N_{2}$ -BET. As displayed in Table 1, the addition of barium halide has decreased the specific surface area of the modified catalysts in comparison with the individual SnO<sub>2</sub>. Compared with the fresh catalysts, after OCM reaction, all the samples have only insignificant surface area decrease, indicating that these SnO<sub>2</sub>-based samples are stable during the high temperature reaction.

#### 3.2. Raman spectra characterization of the catalysts

Raman technique was also used to investigate the compositions and properties of the catalysts. For comparison, the spectra of individual barium halides and  $BaSnO_3$  were also collected and shown in Fig. S2. Compared with fresh barium halides, the Raman spectra of the spent ones have no any change in Raman modes, testifying that they are chemically stable during OCM process, well consistent with the XRD results.

As formerly reported, SnO<sub>2</sub> with a rutile crystalline phase belongs to  $D_{4h}^{14}$  space group, whose active Raman modes can be distributed as  $B_{1g}$ ,  $E_g$ ,  $A_{1g}$  and  $B_{2g}$  according to the group theory [24,25]. For the fresh BaX<sub>2</sub>/SnO<sub>2</sub> catalysts, as shown in Fig. 2(a), three typical Raman vibration modes at 478 cm<sup>-1</sup>, 633 cm<sup>-1</sup> and 774 cm<sup>-1</sup> corresponding to  $E_g$ ,  $A_{1g}$  and  $B_{2g}$  modes can be obviously observed, which indicates that SnO<sub>2</sub> is the major phase in all the catalysts [24,25]. For spent

 $BaF_2:SnO_2 = 1:1$  and  $BaCl_2:SnO_2 = 1:1$  catalysts, no obvious phase change can be observed after OCM reaction, well consistent with the XRD results. Nevertheless, it is apparent that significant phase change is detectable for the spent  $BaBr_2:SnO_2 = 1:1$  catalyst. To clarify this, the Raman spectroscopy of the pure  $BaSnO_3$  compound was collected and compared with the spent  $BaBr_2:SnO_2 = 1:1$  catalyst in Fig. S2(c).

It was previously reported that in a perfect cubic BaSnO<sub>3</sub> perovskite structure with space group of Pm3m, three IR active modes with  $F_{1u}$ symmetry can be detected, but no Raman active modes can be observed [29,30]. As hown in Fig. S2(c), the Raman bands observed for BaSnO<sub>3</sub> and the spent  $BaBr_2:SnO_2 = 1:1$  catalyst are likely to present defects in the samples, which may locally lower the internal symmetry of the perovskite phase, thus leading to unexpected Raman modes. A sharp peak at 1060  $\text{cm}^{-1}$  is observed, which is ascribed to the BaCO<sub>3</sub> phase [29,30]. Because the defective cubic BaSnO<sub>3</sub> perovskite structure is an A-site Schottky type disorder, which possesses an A-site vacancy coupled with an oxygen vacancy [29]. In this case, the elimination of the structure Ba cations happens, which would eventually convert into  $BaCO_3$  in contact with the atmosphere  $CO_2$  or OCM byproduct  $CO_2$ . Except for the Raman peaks of BaSnO<sub>3</sub>, some Raman peaks belonging to  $BaBr_2$  can be observed for the spent  $BaBr_2:SnO_2 = 1:1$  catalyst, suggesting that solid phase reaction between SnO<sub>2</sub> and BaBr<sub>2</sub> is not very complete during the high temperature OCM process.

Compared to pure SnO<sub>2</sub>, all the fresh BaX<sub>2</sub>/SnO<sub>2</sub> catalysts exhibit a new peak at  $575 \text{ cm}^{-1}$ , which can be attributed to interface or surface phonon modes corresponding to lattice disorder and oxygen vacancies [24,25]. We hence quantified the integrated area ratios  $(A_1/A_{1g})$  of the fresh and spent samples in Table 1. For the fresh catalysts, the  $A_1/A_{1g}$ ratios follows the order of  $BaBr_2:SnO_2 = 1:1 >$  $BaCl_2:SnO_2 = 1:1 > BaF_2:SnO_2 = 1:1 > SnO_2$ , indicating that the addition of barium halide to SnO2 can improve the vacancy amount on the catalyst surface. For the spent catalysts, except for  $BaBr_2:SnO_2 = 1:1$ , it is obvious that the  $A_1/A_{1g}$  ratios are larger than the corresponding fresh catalysts and follow the order of  $BaCl_2:SnO_2 = 1:1 >$  $BaF_2:SnO_2 = 1:1 > SnO_2$ . This supports the XRD results to testify that anion substitution occurs to the modified catalysts, which also continues during the OCM process. The presence of surface vacancies/defects are believed to be favorable for the generation of surface active sites, such as electrophilic oxygen species [16,17].

#### 3.3. Reaction performance of the catalysts

The reaction performance of the catalysts has been evaluated for OCM, with the results displayed in Fig. 3 and Table 2. For comparison, the related pure barium halides were also tested for the reaction. Fig. S3 displays that all of them have poor reaction performance.

As depicted in Fig. 3, pure SnO<sub>2</sub> exhibits constant CH<sub>4</sub> conversion around 10 % from 600 to 800 °C, but has low selectivity to C<sub>2</sub> products. In contrast, all the BaX<sub>2</sub>/SnO<sub>2</sub> catalysts exhibit evidently lower activity than pure SnO<sub>2</sub> below 650 °C. But starting from 700 °C, the reaction performance of these modified catalysts begins to output it. Above this temperature, the CH<sub>4</sub> conversion, C<sub>2</sub> product selectivity and yield improve quickly with the increasing of the temperature. Obviously, the



Fig. 2. Raman spectra of the catalysts, (a) fresh, (b) spent.

catalytic performance of the catalysts follows the order of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 > SnO<sub>2</sub>. BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 possesses the best OCM reaction performance among

BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 possesses the best OCM reaction performance among all the catalysts. Particularly, it is noted here that this catalyst displays also the highest C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio in all the samples (Fig. 3(d) and Table 2), demonstrating that it owns also the surface active sites facilitating the formation of ethylene. The C<sub>2</sub>H<sub>4</sub> selectivity, C<sub>2</sub>H<sub>4</sub> yield and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratios follow the sequence of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 > SnO<sub>2</sub> at 800 °C.

As evidenced by XRD and Raman results, in the spent  $BaBr_2:SnO_2 = 1:1$ , a large amount of  $BaSnO_3$  has been formed during OCM reaction, which could play a critic role for the reaction performance and selectivity to ehtylene. Therefore, the OCM performance of pure  $BaSnO_3$  has also been evaluated. Fig. 3 shows that  $BaSnO_3$  has much better OCM performance than  $SnO_2$ , which is close to  $BaF_2:SnO_2 = 1:1$ . However, its performance is still much lower than  $BaBr_2:SnO_2 = 1:1$ . In this sample, beside the large amount of  $BaSnO_3$ , a

Table 2
The OCM performance of different catalysts at 800 °C.

Catalysts	Conversion (%)	ion (%) Selectivity (%)		Yield (%)		C <sub>2</sub> H <sub>4</sub> /
		C <sub>2</sub>	$C_2H_4$	C2	$C_2H_4$	C <sub>2</sub> n <sub>6</sub>
$\label{eq:snO2} \begin{split} &SnO_2\\ BaF_2:SnO_2 = 1:1\\ BaCl_2:SnO_2 = 1:1\\ BaBr_2:SnO_2 = 1:1\\ BaSnO_3 \end{split}$	11.6 22.5 28.0 28.9 28.4	11.8 56.4 63.9 62.6 49.3	3.0 26.2 38.3 50.1 30.3	1.4 12.7 17.9 18.1 14.0	0.4 5.9 10.7 14.5 8.6	0.3 0.9 1.5 4.0 1.6

small amount of  $BaBr_2$  is still present. This seems to indicate that the concerted interaction between  $BaSnO_3$  and  $BaBr_2$  is necessary to get an improved OCM reaction performance.

To get deeper understanding on the reaction process, both of  $CO_2$ and CO selectivity over the catalysts are also shown in Fig. S4. Fig. S4 (A) demonstrates that the  $CO_2$  selectivity on the catalysts decreases



Fig. 3. The OCM performance of the catalysts. (a)  $CH_4$  conversion, (b)  $C_2$  selectivity, (c)  $C_2$  yield, (d)  $C_2H_4/C_2H_6$  ratio. Reaction conditions:  $CH_4/O_2 = 4:1$  (nitrogen as balance gas), WHSV = 18,000 mL<sup>-1</sup> h<sup>-1</sup> g<sup>-1</sup>.



Fig. 4. Long-term stability test of the catalysts at 800 °C. Reaction conditions:  $CH_4/O_2 = 4:1$ , (nitrogen as balance gas), WHSV = 18,000 mL<sup>-1</sup> h<sup>-1</sup> g<sup>-1</sup>.

with the sequence of  $SnO_2 > BaF_2:SnO_2 = 1:1 > BaCl_2:SnO_2 = 1:1 > BaBr_2:SnO_2 = 1:1 > BaBr_2:SnO_2 = 1:1$ , which is opposite to their  $C_2$  selectivity trend. For the convenience of comparison, the added  $CO_x$  selectivity is displayed in Fig. S4 (C). In comparison with the un-modified  $SnO_2$ , with the addition of different barium halides, the  $CO_x$  selectivity over all the modified catalysts is significantly dropped above 650 °C. This indicates that the presence of surface halogen anions can evidently inhibit the deep oxidation of methane and  $C_2$  products, especially at elevated temperature, which is favorable for the formation of coupling products. Among the three kinds of barium halides, BaBr\_2 possesses the strongest ability to restrict  $CO_2$  formation, which might explain its best OCM reaction performance in all the samples.

The spent catalysts have been used to estimate their reaction stability at 800 °C. Fig. 4 exhibits that during 50 h's tests, all the catalysts possess very stable reaction performance, indicating that these catalysts can stand high temperature, which is important for an OCM catalyst.

#### 3.4. $H_2$ -TPR analysis of the catalysts

H<sub>2</sub>-TPR was used to investigate the redox properties of the fresh and spent catalysts. As shown in Fig. 5(a), pure SnO<sub>2</sub> depicts an unsymmetrical reduction peak, which is attributed to the stepwise reduction of SnO<sub>2</sub> via Sn<sup>4+</sup>  $\rightarrow$  Sn<sup>2+</sup>  $\rightarrow$  Sn<sup>0</sup> [24,25,28]. In contrast, though all the BaX<sub>2</sub>/SnO<sub>2</sub> catalysts still display the major reduction peak at the same temperature region, it is obviously broadened. On the profiles of fresh BaCl<sub>2</sub>:SnO<sub>2</sub> and BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1, two seperated reduction peaks can be evidently discerned. This indicates that barium halide addition can influence the redox behavior of SnO<sub>2</sub>. However, in the fresh samples, no solid phase reaction occurred between BaX<sub>2</sub> and SnO<sub>2</sub> during the calcination process, in good accordance to the XRD and Raman results.

Fig. 5(b) displays the H<sub>2</sub>-TPR profiles of all the spent catalysts. on the profiles of  $BaF_2$ :SnO<sub>2</sub> = 1:1 and  $BaCl_2$ :SnO<sub>2</sub> = 1:1 catalysts, two reduction peaks corresponding to the stepwise reduction process are

obviously observed, testifying that BaF<sub>2</sub> and BaCl<sub>2</sub> re-dispersed on the catalyst surface during the OCM reaction, and their interaction with SnO<sub>2</sub> could be altered. On the profile of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 and BaSnO<sub>3</sub>, the reduction becomes negligible, proving that the Sn<sup>4+</sup> cations in the lattice of BaSnO<sub>3</sub> becomes non-reducible. The small peak observed for BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 is attributed to the reduction of the residual amount of remaining SnO<sub>2</sub> in the catalyst.

#### 3.5. O<sub>2</sub>-TPD analysis of the catalysts

Since surface oxygen sites are of great importance for  $CH_4$  activation and  $C_2$  product formation during an OCM process,  $O_2$ -TPD experiments were conducted for the fresh and spent catalysts. Fig. 6 demonstrates that two or three distinct desorption peaks can be observed for all the samples, which can be classified into three groups.

As formerly reported, the peaks below 400 °C are attributed to the desorption of loosely bonded oxygen species, and the peaks at 400 ~ 600 °C can be ascribed to the desorption of reactive oxygen species beneficial to CH<sub>4</sub> activation and C<sub>2</sub> product formation [31–33]. The peaks above 600 °C can be attributed to the desorption of some lattice oxygen species, which might not be important for OCM reaction. After reaction, the part of OCM reactive oxygen species obviously increases, as evidenced by the enlarged peaks at 400 ~ 600 °C in Fig. 6 (b). Therefore, the oxygen desorption amount on the fresh and spent catalysts are quantified in Table 3.

For the fresh catalysts, the addition of barium halides significantly improves the amount of the OCM reactive oxygen sites as well as the total amount of the desorbed oxygen species, which indicates that barium halides can interact and modify the SnO<sub>2</sub> surface property. Raman results in Table 1 have testified that the addition of barium halides can create more surface vacancies, thus being favorable for the generation of surface active oxygen sites. For the fresh catalysts, the OCM reactive oxygen amount follows the order of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 > SnO<sub>2</sub>,



Fig. 5. H<sub>2</sub>-TPR profiles of the catalysts, (a) fresh, (b) spent.

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matching very well the reaction performance of the catalysts. After reaction, no significant change is observed for the O<sub>2</sub>-TPD profile of pure SnO<sub>2</sub>, together with the amount of its OCM reactive oxygen species. For the modified catalysts, the amount of the OCM reactive oxygen species together with the total oxygen desorption amount became evidently larger, indicating that the surface active sites experienced an adjustment during the OCM reaction process, possibly due to the redispersion of the BaX<sub>2</sub> at high temperature. The oxygen desorption amount obeys also the sequence of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 for the spent catalysts, which is consistent to the reaction performance.

In brief, O<sub>2</sub>-TPD results have substantiated that the amount of surface active oxygen sites plays a crucial role for OCM reaction on  $BaX_2/SnO_2$  catalysts. During the OCM reaction, the amount of the reactive oxygen sites can be further improved.

#### 3.6. CO<sub>2</sub>-TPD analysis of the catalysts

It has been reported that  $C_2$  selectivity is closely related to the basic properties of an OCM catalyst [14,25,31–33]. Therefore,  $CO_2$ -TPD experiments were performed to analyze the basic sites on the fresh and spent catalysts, with the profiles shown in Fig. 7.

Some researchers pointed out that those active basic sites beneficial to C<sub>2</sub> selectivity are generally inactive at low temperature, because they could be blocked by CO<sub>2</sub> adsorption during the OCM reaction. By increasing the reaction temperature, these active basic sites start to be progressively available for methane activation due to desorption of CO<sub>2</sub>. On the other hand, the strong basic sites can capture CO<sub>2</sub> easily to form stable carbonates, which also contribute negligibly to OCM reaction [31,34,35]. Therefore, surface basic sites with moderate strength could devote mostly to C<sub>2</sub> product selectivity. Based on former reports, the CO<sub>2</sub> desorption peak below 300 °C can be attributed to weak basic sites, the peak at  $300 \sim 600$  °C corresponds to moderate basic sites and

Table 3

Samples	O <sub>2</sub> Desorption Anount (µnior/g)						
	Fresh			Spent			
	Loosely bounded	OCM reactive	Total	Loosely bounded	OCM reactive	Total	
SnO <sub>2</sub>	22.0	4.4	26.4	22.7	5.2	27.9	
$BaF_2:SnO_2 = 1:1$	30.6	14.5	45.1	15.1	29.3	44.4	
$BaCl_2:SnO_2 = 1:1$	27.3	20.7	47.3	18.3	46.7	65.0	
$BaBr_2:SnO_2 = 1:1$	8.9	26.2	35.1	7.8	59.9	67.7	

the peak above 600 °C can be ascribed to strong basic sites [19,25,31–33].

According to this classification, the CO<sub>2</sub> desorption amount on the fresh and spent catalysts is quantified in Table 4. Again, it is observed that the addition of barium halides into SnO<sub>2</sub> can significantly improve the amount of the moderate basic sites, following the sequence of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 for both the fresh and spent catalysts, no significant change is observed for the pure SnO<sub>2</sub> sample. In comparison with the modified fresh catalysts, the amount of the moderate basic sites beneficial to the reaction is also improved evidently for all the spent catalysts.

It has been generally accepted that surface basic sites can be attributed to the chemisorbed electrophilic oxygen species such as  $O_2^-$ ,  $O_2^{-2}$ ,  $O^-$  and surface defects [31,34]. For example, by doping Li<sup>+</sup> into MgO lattice, Li<sup>+</sup>O<sup>-</sup> electron pair defects can be formed, which contribute either to the basicity of the catalyst [31,33,36,37]. Therefore, it believed that the improved basicity of the BaX<sub>2</sub>/SnO<sub>2</sub> catalysts comes from the formation of more OCM reactive oxygen species and surface oxygen vacancies, as evidenced by the Raman and O<sub>2</sub>-TPD results. The anion substitutions continued during the OCM process, thus resulting in



Fig. 6. O2-TPD analysis of the catalysts, (a) fresh, (b) spent.



Fig. 7. CO<sub>2</sub>-TPD analysis of the catalysts, (a) fresh catalysts, (b) spent catalysts.

Table 4CO2-TPD Quantification Results of the fresh and spent catalysts.

Samples	CO <sub>2</sub> Desorption Amount (µmol/g)							
	Fresh			Spent				
	Weak	Moderate	Total	Weak	Moderate	Total		
$SnO_2$	0.10	0.24	0.34	0.07	0.30	0.37		
$BaF_2:SnO_2 = 1:1$	0.08	0.50	0.58	0.22	0.71	0.93		
$BaCl_2:SnO_2 = 1:1$	0.05	0.62	0.67	0.08	1.16	1.24		
$BaBr_2:SnO_2 = 1:1$	0.12	0.92	1.04	0.07	1.29	1.36		

the formation of more oxygen vacancies and improved basicity in the spent catalysts.

#### 3.7. In situ Raman analysis of the catalysts

Former publications have indicated that  $O_2^{-}$  superoxide species can be stabilized at 200 °C on MgO-based catalysts and is the active oxygen site for OCM [38]. Over CaO/Y<sub>2</sub>O<sub>3</sub> OCM catalyst, Osada et al. found that  $O_2^{-}$  can even be stabilized up to 750 °C [39]. Moreover, over Na<sub>2</sub>O<sub>2</sub>, SrO<sub>2</sub>, and BaO<sub>2</sub> catalysts, Otsuka et al. proved that  $O_2^{2^{-}}$  peroxide could be another type of reactive oxygen species for OCM reaction [40]. Lunsford et al. have provided the first evidence that  $O_2^{2^{-}}$  is the OCM reactive species over Ba/MgO, La<sub>2</sub>O<sub>3</sub> and Sr/La<sub>2</sub>O<sub>3</sub> by using *in situ* Raman spectroscopy [41,42]. Wan et al. have systematically investigated active oxygen species of the fuoride-containing rare earth and alkaline earth-based catalysts for OCM by using *in situ* FTIR and Raman techniques [43]. They concluded that  $O_2^{-}$  species can be considered as OCM reactive oxygen species over the fuoride-containing rare earth and alkaline earth metal oxide based catalysts [43].

# 3.7.1. Identifying surface oxygen species on the fresh and spent $BaX_2/SnO_2$ catalysts with in situ Raman

To discern the active oxygen species over the fresh and spent catalysts for OCM reaction, *in situ* Raman experiments have thus been performed. All the samples were pretreated in a 30 mL/min O<sub>2</sub> gas flow at 800 °C for 1 h before taking the Raman spectra. Fig. 8(a) displays that a peak at ~ 1050 cm<sup>-1</sup> can be evidently observed for all the fresh catalysts, which is attributed to O<sub>2</sub>- oxygen species [43,44]. As manifested in Fig. 8(b), on the spent BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 and BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalysts, this O<sub>2</sub>- Raman peak can still be observed. As testified by XRD and Raman results in above sections, during OCM reaction, no solid phase reaction between SnO<sub>2</sub> and BaF<sub>2</sub>/BaCl<sub>2</sub> occurred, thus these two samples are composed majorly of SnO<sub>2</sub> phase. However, for the spent BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalyst, a solid phase reaction between SnO<sub>2</sub> and BaBr<sub>2</sub> happened during the OCM reaction to form defect BaSnO<sub>3</sub>, which accompanies the generation of BaCO<sub>3</sub>. Therefore, the 1060 cm<sup>-1</sup> peak on its Raman profile is assigned to micro crystalline BaCO<sub>3</sub> instead of O<sub>2</sub>-. In the following section, the *in situ* Raman results will prove that this peak is inert to CH<sub>4</sub>, providing extra evidence to testify this assignment. Whereas, on the profile of the spent BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1, a new peak at 862 cm<sup>-1</sup> is observed, which can be ascribed to active surface O<sub>2</sub><sup>2-</sup> species [41,42,44], possibly induced by the formation of the new BaSnO<sub>3</sub> phase.

## 3.7.2. The reactivity of the surface oxygen sites on the spent $BaX_2/SnO_2$ catalysts probed by in situ Raman

To further identify the active surface oxygen species and probe its reactivity toward OCM reaction, another series of in situ Raman experiments have been designed and performed with the spent catalysts. Typically, a catalyst was first treated in a 30 mL/min O2 flow at 800 °C for 1 h and then flushed briefly in a 30 mL/min He flow. After these steps, the feed gas was switched to a 30 mL/min CH<sub>4</sub> flow. As shown in Fig. 9 (a) and (b), over the spent  $BaF_2:SnO_2 = 1:1$ and  $BaCl_2:SnO_2 = 1:1$  catalysts, the  $O_2^-$  peak at ~1060 cm<sup>-1</sup> decreases gradually with the increase of the exposing time, and disappears completely after 15 min. After flushing briefly in a 30 mL/min He flow, the feed was switched to a  $30 \text{ mL/min CH}_4:O_2 = 4:1$  gas mixture flow for 5 min. It is apparent that the ~1060 cm<sup>-1</sup> Raman peak of  $O_2^-$  species can be restored. These results have indicated strongly that the surface O<sub>2</sub><sup>-</sup> is reactive to CH<sub>4</sub> and is the reactive sites for OCM reaction. Under reaction condition, it can be consumed and regenerated easily by the gas phase O<sub>2</sub>.

For the spent BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalyst, the species corresponding to the ~1060 cm<sup>-1</sup> band is obviously inert to CH<sub>4</sub> at 800 °C, as substantiated by Fig. 9 (c). Therefore, this confirms that it should be ascribed to the stable BaCO<sub>3</sub> instead of surface O<sub>2</sub>- sites. Whereas, the O<sub>2</sub><sup>2-</sup> oxygen species corresponding to the peak at 862 cm<sup>-1</sup> is obviously reactive to CH<sub>4</sub>, and which can be regenerated by the gas phase O<sub>2</sub>.

In summary, *In situ* Raman results have proved strongly on BaX<sub>2</sub>/SnO<sub>2</sub> catalysts modified by different barium halides, varied surface active oxygen sites contributing to OCM reaction have been generated. On BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 and BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalysts, superoxide O<sub>2</sub><sup>-</sup> anions are formed as the active oxygen sites, but on BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalyst, peroxide O<sub>2</sub><sup>2-</sup> anions are formed as the active oxygen sites. The generation of active O<sub>2</sub><sup>2-</sup> species may come from the interaction between BaBr<sub>2</sub> and BaSnO<sub>3</sub>, which was formed by the solid phase reaction between SnO<sub>2</sub> and BaBr<sub>2</sub> during the high temperature OCM reaction process.

## 3.8. XPS analysis of the oxygen properties on the surface of the fresh and spent catalysts

It has been reported that surface electrophilic oxygen species such as  $O_2^{-}$ ,  $O_2^{2^{-}}$  and O- are beneficial to  $C_2$  product formation, but surface lattice  $O^{2^{-}}$  could contribute to deep oxidation of CH<sub>4</sub> and the OCM

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Fig. 8. In situ Raman spectra of the catalysts treated in O2 at 800°C for 1 h, (a) fresh, (b) spent.

products [19,25,31,32]. The ratio of electrophilic oxygen species ( $O_2^-$  and  $O_2^{2-}$ ) to lattice ( $O^{2-}$ ) could be used to estimate the reaction performance of an OCM catalysts, which can be quantified by XPS O1s spectra [19,25,31,32]. Therefore, the surface oxygen properties of the fresh and spent catalysts were particularly analyzed with XPS to get supplementary information to other characterizations.

#### 3.8.1. XPS analysis of the O1s peaks for the fresh catalysts

Over the fresh catalysts, *in situ* Raman results have proved that  $O_2^-$  is the OCM reactive oxygen species. As depicted in Fig. 10, the O1s spectra of the fresh catalysts can be deconvoluted into three peaks corresponding to different oxygen species by assuming a single peak having 80 % Gaussian plus 20 % Lorentzian peak shape, and fixing the FWHM (full widths at half maximum) of a single XPS oxygen peak between 1.8 and 2.0 eV. In sequence, they are  $O_2^-$  anions at 533.1 ~ 533.2 eV, oxygen species of the - OH groups on the SnO<sub>2</sub> surface at 532.2 ~ 532.4 eV and surface lattice  $O^{2^-}$  anions at 530.5 ~ 530.8 eV [19,25,29,30]. On the basis of this, the  $O_2$ -/  $O^{2^-}$  ratios of all the fresh catalysts are quantified in Table 5, which obeys the order of

 $SnO_2 < BaF_2:SnO_2 = 1:1 < BaCl_2:SnO_2 = 1:1 < BaBr_2:SnO_2 = 1:1$ . By adding barium halides, the  $O_2$ -/  $O^2$ - ratios of the fresh catalysts was obviously increased, which could be a result of the anionic substitution between halogen anions and lattice  $O^2$ -, as observed by XRD. As a consequence, a larger amount of oxygen vacancies can be formed, as testified by Raman. The O1s analysis results of the fresh samples are well consistent with the Raman, H<sub>2</sub>-TPR and O<sub>2</sub>-TPD results, and explain well the reaction performance.

#### 3.8.2. XPS analysis of the O1s peaks for the spent catalysts

The deconvoluted and curve-fitted O1s spectra of the spent catalysts are exhibited in Fig. 11. According to Raman results, defect BaSnO<sub>3</sub> compound is detected on the spent BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalyst as a major component. For comparison, the O1s spectra of the pure defect BaSnO<sub>3</sub> was thus also included in the figure. With the same method described as above, the O1s spectra of the spent catalysts are also deconvoluted and fitted, with the  $O_2^{2^-}/O^{2^-}$  or  $O_{2^-}/O^{2^-}$  ratios quantified in Table 6. Notably, five kinds of surface oxygen anions with different chemical environments are totally detected on the spent catalysts



Fig. 9. In situ Raman spectra of the spent catalysts. (a)  $BaF_2:SnO_2 = 1:1$ , (b)  $BaCl_2:SnO_2 = 1:1$ , (c)  $BaBr_2:SnO_2 = 1:1$ .



Fig. 10. XPS analysis of the O1s peaks for the fresh catalysts. (a)  $SnO_2$ , (b)  $BaF_2:SnO_2 = 1:1$ , (c)  $BaCl_2:SnO_2 = 1:1$ , (d)  $BaBr_2:SnO_2 = 1:1$ .

Table 5 Curve-fitting and quantification results of XPS O1s spectra for the fresh catalysts.

Catalysts	O1s B.E., FWHM	$0_2^{-}/0^{2-}$		
	02-	OH-	02-	
$SnO_2$ $BaF_2:SnO_2 = 1:1$ $BaCl_2:SnO_2 = 1:1$ $BaBr_2:SnO_2 = 1:1$	533.1/2.0/1.0 533.2/1.9/4.9 533.2/1.8/5.6 533.1/2.0/8.0	532.2/1.9/27.3 532.4/1.8/28.4 532.2/1.8/15.3 532.2/1.8/16.4	530.7/1.3/71.7 530.6/1.7/78.1 530.7/2.0/79.1 530.7/1.8/75.6	0.01 0.05 0.07 0.11

[19,25,31–33], as listed in Table 6.

In comparison with the corresponding fresh catalysts, all the spent catalysts have improved  $O_2^{2^-}/O^{2^-}$  or  $O_2^{-}/O^{2^-}$  ratios, testifying the further formation of the OCM reactive and selective oxygen sites during the reaction process, possibly due to the continued substitution of the lattice  $O^{2^-}$  by halogen anions to generate more oxygen vacancies. For the spent BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1, it is obviously observed that the amount of lattice oxygen was decreased accompanying the amount increase of the active peroxide  $O_2^{2^-}$  species. The similar phenomenon is observed on the pure defect BaSnO<sub>3</sub> sample. This indicates that the presence of BaBr<sub>2</sub> and BaSnO<sub>3</sub> phase in the sample contributes significantly to the generation of more amount of  $O_2^{2^-}$  and  $O_2^{-}$  are 1.0 and 1.5 in sequence. Therefore, surface  $O_2^{2^-}$  anions are more reactive than  $O_{2^-}$  anions, which might be an important cause that BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 has the best reaction performance among all the catalysts.

#### 3.9. A brief discussion

It was reported that exchange equilibrium between lattice  $O^{2-}$  and F- in the lattice of some fluoro-oxide can take place, thus leading to the formation of  $O_{2^-}$  species and anion vacancies, which is beneficial to  $C_2$  selectivity for OCM reaction [45]. In addition, the diffusion of Cl- into the Gd<sub>2</sub>O<sub>3</sub> matrix to substitute part of the lattice  $O^{2-}$  was also observed

for a 30 mol%  $BaCl_2/Gd_2O_3$  catalyst which eventually induces the formation of OCM reactive  $O_2$ - species [23]. Therefore, it is rational to believe that the same phenomenon occurs to the  $BaX_2/SnO_2$  catalysts in this study, as  $O_2$ - species is detected on all the fresh catalysts.

During the high temperature OCM reaction, no solid phase reaction happened between  $BaF_2/BaCl_2$  and  $SnO_2$  for  $BaF_2:SnO_2 = 1:1$  and  $BaCl_2:SnO_2 = 1:1$  catalysts, due to the high bonding energies of Ba-F (487 kJ/mol) and Ba-Cl (444 kJ/mol). Therefore, in comparison with the fresh samples, the catalyst compositions have no evident change, and  $O_2^-$  species is still the major OCM reactive sites on the two spent catalysts. However, due to the much lower bonding energy of Ba-Br (370 kJ/mol), a significant solid phase reaction took place between  $BaBr_2$  and  $SnO_2$  during the OCM reactive  $O_2^{-2}$  species on the spent  $BaBr_2:SnO_2 = 1:1$  catalyst. With the concerted interaction between the left  $BaBr_2$  and  $BaSnO_3$ , this catalyst displays the best reaction performance among all the catalysts.

It has been commonly accepted that OCM reaction involved two typical steps, that is, a heterogeneous step to activate CH<sub>4</sub> molecules into gas-phase CH3 radicals on the catalyst surface, and a homogeneous gas-phase step to combine two CH<sub>3</sub> radicals to form an C<sub>2</sub>H<sub>6</sub> molecule [2,5,6]. The production of  $C_2H_4$  in OCM reaction can go through two ways. One way can be attributed to the dehydrogenation of the formed C<sub>2</sub>H<sub>6</sub>, and another way can be attributed to coupling of carbene species generated by active oxygen species [46-48]. Actually, in most of the cases, these two ways exist simultaneously during OCM reaction [46–48]. As formerly reported, both  $O_2^-$  and  $O_2^{2-}$  anions are the active oxygen species contributing to C<sub>2</sub>H<sub>6</sub> dehydrogenation [49]. However,  $O_2^{2^2}$  anions can active CH<sub>4</sub> to form carbene species, which can be directly coupled into form  $C_2H_4$  [48,49]. As mentioned above,  $O_2$ - anions are the active oxygen sites on both  $BaF_2:SnO_2 = 1:1$  and  $BaCl_2:SnO_2 = 1:1$  catalysts, thus the way of  $C_2H_4$  formation on these two catalysts may preferentially go through the dehydrogenation of  $C_2H_6$ . In contrast, on BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalyst,  $O_2^{2-}$  anions is the predominant active oxygen sites, which were generated during the OCM process due to the formation of defect BaSnO<sub>3</sub>. Therefore, the way



Fig. 11. XPS analysis of the O1s peaks for the spent catalysts. (a) BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1, (b) BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1, (c) BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 catalysts and (d) BaSnO<sub>3</sub>.

Table 6		
Curve-fitting and quantification r	esults of XPS O1s spectra	for the spent catalysts.

Catalysts	O1s B.E., FWHM (eV)	$O_2^{2^-}$ or $O_2^{-}/O^{2^-}$				
	02 <sup>-</sup>	OH/CO <sub>3</sub> <sup>2-</sup>	02 <sup>2-</sup>	02-	ratio	
$BaF_2:SnO_2 = 1:1$	533.2/1.8/4.2	532.4/1.8/17.7	-	530.6/1.4/66.7	0.07	
$BaCl_2:SnO_2 = 1:1$	533.2/1.8/5.8	532.3/1.9/26.3	-	530.7/1.3/67.9	0.09	
$BaBr_2:SnO_2 = 1:1$	-	532.1/2.0/23.7	531.2/1.7/61.3	529.5/1.8/15.0	4.08	
$BaSnO_3$	-	532.1/1.9/12.0	531.1/1.8/50.3	529.4/1.8/37.7	1.33	

of C<sub>2</sub>H<sub>4</sub> formation may preferentially go through the coupling of carbene species, but include also the dehydrogenation of the formed C<sub>2</sub>H<sub>6</sub>. As a result, BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 exhibits extremely high C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio in comparison with other catalysts.

#### 4. Conclusion

Aiming to design and develop improved catalysts for OCM reaction,  $SnO_2$  modified by different barium halides have been purposely designed and prepared as catalysts in this work. By using different physical chemical means, the surface and bulk properties of the catalysts have been characterized thoroughly, and correlated with the reactivity.

- (1) In comparison with pure SnO<sub>2</sub>, all the catalysts modified by different barium halides exhibit evidently improved OCM reaction performance above 650 °C, following the sequence of BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaCl<sub>2</sub>:SnO<sub>2</sub> = 1:1 > BaF<sub>2</sub>:SnO<sub>2</sub> = 1:1 > SnO<sub>2</sub>. BaBr<sub>2</sub> displays the best promotional effects among all the halides. Over BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1, the highest C<sub>2</sub> product yield of 18.1 % can be obtained at 800 °C, which accompanies an extremely high C<sub>2</sub>H<sub>4</sub>/ $C_2H_6$  ratio of 4/1.
- (2) XRD and Raman results have testified that the addition of different barium halides into SnO<sub>2</sub> can generate more surface vacancies/ defects due to anion substitution effect, thus producing obviously

larger amount of surface  $O_2^-$  sites contributing to OCM reaction on the fresh samples, as evidenced by  $O_2$ -TPD, *in situ* Raman and XPS results.

- (3) During the reaction process, the amount of  $O_2^-$  sites can be further improved on all the spent catalysts except for BaBr<sub>2</sub>:SnO<sub>2</sub> = 1:1. On this catalyst, a new type of more active oxygen sites, peroxide  $O_2^{2^-}$ anions, are generated due to the solid phase reaction between BaBr<sub>2</sub> and SnO<sub>2</sub> to form BaSnO<sub>3</sub> perovskite phase. Moreover,  $O_2^{2^-}$  anions are also favourable for the direct formation of  $C_2H_4$  through carbene mechanism, which explains that an extremely high  $C_2H_4/C_2H_6$ ratio is obtained on this catalyst.
- (4) The amount and properties of the surface active oxygen species and basic sites are important for OCM reaction, and their concerted interaction determines the reaction performance of  $BaX_2/SnO_2$  catalysts.  $BaBr_2:SnO_2 = 1:1$  contains the apporiate amount of both types of active sites, hence displaying the best OCM performance among all the catalysts.

#### CRediT authorship contribution statement

**Rong Xi:** Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft. **Junwei Xu:** Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft. **Yan Zhang:** Investigation, Formal analysis,

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Methodology, Validation. Zhixuan Zhang: Investigation, Formal analysis. Xianglan Xu: Project administration, Resources, Software, Funding acquisition. Xiuzhong Fang: Project administration, Resources. Xiang Wang: Conceptualization, Data curation, Formal analysis, Funding acquisition, Validation, Project administration, Supervision, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2020.04.010.

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