Oxidative coupling of methane over Ce^{4+}-doped Ba_3WO_6 catalysts: investigation on oxygen species responsible for catalytic performance

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Ce^{4+} doped Ba_3WO_6 complex oxides were used as catalysts for methane oxidative coupling (MOC), and characterized by XPS and O_2-TPD-MS techniques. The results indicate that the ratio of electrophilic oxygen species O^- and O_2^- to lattice oxygen on the surface is crucial for C_2 selectivity. By adjusting the relative amount of cations in Ba–W–Ce complex oxides with perovskite superstructure interstitial oxygen species can be created which benefits C_2 selectivity by raising the relative amount of $(O^- + O_2^-)$ on the surface.

Keywords: Methane oxidative coupling; perovskite-type catalyst; electrophilic oxygen species; Ce^{4+}-doped Ba_3WO_6

1. Introduction

Studies on searching an effective catalyst for methane oxidative coupling (MOC) to ethylene have shown that many metal oxides are catalytically active [1,2]. In the past decade considerable efforts have been made in correlating the properties of various oxide systems with their catalytic behaviors, but the nature of the catalytic active sites for the reaction is still an active topic in related literature. The complexity comes from the facts that the high reaction temperature makes in situ spectroscopic methods difficult to apply, and the active sites on a great variety of oxide systems might not be the same. However, there is general agreement that oxygen species on the surface of the catalysts play an important role in methane activation. For example, as pointed out by Ito and Lunsford, the $[Li^+O^-]$ site on Li/MgO catalyst pretreated at high temperature in oxygen atmosphere is responsible for the formation of methyl radicals during methane oxidative coupling reaction [3,4]. As mentioned by Otsuka et al., peroxide ions can be related to the activity

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of methane oxidative coupling, and several metal peroxides, e.g. Na_2O_2, and SrO_2 etc. can oxidize methane stoichiometrically [5,6]. Lin et al. [7] further suggested that the active O^- species might form from superoxide O_2^- on La_2O_3, and a similar suggestion has been proposed by Wang et al. [8], i.e., the superoxide species were in equilibrium with the surface peroxide ions and oxygen. It has been generally established that on metal oxide catalysts the surface oxygen species may consist of lattice oxygen O^{2-}, peroxide O_2^{2-}, superoxide O_2^-, carbonate CO_3^{2-}, hydroxide OH^- ions, etc. The surface electrophilic oxygen species can be produced via different ways such as: (1) gaseous oxygen interacting with oxygen vacancy on the catalyst, e.g. $[Li^+O^-]$ on Li/MgO [3]; (2) oxygen adsorbed on the catalyst, e.g. O_2^- on La_2O_3 [7]; and (3) oxygen species already existing in the bulk phase of the catalyst, e.g. Na_2O_2 [6]. Among the oxide systems investigated for the oxidative coupling of methane, perovskite-type compounds are of particular interest for their good thermal stability and interesting catalytic properties [9]; moreover, it is known that oxygen vacancy or interstitial oxygen can be introduced to these compounds by doping cations with different valence [10], this interesting property providing the possibility of adjusting the catalytic property of perovskite-type catalysts. In this respect, recent studies on oxide superconductors have proved that, by doping cations with lower valence, holes in the oxygen 2p valence band and peroxide-like species can be created [11,12]. The existence of peroxide-like ions has been observed experimentally by Kharas and Lunsford in their study of $BaPbO_3$ catalyst, and the formation of the so-called non-classic peroxide has been related to the change of the valence of lead, and also to the good catalytic performance of $BaPbO_3$ for methane oxidative coupling [13,14]. In this report, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and oxygen temperature programmed desorption mass spectroscopy (O_2-TPD-MS) are used to study the properties of Ba–W–Ce oxide systems, in particular, the formation of various oxygen species by adjusting the ratio of Ba, W, and Ce cations in Ba_3WO_6 catalyst with perovskite superstructure [15]. Along these lines, the relation between the surface oxygen species and the catalytic properties of the catalysts for methane oxidative coupling are discussed.

2. Experimental

2.1. SAMPLE PREPARATION

Appropriate amounts of CeO_2 (AR), $BaCO_3$ (AR), and WO_3 (AR) were calcined at 1023 K for 5 h, then mixed., ground extensively, and calcined in an alumina crucible at 1373 K for 48 h in air. The catalysts studied were Ba_3WO_6 (denoted as BWO), $BaCeO_3$ (BC), $Ba_{1.35}W_{0.45}Ce_{0.2}O_3$ (BWC3), and $Ba_{1.4}W_{0.4}Ce_{0.2}O_3$ (BWC4).

2.2. CATALYTIC PROPERTIES

The catalytic activity and selectivity of the catalysts were measured by using a continuous flow, U-type quartz reactor. In short, 0.100 g catalyst was used, and the flow rates of CH_4 and air were 30 and 70 ml min^{-1} respectively. The mole ratio of methane-to-oxygen was ca. 2.2.

Products were analyzed by two on-line GC units with a 406 (Porapak Q-like) column and a 13X-molecular sieve column respectively. The first GC detected the amounts of (CH_4 + air + CO), CO_2, C_2H_4, and C_2H_6, whereas the second one gave the amounts of O_2, N_2, CH_4, and CO. Carbon balances for all the measurements were better than 97%.

2.3. CHARACTERIZATION METHODS

X-ray diffraction. XRD results were obtained with a Shimadzu XD-3A diffractometer employing Ni filtered Cu K_α radiation, and the X-ray source power was 525 W.

X-ray photoelectron spectroscopy. XPS measurements were carried out on an ESCALAB MKII spectrometer using Mg K_α (1253.6 eV) irradiation. The C 1s peak of residual carbon was assigned a binding energy of 284.6 eV, and used as reference. Samples before reaction were pretreated at 1093 K first in vacuum and in oxygen (ca. 15 Pa) to clean the surface before XPS measurements. After smoothing and background subtraction, the O 1s envelopes were deconvoluted into the contributions of corresponding surface oxygen species each with reasonable binding energy and peak width. For all the computer fits, the XPS peaks were assumed to have 80% Gaussian plus 20% Lorentzian peak shape. The correctness of the analysis method has been tested with the deconvolution of a simulated peak composed of four single peaks with known binding energy and peak width values. The result shows that the deviations of the binding energy values obtained are not more than 0.02 eV in all cases, and the errors in peak area are not more than 5%.

Oxygen temperature programmed desorption. 0.1 g sample was heated in a sample tube connected to an AGA-100 quadrupole mass spectrometer at 1233 K for 1 h under vacuum, and cooled slowly to room temperature in ca. 0.1 Torr oxygen. The sample was reevacuated and then the temperature was linearly increased at a rate of 20 K min^{-1} up to 1233 K for spectrum recording. The apparatus used are schematically shown in fig. 1. It is difficult to make quantitative analyses of the desorption peaks observed because, in fact, the experiments are running under continuous pumping condition; however, the different oxygen species existing on the surface can be clearly examined.

3. Results and discussion

Results for the oxidative coupling of methane over the catalysts are listed in

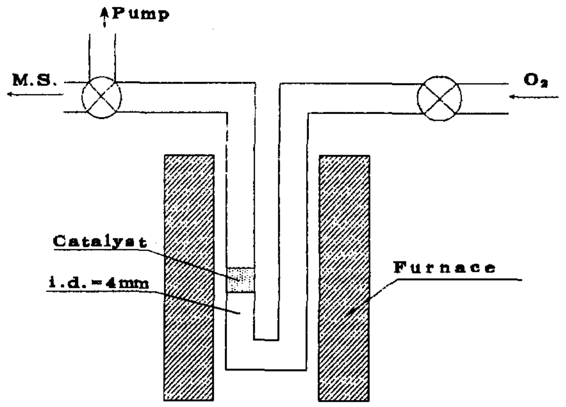

Fig. 1. Schematic diagram of the apparatus used in O_2-TPD experiment.

table 1. The data were obtained after reaction for 0.5 h. It can be seen that the methane conversion and C_2 selectivity are greatly improved by doping cerium ions to BWO catalyst, i.e. a yield of 18.8% for the C_2 compounds was obtained with 48.9% selectivity and 38.4% conversion over BWC3 catalyst. For these Ba–W–Ce oxide catalysts, e.g. BWC3 or BWC4, XRD results have revealed that they have the same bulk phase structure as BWO, thus indicating the even distribution of cerium without the formation of any new phase.

Fig. 2 shows that the C_2 yield of BWC3 catalyst, at least in a reaction period of 90 h, actually maintains a constant value due to the compensation of a gradual decrease in the conversion of methane and a gradual increase in C_2 selectivity with the reaction time. The lack of an induction period reveals that the surface of the catalyst is responsible for its catalytic activity [13].

Table 2 shows the effects of space velocity on CH_4 conversion and C_2 selectivity of BWC3 catalyst. For these measurements a CH_4 : air ratio of 2 : 3 was used, and the results show that the BWC3 catalyst has a good performance at high space velocity.

Table 3 summarizes the results obtained by XPS analyses on the binding energies of the metal cations in the catalysts. The results indicate that all the metal

Table 1
Catalytic performance of the catalysts for methane oxidative coupling

Catalyst	Conversion (%)		Selectivity (%)		C_2 yield (%)
	CH_4	O_2	C_2	CO_x	
BWO	4.1	9.1	72.1	27.9	3
BC	31.5	94.9	33.6	66.4	10.6
BWC3	38.4	90.9	48.9	51.1	18.8
BWC4	36.8	91.7	45.4	54.6	16.7

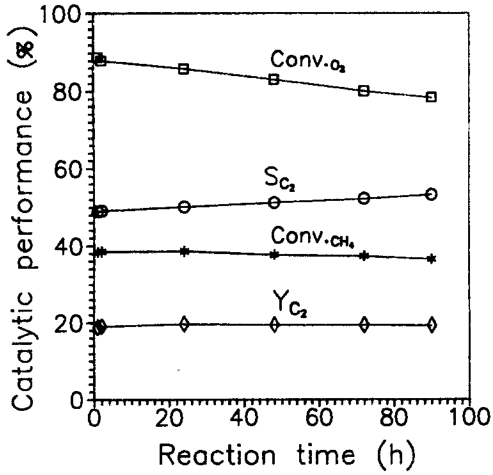

Fig. 2. Catalytic performance of BWC3 catalyst during a reaction period of 90 h.

cations in BWO, BC, and BWC4 are in their highest oxidation states, i.e. Ba^{2+}, W^{6+}, and Ce^{4+}, which are consistent with the stoichiometric composition of the catalysts, and are reasonable results derived from the oxidation atmosphere used for sample calcination. In the case of the BWC3 sample, if it were expressed as $Ba_{1.35}W_{0.45}Ce_{0.2}O_3$, one should expect that all the cerium ions be Ce^{3+}, which is in contradiction with the XPS results indicating that the binding energy of cerium ions in BWC3 is slightly lower than that of Ce^{4+} but still far from that of Ce^{3+} ions. Taking into consideration the preparation conditions, i.e. CeO_2 was the starting material and the calcination process was carried out in oxidation atmosphere, it is suggested that the BWC3 catalyst should be written as $Ba_{1.35}W_{0.45}Ce_{0.2}O_{3+x}$ with $0<x<0.1$, and the O_x is tentatively attributed to interstitial oxygen in the complex oxide structure. The assumption that there are interstitial oxygen species in BWC3 catalyst was supported by O_2-TPD-MS results (cf. below).

The O 1s spectra of the samples as shown in fig. 3 are used to identify the coexisting oxygen species on the catalysts. One can see that the FWHM (full widths at half maximum) of all the O 1s spectra measured are larger than that of a single species, which was usually about 2 eV [16]. For this purpose, all of the O 1s spectra are consistently deconvoluted into contributions from four different oxygen spe-

Table 2
The dependence of the space velocity on the catalytic performance of BWC3 sample

Space velocity ($ml\,g^{-1}\,h^{-1}$)	Conversion (%)		C_2 selectivity (%)
	CH_4	O_2	
60000	28.7	92.1	59.5
120000	27.2	84.3	63.6
180000	25.2	80.2	59.6

Table 3
XPS binding energies and corresponding FWHM (eV) for cations in the catalysts

Catalyst	BWO	BC	BWC3	BWC4
Ba($3d_{5/2}$)	779.80(2.1)	779.65(2.0)	779.55(2.0)	779.5(2.0)
Ba($3d_{3/2}$)	795.25(2.2)	795.21(2.0)	795.10(2.05)	795.0(2.1)
W($4f_{7/2}$)	35.00(2.3)	–	34.85(2.0)	34.85(2.0)
W($4f_{5/2}$)	37.05(1.9)	–	36.85(2.0)	36.85(2.0)
Ce($3d_{5/2}$)	–	881.85	881.05	881.6
Ce($3d_{3/2}$)	–	900.65	898.95	900.4

cies. These can be assigned to (i) O_2^-, 532.9 eV; (ii) CO_3^{2-}, 531.1 eV; (iii) O^-, 530.1 eV; and (iv) O^{2-}, 529.1 eV [13,14,17–19]. The experimental strategy used to computer fit the spectra was to assign a fixed binding energy and reasonable peak width

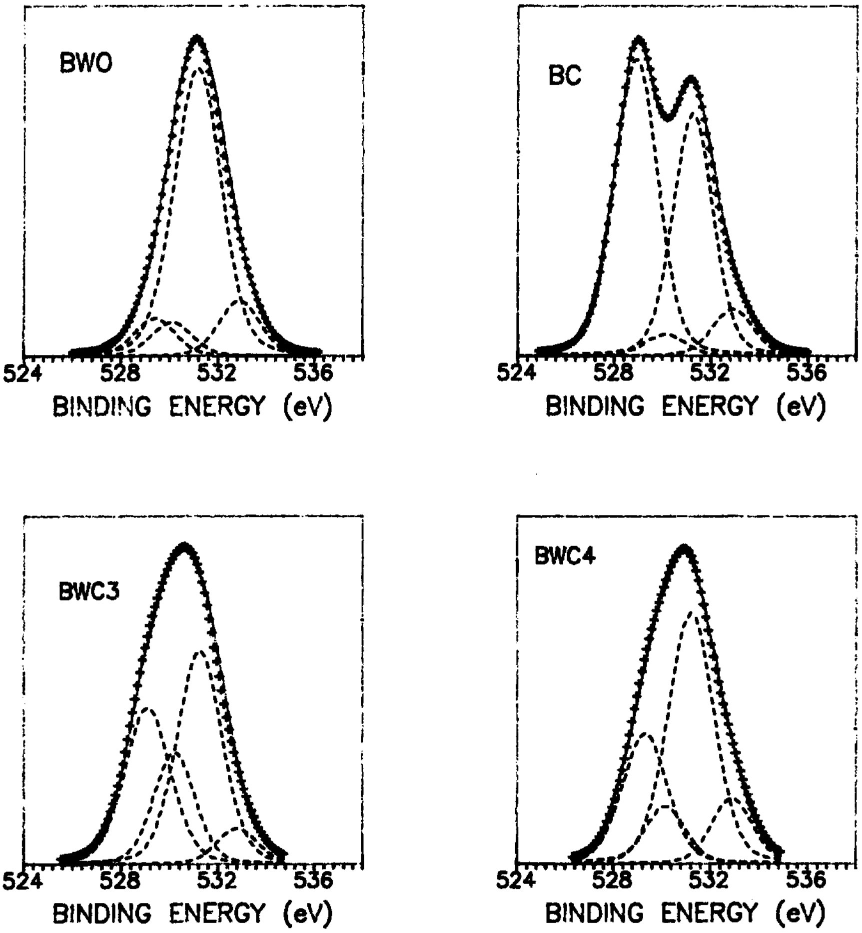

Fig. 3. O 1s binding energy spectra of the various samples. (——) Referring to experimental data, (- - -) showing contributions of single species calculated using 80% Gaussian–20% Lorentzian peak shape, (+) showing sum of the computer fitted contributions of each single species.

to each oxygen species and to let the computer determine the relative intensities of these peaks from each experimental spectrum in fig. 3. Based on these primary results, the computer was allowed to vary the binding energies and the peak widths of the four peaks in the fits of each spectrum. The binding energies, peak widths, and relative peak intensities thus obtained typically differed by less than 0.2 eV, 0.2 eV, and 5% respectively from those primary values resulting from the constrained fits. This indicates that the fits are, in fact, good fits of the experimental data; moreover, reasonable physical meanings can be derived. The results are shown in fig. 3 and summarized in table 4. These results point to the fact that both atomic and molecular oxygen species with various charges, i.e. O^-, O_2^-, and O^{2-}, are present on the surface of the catalysts.

The above results were further confirmed by O_2-TPD-MS profiles of the samples, as shown in fig. 4. The general feature of these profiles is the existence of two types of desorption peak, i.e. I and II, desorbed around 873 K and at around 1193 K respectively. As reviewed by Kung [20], the general feature of the TPD profiles of a number of oxides consists of three peaks corresponding respectively to the desorption of adsorbed molecular oxygen (<573 K), adsorbed atomic oxygen (<873 K), and the vaporization of lattice oxygen at high temperatures. In comparison, all the peaks I (<800 K) in fig. 4 can be attributed to the desorption of adsorbed molecular oxygen and atomic oxygen, i.e. O_2^- and O^- species, when the high heating rate (20 K min^{-1}) used in this study and its asymmetric shape indicating an unresolved shoulder peak around 600 K are taken into consideration. All the peaks II (>1200 K) obviously result from the release of lattice oxygen. The peak I′ in the profile of BWC3 sample deserves comments. This unique feature has tentatively been correlated with the existence of interstitial oxygen species in this sample. In addition, the intermediate peak temperature of I′ as compared with those of peak I and peak II supports this assignment, since interstitial oxygen is expected to release more easily than lattice oxygen but harder than adsorbed oxygen respectively. A comparison between the relative amount of various oxygen spe-

Table 4
Curve-fitting results from XPS data on the O 1s binding energies, the corresponding FWHM (eV), and the relative amount (%) of the oxygen containing species in various samples

Catalyst	BWO	BC	BWC3	BWC4
O 1s CO_3^{2-}	531.15 (70%, 2.3)	531.25 (38%, 2.0)	531.25 (42%, 2.2)	531.2 (51%, 2.2)
O 1s O^{2-}	529.3 (10%, 2.0)	528.9 (50%, 2.1)	529.2 (31%, 2.2)	529.25 (27%, 2.2)
O 1s O_2^-	532.9 (13%, 2.0)	532.9 (8%, 2.0)	532.8 (7%, 2.0)	532.9 (12%, 2.0)
O 1s O^-	530.1 (7%, 2.0)	530.1 (4%, 2.0)	530.15 (20%, 2.0)	530.15 (10%, 2.0)
$(O^- + O_2^-)/O^{2-}$	2.0	0.24	0.87	0.81

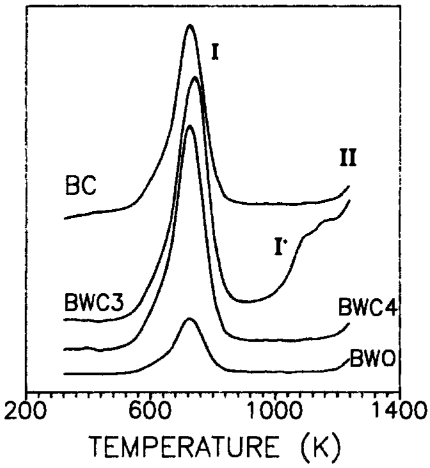

Fig. 4. O_2-TPD-MS profiles of the catalysts.

cies in BWC3 and BWC4 samples obtained from XPS analyses, as listed in table 4, leads to the argument that the interstitial oxygen exists mostly as O^- species. Accordingly, by adjusting the cation ratio in the Ba–W–Ce–O system one might create interstitial oxygen and thus the O^- species in the complex oxide with perovskite structure. To answer the question as to which oxygen species are responsible for the activity of methane oxidative coupling to C_2 hydrocarbons, the ratios of surface electrophilic oxygen to lattice oxygen species, i.e. $(O^- + O_2^-)/O^{2-}$, in all of the samples were evaluated from table 4 and related to their CH_4 conversion as well as C_2 selectivity. The results are shown in fig. 5. The linear relationship

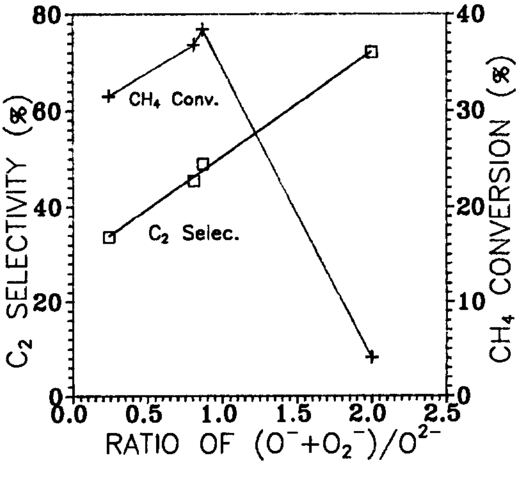

Fig. 5. Variation in C_2 selectivity and CH_4 conversion with the $(O^- + O_2^-)/O^{2-}$ ratio of the catalysts.

between the ratio and C_2 selectivity clearly points to the relative effectivity of the electrophilic oxygen species as compared to lattice oxygen on C_2 selectivity. For the conversion of CH_4, a similar trend can be seen, with the exception of the BWO sample which shows a much lower conversion than other samples. This could be due to the lacking of cerium ions in this sample, since cerium ions are expected to work as a redox component during the reaction and hence to promote the activation of dioxygen into electrophilic oxygen species. Although it is hard to distinguish the contribution of O^- and O_2^- species from the above results, O^- is considered to be the main species responsible for enhancing the selectivity to C_2 hydrocarbons, since it is known that O_2^- is only weakly adsorbed on the surface, thus under high reaction temperature it might have already desorbed or transformed into O^- species. It may be argued that the desorption temperature of O^- species measured by TPD-MS is also lower than the reaction temperature. However, it should be reminded that the much higher partial pressure of oxygen under reaction condition should benefit the formation of O^- species on the surface; moreover, in some complex oxide systems the peroxide ions might exist in a through-bond isomer as suggested by Kharas and Lunsford [13]. As a matter of fact, a number of workers have proposed O^- species to be the key oxidant in the oxidative coupling and/or partial oxidation of methane [21].

Another conclusion that can be derived from fig. 5 is that lattice oxygen is relatively effective on non-selective oxidation of methane. Lane et al. [22], in their study of methane oxidative coupling over Li/TiO_2 catalysts, have also evidenced that lattice oxygen activates methane non-selectively. However, the above results seem in contrast with the general idea that lattice oxygen usually oxidizes hydrocarbons selectively. The recent results reported by Otsuka et al. [23] provide one possible explanation for this dilemma, as they mentioned that lattice oxygen selectively catalyzes CH_4 with the formation of HCHO which is then decomposed to CO under high reaction temperature. It seems reasonable to argue that if there are oxygenate compounds formed during methane oxidative coupling reaction, they will further decompose into CO_x at the high temperature used for methane oxidative coupling.

4. Conclusions

The results of this study can be rationalized as follows. The selectivity of methane oxidative coupling to C_2 hydrocarbons is controlled by the relative amount of electrophilic oxygen species to lattice oxygen on the surface of the catalysts, and the higher the ratio, the better the selectivity for C_2 products. By adjusting the relative amounts of cations in Ba–W–Ce oxides, interstitial oxygen species can be created, which leads to an abundance of electrophilic oxygen species in the catalysts and hence the C_2 selectivity is improved.

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