Oxidative Coupling of Methane Over Mixed BaCl₂-TiO₂-SnO₂ and Na₂WO₄-Mn/SiO₂ Catalysts

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Oxidative coupling of methane (OCM) has been studied over a mixed catalyst constituted by Na₂WO₄-Mn/SiO₂ (W) and BaCl₂-TiO₂-SnO₂ (B). The effects of reaction temperature, gas hourly space velocity (GHSV) and CH₄/O₂ ratio on catalytic performance were systematic investigated. Compared with the single component counterpart, the results indicated that ethylene yield was significantly enhanced over the mixed catalysts. When the BaCl₂-TiO₂-SnO₂/Na₂WO₄-Mn/SiO₂ (B/W) ratio was controlled at 1/5 (v/v), the ethylene yield reached 22.2 %, which was 7.1 %, 2.1 % higher than the single Na₂WO₄-Mn-SiO₂, BaCl₂-TiO₂-SnO₂ catalyst, respectively. Besides, the ethylene yield was higher than 20 % over the mixed catalyst in wide reaction condition range.

Key Words: Oxidative coupling of methane, Mixed catalyst, Ethylene.

INTRODUCTION

Oxidative coupling of methane (OCM) to higher hydrocarbons has been extensively investigated in last decades, because it can directly and effectively convert methane to more active compounds for further chemical application. Up to date, a large number of catalysts have been tested for oxidative coupling of methane[1-16], such as Li/Sm₂O₃[6], Li/MgO[8], Ba/MgO[11], BaCO₃/LaOCl[12] and Na₂WO₄-Mn/SiO₂[16], *etc*. Among those catalysts, the Na₂WO₄-Mn/SiO₂ catalyst has received much more attention due to its outstanding performance in OCM[17-25]. Over the Na₂WO₄-Mn/SiO₂ catalyst, 80 % C₂ selectivity together with 33 % CH₄ conversion have been reported by Lambert *et al.*[17]. However, the present ethylene yield is still too low to meet the industrial demand. Therefore, in order to further improve ethylene yield, some strategies have been proposed for the application of Na₂WO₄-Mn/SiO₂ catalyst in OCM reaction[26-29]. A typical example is the utilization of monolithic foam-structured SiC as support to avoid significant hot spots in the catalyst bed[27]. In parallel with catalyst studies, many publications have focused on developing various types of reactors[28-34] for commercial applications. Ji *et al.*[28] establishes a dual-bed reactor of Na₂WO₄-Mn/SiO₂ catalyst and Ce-Na₂WO₄-Mn/SiO₂/cordierite monolithic catalyst. They have achieved higher methane conversion and ethylene selectivity than either of them. Hu *et al.*[29] also establishes a similar dual catalyst bed system using Na₂WO₄-Mn/SiO₂ and Co-La/SiO₂

catalysts. Methane is converted to ethylene and syngas simultaneously. Besides, this process can also adjust the distribution of reaction products; therefore, the products can be used as feedstock for hydro-formylation of ethylene to produce propanal. Although all these researches have improved the utilization of methane to a certain extent, the process needs to be further optimized for commercialization.

Recently, we have demonstrated that the BaCl₂-TiO₂-SnO₂ catalysts show excellent performance in both OCM and oxidative dehydrogenation of ethane (ODE) reactions[35,36]. The yield of ethylene in OCM is as high as 20.1 % with CH₄ conversion of 43.8 % and C₂ selectivity of 53.3 %. In the ODE reaction, the ethylene selectivity is as high as 92.9 %, which denotes the BaCl₂-TiO₂-SnO₂ catalyst can efficiently convert OCM product, ethane, to ethylene. On the other hand, the Na₂WO₄-Mn/SiO₂ catalyst shows both high and longtime stable activity[17-20]. Therefore, the coupling of the Na₂WO₄-Mn/SiO₂ catalyst with the BaCl₂-TiO₂-SnO₂ catalyst is expected to further elevate the ethylene yield in OCM, which constitutes the objective of our present work.

EXPERIMENTAL

Catalyst preparation: The Na₂WO₄-Mn/SiO₂ catalyst was prepared by sequential wet impregnation method[16]. Commercial silica supports (30-50 mesh, Chemical Industry Co., Ltd., Qingdao Defeng, China) were immersed in appropriate concentrations of manganese (II) acetate tetrahydrate (Aldrich,

purity > 99 %) and sodium tungstate dehydrate (Aldrich, purity > 99 %). The samples were dried in air at 120 ºC for 10 h and then calcined at 830 ºC for 5 h. The final composition of the catalyst was 5 wt % Na_2WO_4-2 wt % Mn/SiO_2.

The $BaCl_2$-TiO_2-SnO_2 catalyst was prepared according to previous study[35]. All chemicals were purchased from Aldrich (purity > 99 %). A typical preparation of $BaCl_2$-TiO_2-SnO_2 catalyst was as follows: the mixture of 1.50 g $BaCl_2 \cdot 2H_2O$, 0.49 g TiO_2 and 0.92 g SnO_2 was moistened with trace amount of deionized water and ground in a mortar until it became a hard paste. The sample was then dried at 110 ºC overnight, ground to powder and extruded to pellets at 400 kg cm^{-2} pressure. The pellets were calcined in air at 800 ºC for 5 h, crushed and sieved to 30-50 mesh before testing.

Catalyst characterization: The N_2 adsorption-desorption isotherms of the catalysts were performed on a Quantachrome autosorb iQ gas-sorption apparatus at -196 ºC. The samples were degassed at 200 ºC for 2 h before measurements. X-Ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert PRO X-ray diffractometer using CuK$_\alpha$ radiation (40 kV, 40 mA). X-Ray photoelectron spec troscopic (XPS) analysis was performed on a VGESCALAB 210 spectrometer with MgK$_\alpha$ radiation (hν = 1253.6 eV). Surface compositions were calculated from peak areas using the sensitivity factors provided by the software of the instrument.

Reactivity study: The reaction was performed in a quartz fixed-bed reactor at atmospheric pressure. For each test, both of the catalysts were mixed in a proper proportion and then loaded in the reactor. The temperature in the middle of reaction bed was monitored with a coaxial thermocouple and it was protected by a small quartz thermocouple well. The flow rates of reactants, methane and oxygen (all the gases were purchased from Foshan Kodi Chemical with purities > 99.9 %), were regulated by mass flow controllers (Brooks, Model 5850E). The feed gases were mixed and preheated to 400 ºC before introducing to the reactor. According to the former results of OCM reaction[35], the measurement of catalytic activity of the samples as a function of mixed proportion was performed under given conditions: 800 ºC, GHSV = 6600 h^{-1}, CH_4/O_2 = 2. In view of the complete consumption of oxygen at 800 ºC, the reaction temperature was kept at 780 ºC when studying the catalytic performance as functions of gas hourly space velocity (GHSV) and CH_4/O_2 ratio.

The reaction products were analyzed on-line by two gas chromatographs (Perkin-Elmer Autosystem XL) equipped with TCD/FID detectors. A Porapak Q column was utilized to analyze CO_2. An Al_2O_3 capillary column was used for the analysis of CH_4, C_2H_4, C_2H_6 and other higher hydrocarbons and a 5A molecular sieve column for the O_2 and CO. The conversion of

methane and the selectivity to products were calculated based on the balance of carbon, which were estimated within 100 ± 1 %. All the data were obtained after 0.5 h of operation.

RESULTS AND DISCUSSION

Catalyst characterization: Table-1 listed the surface composition determined by XPS and BET surface area, pore volume and pore size of the fresh and used mixed catalyst. The surface area, pore volume and pore size changed slightly for the samples before and after reaction, but the surface composition had changed obviously. The Ti, Ba and Cl depleted while O enriched on B catalyst surface. And the Mn and W content on W catalyst were decreased obviously after reaction.

XRD analysis was performed to find out the changing of crystalline phases on mixed catalyst. The XRD diffraction patterns were obtained as shown in Fig. 1. For B catalyst, the fresh catalyst exhibited strong signals of monoclinic $BaCl_2 \cdot 2H_2O$ [JCPDS 70-1113], tetragonal SnO_2 [JCPDS 88-0287] and tetragonal TiO_2 [JCPDS 04-0551]; although the used catalyst exhibited the same diffraction patterns as the fresh one, the diffractions of $BaCl_2 \cdot 2H_2O$ at 16.2, 18.0 and 19.8º became weaker (Fig. 1a,a'). This confirmed the measurement results of surface composition based on XPS. Comparing to B catalyst, the pattern of W catalyst exhibited the weak diffraction peaks for Na_2WO_4 and Mn_2O_3 and clear peak for α-cristobalite [JCPDS 39-1425] and α-tridymite [JCPDS 42-1401]. In Fig. 1b, the initially amorphous SiO_2 support (the XRD pattern for the precursor silica support was not shown here) underwent to complete crystallization with the formation of highly crystalline α-cristobalite during calcinations at 830 ºC. This was consistent with the results of reports[16,17]. However, as shown in Fig. 1b', it transformed completely into α-tridymite during the OCM reaction. Although the α-tridymite phase has been noted in the fresh W catalyst before[16], it was seldom reported in the used W catalyst in OCM reaction. This proposed that the B catalyst had caused the transformation of crystal structure of SiO_2 and the possible changing of active oxygen species on catalyst surface.

Catalytic performance: The catalytic performances over the catalysts with various B/W ratios, as well as B and W single component catalysts were exhibited in Table-2. Obvious variation could be observed in the selectivity of samples, with ethylene selectivity ranging from 34.3 % for W to 47.4 % for B/W = 1/5 catalyst. When a small amount of B catalyst was added to the W catalyst (B/W = 1/8, v/v), the ethylene selectivity increased from 34.3-44.5 %. With the amount of the B catalyst increased in the mixed catalyst, both methane conversion and ethylene selectivity initially increased and then decreased. Over catalyst with B/W = 1/5 ratio, the highest ethylene selectivity,

TABLE-1
SPECIFIC BET SURFACE AREA AND SURFACE COMPOSITION OF MIXED CATALYST

Catalyst	Surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)	Surface composition[a] (at. %)				
				Ba/Na	Sn/Mn	Ti/W	Cl/Si	O
B-fresh	9.5	0.05	3.7	12.4	13.7	6.3	15.5	52.2
B-used	7.8	0.05	3.2	9.2	13.8	2.3	8.5	66.3
W-fresh	2.5	0.01	8.6	8.9	1.2	1.9	23.9	64.1
W-used	2.2	0.01	8.3	7.9	0.6	0.7	25.0	66.0

[a]C1s was not included; B = $BaCl_2$-TiO_2-SnO_2; W = Na_2WO_4-Mn/SiO_2.
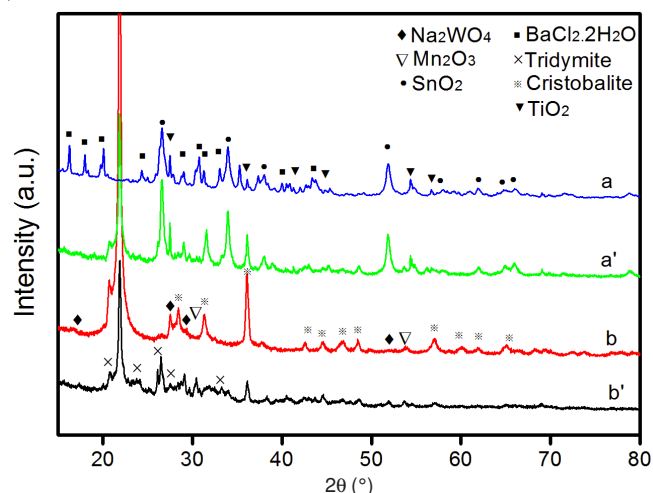
Fig. 1.   X-Ray diffraction patterns of the (a) fresh and (a') used B catalyst and (b) fresh and (b') used W catalyst

TABLE-2
PERFORMANCE OF MIXED CATALYST, B AND W
CATALYSTS FOR OCM REACTION (C₂ STANDS FOR
ETHANE, ETHYLENE AND ACETYLENE)

Catalyst	Conversion (%)		Selectivity (%)			Yield (%)
	CH_4	O_2	CO_x	C_2H_4	C_2	C_2H_4
W	43.9	98.8	50.4	34.3	47.1	15.1
B/W = 1/8	42.7	97.4	41.4	44.5	54.3	19.0
B/W = 1/5	46.9	97.6	42.1	47.4	54.3	22.2
B/W = 1/2	45.0	93.2	42.4	45.9	53.7	20.7
B/W = 1/1	44.3	90.2	43.4	46.4	53.2	20.6
B	43.8	88.8	43.3	45.8	53.3	20.1

CH_4 conversion and ethylene yield were obtained. In this case, 46.9 % CH_4 conversion and 47.4 % ethylene selectivity were observed and the ethylene yield increased by 7.1 and 2.1 % in comparison to B and W single component catalysts. Since methane conversion changed slightly from 42.7-46.9 % with the variation of B/W ratio, the enhancement in ethylene yield for the mixed catalyst was mainly due to the improvement in ethylene selectivity.

The effect of reaction temperature on catalytic performance was investigated under identical conditions and their catalytic behaviours were exhibited in Fig. 2. For the mixed catalyst, the sample with B/W = 1/5 ratio was selected as the representative for the following study. As shown in Fig. 2a, the conversion of methane suffered continuous increase with the reaction temperature elevated from 740-800 ºC. In this case, the activities of the catalysts were in the order of mixed catalyst > B catalyst > W catalyst. As the reaction temperature increased above 800 ºC, the activity of the three catalysts changed in a different way. Specifically, methane conversion continued to increase over B catalyst, remained constant over the W catalyst and decreased slightly over the mixed catalyst. It was also worth noting that the oxygen was almost completely consumed (Fig. 2b) over B and W catalysts at the temperature above 800 ºC. Therefore, the shortage of oxygen in the reaction led to the steadiness or decline in methane conversion over above both catalysts when the temperature was higher than 800 ºC.
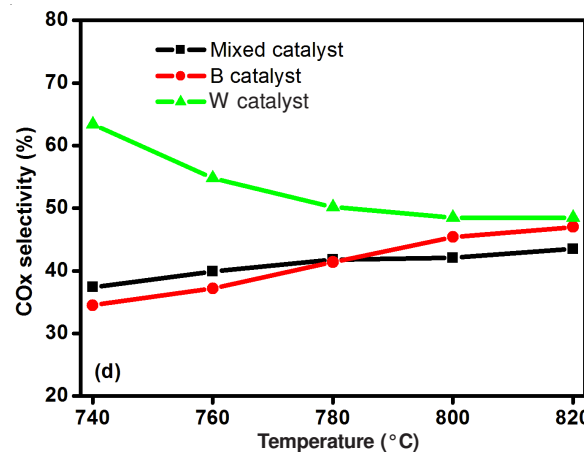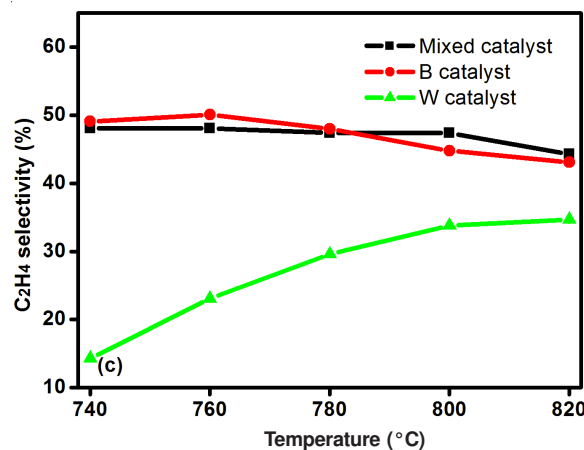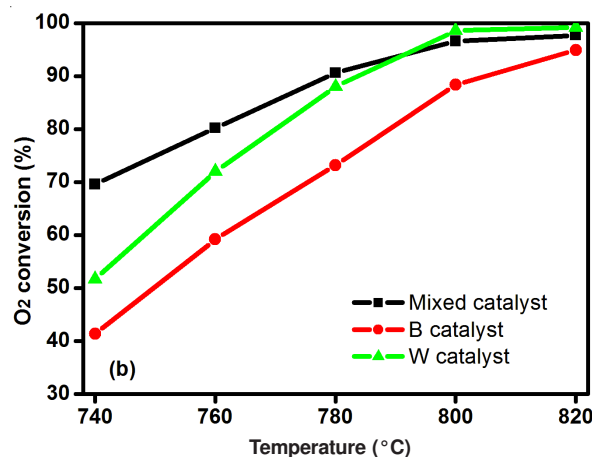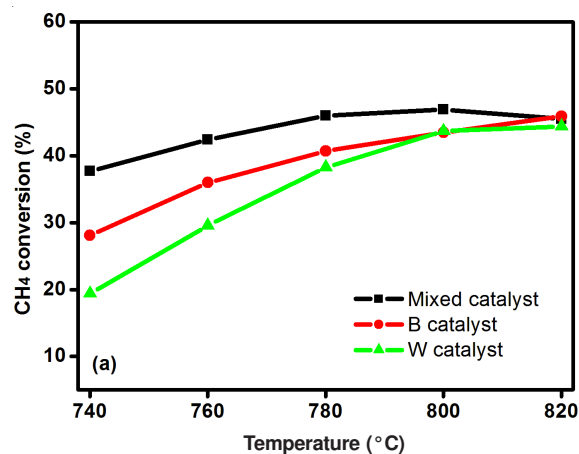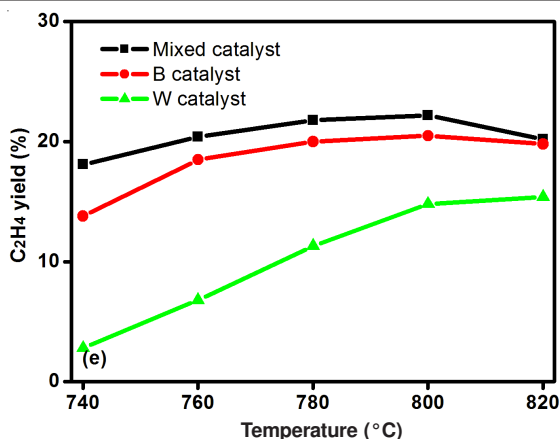
Fig. 2. Effect of the reaction temperature on the catalytic performance over mixed catalyst, W and B catalysts

With the increase of the temperature, the ethylene selectivity only suffered a little decline over the mixed catalyst and the B catalyst. On the contrary, the ethylene selectivity over the W catalyst monotonously increased among the whole temperature range studied (Fig. 2c). Correspondingly, the COx selectivity increased gradually over the mixed catalyst and B catalyst and decreased over the W catalyst (Fig. 2d). As a result, in the range of 760-820 °C, the ethylene yield changed slightly, from 20.2-22.2 %, over the mixed catalyst, which would be favorable for industrial application.

The effect of the CH_4/O_2 ratio on catalytic performance was displayed in Fig. 3. It's found that with the increase of CH_4/O_2 ratio, methane conversion and COx selectivity decreased over each catalyst (Fig. 3a,c); while ethylene selectivity increased continuously (Fig. 3b). Although these three catalysts showed similar tendency in catalytic performance, the mixed catalyst and B catalyst showed higher activity and ethylene selectivity than those of W catalyst. The highest ethylene yield was observed over the mixed catalyst at the CH_4/O_2 ratio of 2. In a high CH_4/O_2 ratio condition, the low oxygen concentration would limit the activation of methane and deep oxidation of ethylene. In contrast, in a low CH_4/O_2 ratio condition, the excessive oxygen in reaction conditions not only activated methane but also deeply oxidized the products in the OCM reaction. Thus, with the decrease of CH_4/O_2 ratio, the methane conversion and COx selectivity increased while the ethylene selectivity decreased. The results were in good agreement with literatures[19,29].
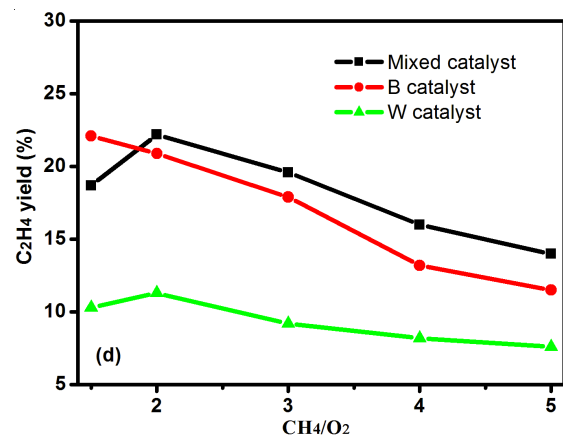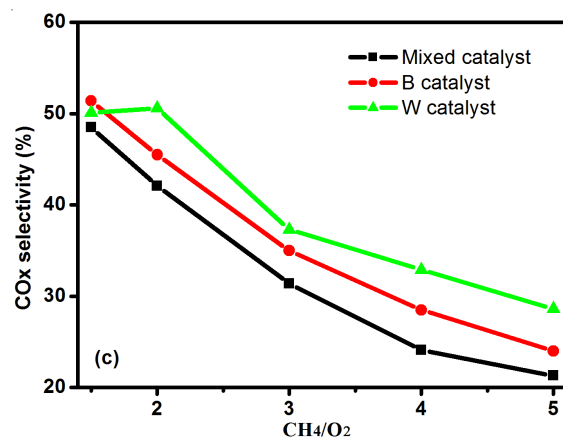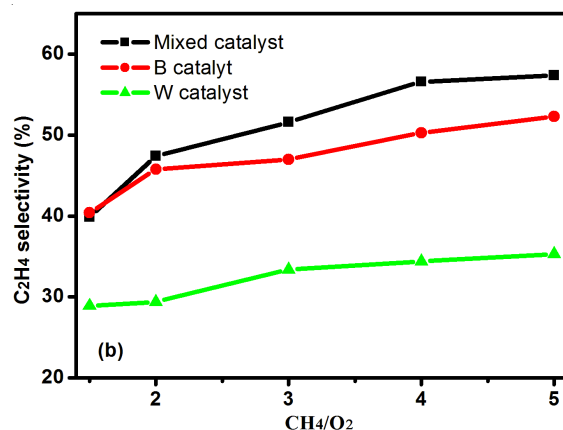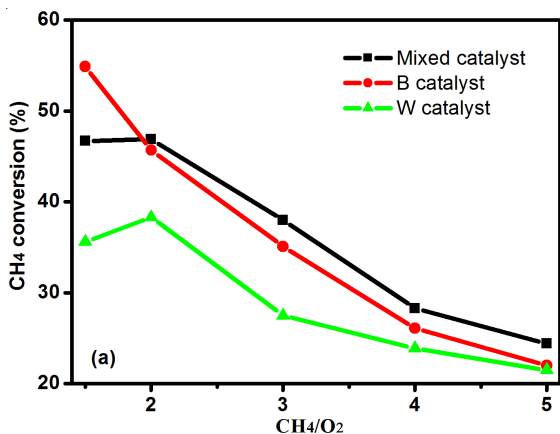

Fig. 3. Effect of CH_4/O_2 ratio on the catalytic performance over mixed catalyst, W and B catalysts

The effect of GHSV on catalytic performance was shown in Fig. 4. As shown in the figure, with the increase of GHSV, the conversion of methane gradually decreased (Fig. 4a); at the same time, the selectivity to ethylene continued to increase (Fig. 4b). Since the contact time between the feed gases and active sites became shorter; therefore, the deep oxidation of ethylene was obviously suppressed (Fig. 4c). The ethylene yields over the catalysts under various GHSVs followed the same order: mixed catalyst > B catalyst > W catalyst (Fig. 4d). Moreover, it was also noticeable in Fig. 4d that the ethylene yield over mixed catalyst could still remained higher than 20.1 % even the GHSV up to 10000 h^{-1}.

To account for the catalytic performance on the mixed catalyst, the XPS spectra of O 1s was also considered in the
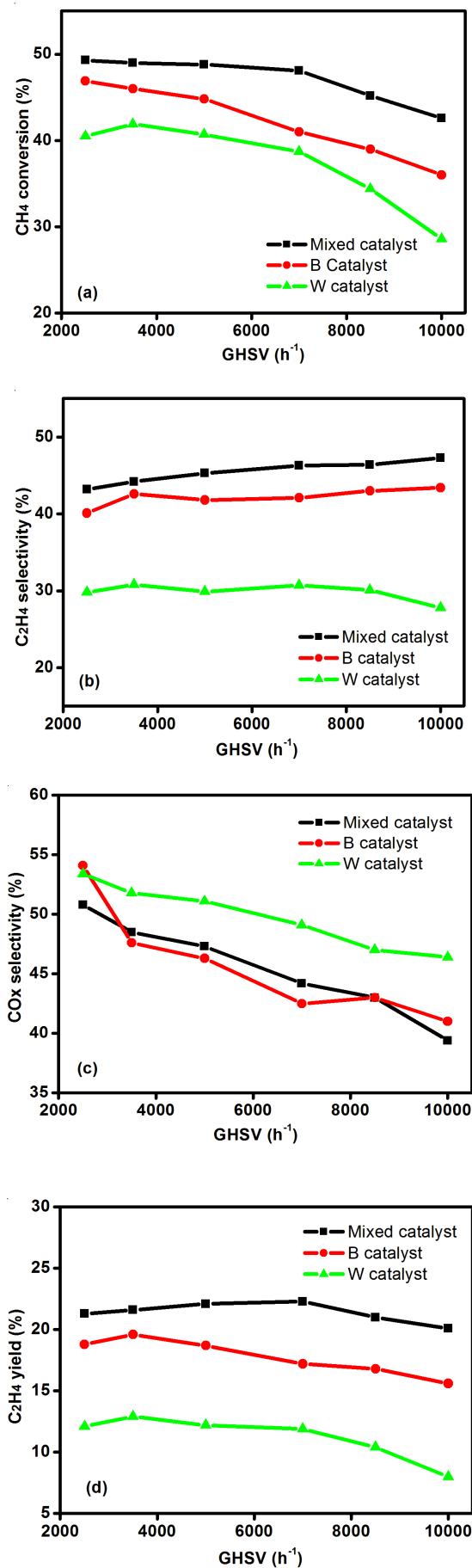
Fig. 4.   Effect of GHSV on the catalytic performance over mixed catalyst, W and B catalysts

peak deconvolution. Fig. 5 compared the surface oxygen species on mixed catalyst before and after OCM reaction. The asymmetric peak was observed for all samples. The peak at 529.6-531.0 eV corresponded to lattice oxygen (O^{2-}) (denoted as O_{1s} A) and the peak at 531.6-532.5 eV was assigned to chemisorbed oxygen (denoted as O_{1s} B). The peak at above 533.0 eV was associated with adsorb molecular water (denoted as O_{1s} C)[16,37]. The relative concentration ratio of O_{1s} A/(O_{1s} A + O_{1s} B) and O_{1s} binding energy were also listed in Table-3. The value of O_{1s} A/(O_{1s} A + O_{1s} B) of fresh B catalyst was much higher than that of fresh W catalyst. However, the values in used catalysts were identical. It was commonly accepted that surface chemisorbed oxygen was the most active oxygen and highly active in oxidation reactions, the lattice oxygen (O^{2-}) was responsible for the selective oxidation of C_2H_6 to C_2H_4. So, the B catalyst would have higher selectivity and lower activity than that of W catalyst. This deduction was consistent well with the results of catalytic performance test (Table-2). When the mixed catalyst was tested for the OCM reaction, the changing of surface composition and the transformation of crystal structure on single component had made the value of O_{1s} A/(O_{1s} A + O_{1s} B) getting identical. So the mixed catalyst exhibited higher activity and ethylene selectivity in OCM reaction.
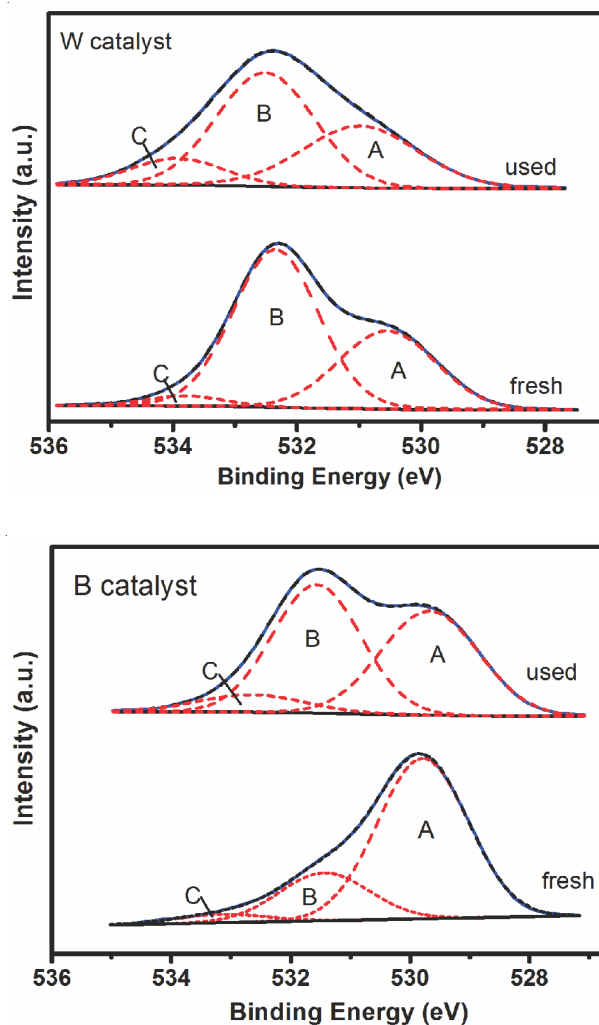

Fig. 5. O 1s XPS spectra of mixed catalysts

TABLE-3
O 1s BINDING ENERGY ON MIXED CATALYST
AND RELATIVE CONCENTRATION
BASED ON XPS MEASUREMENT

Catalyst	O1s (eV)			O1sA/(O1s A + O1s B)
	A	B	C	
B-fresh	530.2	531.7	533.4	71.1
B-used	529.6	531.6	533.6	41.7
W-fresh	530.6	532.4	533.8	35.3
W-used	531.0	532.5	533.9	40.4

For OCM reaction, ethylene was a secondary product. It competed with methane in the formation of COx. The conversion of C_2H_4 to COx was largely a result of a heterogeneous reaction, due to the inhibiting effect of CH_4 on the gas phase oxidation reaction[38]. Over the mixed catalyst, the selectivity to COx decreased appreciably and the ethylene yield increased. This indicated that the heterogeneous reaction, the deep oxidation process, was suppressed, while the ethane oxidative dehydrogenation process was enhanced. Considering the inhibitory effect of Cl^- on deep oxidation of ethylene for B catalyst[35,36] and high catalytic activity for W catalyst[17,18,21,22], the observed enhancement in ethylene yield over mixed catalyst was possibly due to two reasons: one was the Cl^- in the B catalyst suppressing the deep oxidation of ethylene, the other was the W catalyst having high reaction activity.

Conclusion

The performance of the mixed Na_2WO_4-Mn/SiO_2 and $BaCl_2$-TiO_2-SnO_2 catalysts has been investigated for OCM reaction. Overall, the mixed catalysts showed higher activity and ethylene selectivity than their single component counterparts. The proportion of the two single component catalysts (B/W ratio) was found to greatly influence the performance of the mixed catalyst. A 22.3 % ethylene yield was achieved over the mixed catalyst under the optimized conditions. Except for the high ethylene yield, the mixed catalyst can be operated among a large temperature range *i.e.*, from 760-820 °C. Although the ethylene yield decreased slightly when the GHSV exceeded 7000 h^{-1}, it was higher than 20 % in the conditions investigated. The mixed catalyst of Na_2WO_4-Mn/SiO_2 and $BaCl_2$-TiO_2-SnO_2 catalyst for OCM reaction has provided a way for commercial utilization of methane.

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