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Influence of the Composition/Texture of Solid Acid WO₃/TiO₂-Supported Lithium-Manganese Catalysts on the Oxidative Coupling of Methane

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Abstract: The selective oxidation of methane to basic petrochemicals (ethylene and ethane) is desirable and has attracted extensive research attention. The oxidative coupling of methane (OCM) is considered a promising one-step route for the production of C₂ compounds (ethylene and ethane) from methane, and has been the focus of industrial and fundamental studies. It is widely accepted that the composition is a crucial factor governing the activity of a catalyst system. It was found that the phase structures, basicity, existing status and distribution of the active components, oxygen species, and chemical states of the catalyst were influenced by the composition and ratio, resulting in different catalytic performances for the OCM. In this study, a series of solid acid WO₃/TiO₂-supported lithium-manganese oxide catalysts for OCM were synthesized via the impregnation method. The impacts of diverse compositions, such as the individual contents (Li and Mn) and dual contents (Li-Mn), on the OCM were investigated in detail, using inductively coupled plasma optical emission spectrometry, X-ray diffraction, high-resolution transmission electron microscopy, CO₂-temperature-programmed desorption, O₂-temperature-programmed desorption, H₂-temperature-programmed reduction, Raman spectroscopy, X-ray photoelectron spectroscopy, and CH₄-temperature-programmed surface reaction. The addition of Li content to the catalyst not only led to the anatase-to-rutile crystal structure transformation of TiO₂, and the reduction of the high-valence-state Mn species to low-valence-state Mn, but also increased the content of surface lattice oxygen and decreased the surface basicity. The observed effects on the structures and catalytic performance suggest that the Li content is helpful in suppressing the formation of completely oxidized CO₂, and increases the C₂ selectivity. Moreover, increasing the Li content of the catalyst facilitated the mobility of the lattice oxygen, which triggered the promotion of CH₄ activation, thereby enhancing the OCM catalytic performance. The Mn content acted as the active sites for OCM; therefore, the performance of the catalyst was closely related to the Mn concentration and valence state. However, the WO₃/TiO₂-supported catalyst with excessive Mn content exhibited a high surface basicity, high valence state of Mn, and low abundant lattice oxygen, which was unfavorable for C₂ selectivity. The Raman spectroscopy results revealed that MnTiO₃ was formed due to the co-existence of Li and Mn on WO₃/TiO₂, and played an essential role in improving the low-temperature OCM performance. There was a synergic effect of the Li and Mn components on the OCM. The optimal performance (16.3% C₂ yield) was achieved over the WO₃/TiO₂-supported lithium-manganese catalyst with $n(\text{Li}) : n(\text{Mn}) = 2 : 1$ at 750 °C.

Key Words: OCM; Mn species; WO₃/TiO₂; Lattice oxygen; MnTiO₃

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固体酸 WO_3/TiO_2 负载锂锰催化剂组成对其甲烷氧化偶联反应性能的影响

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摘要: 甲烷氧化偶联制乙烷、乙烯是一种最直接有效的甲烷转化工艺路线。催化剂的结构、碱性、活性组分的状态及分布和氧物种的性质是影响甲烷氧化偶联性能的重要因素, 而这些因素与催化剂组成直接相关。以固体酸 WO_3/TiO_2 为载体, 采用浸渍法制备出一系列负载 Li、Mn 活性组分的催化剂。利用电感耦合等离子体发射光谱(ICP-OES)、X 射线衍射(XRD)、高分辨透射电镜(HRTEM)、 CO_2 程序升温脱附(CO_2 -TPD)、 O_2 程序升温脱附(O_2 -TPD)、 H_2 程序升温还原(H_2 -TPR)、拉曼光谱(Raman)、X 射线光电子能谱(XPS)和 CH_4 程序升温表面反应(CH_4 -TPSR)等表征技术对催化剂进行了研究, 发现 Li 的添加提高了 C_2 选择性, 并有效抑制了甲烷深度氧化形成 CO_2 的过程。XRD 分析表明 Li 的添加不仅能够促进锐钛型二氧化钛向金红石型二氧化钛转化而且促使了高价锰离子的还原。XPS 与 CO_2 -TPD 分析表明 Li 的增加有利于增加催化剂表面的晶格氧含量和降低催化剂表面的碱性。 O_2 -TPD 分析表明 Li 含量逐渐升高能够促使晶格氧的移动性增强, 从而提高催化剂的反应性能。催化剂的性能受 Mn 物种的含量与价态的影响, 过多的 Mn 物种对甲烷氧化偶联是不利的, 易造成甲烷的深度氧化。同时, Li 和 Mn 活性组分通过协同作用影响着催化剂的反应性能, 能够形成新的活性物种 MnTiO_3 提高甲烷氧化偶联的低温活性。催化剂在 $n(\text{Li}):n(\text{Mn})=2:1$ 、反应温度 750°C 条件下, C_2 产率达 16.3%, 表现出最佳催化效果。

关键词: 甲烷氧化偶联; 锰物种; WO_3/TiO_2 ; 晶格氧; MnTiO_3

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1 Introduction

The useful basic petrochemicals (ethylene, ethane) can be synthesized by oxidative conversion of methane. The oxidative coupling of methane (OCM) is regarded as a promising high potential single pass reaction for the production of C_2 (ethylene, ethane) from methane, which has been in the focus of industrial and fundamental studies. Up to date, a variety of catalyst systems have so far been investigated¹⁻⁴, after the early work of OCM by Keller and Bhasin⁵. It is widely accepted that catalyst composition is crucial factor to the activity of the catalyst system. And the catalyst composition has significant effects on the performance of the catalyst by generating different catalyst properties. It has also been reported that catalyst properties, such as basicity⁶, specific surface area and phase structure⁷, the existing status of active component⁸, oxygen species⁹, and chemical states of catalyst¹⁰ play an important role for catalyzing the OCM.

According to many statistical analysis of OCM catalysts, multicomponent catalysts have shown typically better performance compared to single metal oxide based catalysts^{11,12}. Some alkali metal and transition metal containing multicomponent catalysts, including Li/MgO ¹³, Mn/TiO_2 ¹⁴, and $\text{Mn/Na}_2\text{WO}_4/\text{SiO}_2$ ¹⁵, had been investigated and shown to be active for OCM. It is widely accepted that Li and Mn content are a promising reactive component for many kinds of OCM process catalysts¹⁶⁻¹⁸. The WO_3/TiO_2 have been widely investigated for many applications

due to their promising properties, such as catalyst supports and heterogeneous catalyst for redox reactions^{19,20}. Moreover, it is notable that Ti and W are effective for increasing the catalytic performance for OCM²¹.

Based on the above results, the present paper design a new class of WO_3/TiO_2 -supported lithium-manganese oxides for OCM. In this study, a series of WO_3/TiO_2 -supported lithium-manganese catalysts have been synthesized by changing the content of Li and Mn. Here, we have investigated the influence of catalyst composition on the catalytic properties of catalysts used for the OCM reaction. We also report how we came to and consequently characterized the WO_3/TiO_2 -supported catalyst using techniques such as X-ray diffraction (XRD), CO_2 -temperature-programmed desorption (CO_2 -TPD), O_2 -temperature-programmed desorption (O_2 -TPD), H_2 -temperature-programmed reduction (H_2 -TPR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and CH_4 -temperature-programmed surface reaction (CH_4 -TPSR). The primary aims are to elucidate the effects of the components Li and Mn on the WO_3/TiO_2 -supported lithium-manganese catalyst, and further understand the catalytic mechanism of the WO_3/TiO_2 -supported lithium-manganese catalyst.

2 Experimental

2.1 Catalysts synthesis

WO_3/TiO_2 support (the loading of WO_3 is 5% (mass fraction))

was prepared *via* wetness impregnation. The TiO₂ (A.R., Tianjin Kemiou Chemical Reagent Co., Ltd., China) was impregnated with the appropriate amount of ammonium metatungstate ((NH₄)₅H₅[H₂(WO₄)₆·H₂O], A.R., Strem Chemicals, Inc., USA) water solution for 20 min ultrasonic treatment, followed by stirring at 80 °C to evaporate water, and calcined in air for 3 h at 800 °C. The calcined sample was denoted as WT.

Catalysts containing the individual components of the mixed oxide (Li, Mn) and their double combinations (Li-Mn) supported on WO₃/TiO₂ support were also prepared by wetness impregnation. The precursors for Li and Mn were lithiumnitrate (LiNO₃, A.R., Sichuan Longxi Chemical Co., Ltd., China) and manganous nitrate (Mn(NO₃)₂, A.R., Shanghai Reagent Factory, China). As before, the catalysts were obtained by the WO₃-TiO₂ impregnation with water solution of the corresponding salts, followed by stirring for 3 h at 80 °C to evaporating water, calcination at 400 °C for 1 h and at 800 °C for 2 h. The catalysts in this work were expressed in this way: lithium-free (denoted as Mn/WT, the mass ratio of Mn : Ti was 1 : 17.2), manganese-free (denoted as 2Li/WT, the mass ratio of Li : Ti was 2 : 17.2) and double combinations (denoted as *x*Li-*y*Mn/WT, the mass ratio of Li : Mn : Ti was *x* : *y* : 17.2), respectively.

2.2 Catalytic activity

The reaction of OCM was performed with catalyst (1.0 g, 40–60 mesh) at atmospheric pressure in a quartz fix-bed system (10 mm I.D.). Before the reaction, the samples were heated to reaction temperature (750 °C) under O₂ and N₂ (O₂ : N₂ = 4 : 10 mL·min⁻¹) and then switched to the reactants consisting CH₄, O₂ and N₂ (CH₄ : O₂ : N₂ = 20 : 8 : 10 mL·min⁻¹). The temperature of reactor was measured by a thermocouple attached to the outer wall of the quartz reactor. The effluent gas was analyzed on-line by the gas chromatography equipped with a hydrogen flame ionization detector (FID) and a thermal conductivity detector (TCD). The calculation of CH₄ conversion and C₂ selectivity were calculated based on total carbon balance (100% ± 2%). In order to get steady state kinetic data, all the data were obtained after 1 h stabilization at 750 °C.

2.3 Catalyst characterization

The actual loadings of metals were analyzed on inductively coupled plasma optical emission spectrometry (ICP-OES) on an Agilent 725-ES (USA).

The phase composition of catalysts was determined by X-ray diffractometer (PANalytical, Inc., The Netherlands) with the Ni-filtered Cu K_α radiation (0.15406 nm).

High resolution transmission electron microscopy (HRTEM) images measurements were performed on a JEM-2010 (Japan) high-resolution transmission electron microscopy under a working voltage of 200 kV.

CO₂-TPD, O₂-TPD and H₂-TPR were all performed on an ChemBET Pulsar TPR/TPD automated chemisorption analyzer (Quantachrome Instruments, USA).

The CO₂-TPD analysis was carried out as follows: The catalysts (150 mg) were first treated at 300 °C for 1 h in flowing

He (30 mL·min⁻¹) to remove adsorbed impurities, and they were then exposed to CO₂ (30 mL·min⁻¹) for 1 h at room temperature. Finally, the catalysts were heated to 900 °C with a ramp rate of 25 °C·min⁻¹ in He gas (30 mL·min⁻¹) to proceed the CO₂-TPD.

The O₂-TPD analysis was carried out as follows: The catalysts (150 mg) were first treated with He stream (30 mL·min⁻¹) at 500 °C for 1 h to remove adsorbed impurities and they were then exposed to O₂ (30 mL·min⁻¹) for 1 h at room temperature. Finally, the catalysts were heated to 900 °C with a ramp rate of 10 °C·min⁻¹ in He gas (30 mL·min⁻¹) to proceed the O₂-TPD.

The H₂-TPR analysis was carried out as follows: The catalysts (15 mg) were first treated with He stream (30 mL·min⁻¹) at 300 °C for 1 h to remove adsorbed impurities and they were then exposed to 10% H₂-Ar (30 mL·min⁻¹) for 30 min at 40 °C. Finally, the catalysts were heated to 900 °C with a ramp rate of 30 °C·min⁻¹ in a flowing 10% H₂-Ar gas (30 mL·min⁻¹) to proceed the H₂-TPR.

The Raman measurements were carried out using a Raman spectrometer (HORIBA jobin Yvon S.A.S., France) with a 532 nm semiconductor laser as excitation, equipped with a charge-coupled device camera enabling microanalysis on a sample point.

XPS analyses were carried out with a Thermo Fisher Scientific ESCALAB250xi spectrometer (USA) with Mg K_α radiation.

The CH₄-TPSR analysis was performed as follows: The sample (500 mg) was pretreated with He stream (30 mL·min⁻¹) at 500 °C for 1 h to remove adsorbed impurities. After cooling to 40 °C, the 10% CH₄-He gas (30 mL·min⁻¹) was adsorbed on the catalyst sample for 60 min. The analysis was performed in a flowing 10% CH₄-He gas (30 mL·min⁻¹) to 900 °C at a heating rate of 10 °C·min⁻¹. The CH₄ consumption and outlet products (C₂H₆, C₂H₄ and CO₂) were measured instantaneously *via* a mass spectrometer (MS, TILON, USA).

3 Results and discussion

3.1 Comparison of performance of catalysts

The catalytic performance of WT, Mn/WT, 2Li/WT and *x*Li-*y*Mn/WT catalysts were systematically investigated at 750 °C for a feed gas of CH₄ : O₂ : N₂ = 20 : 8 : 10 mL·min⁻¹ (Table 1). Blank test with only the support WT as catalyst gave the C₂ selectivity was only 1.2% and C₂H₄ selectivity was close to zero, while the selectivity to CO_x (CO and CO₂) was up to 98.8%. This indicated that the WT was almost inactive for oxidative dehydrogenation of CH₄ under the reaction conditions. The Mn/WT catalyst was active for OCM (CH₄ conversion of 16.1%), but the C₂ selectivity was as low as 11.7%, and the CO_x selectivity was as high as 82.8%, from the catalytic results we could infer that Mn had a significant influence on the deep oxidation of methane. With the continuous increased Mn content in 2Li-*y*Mn/WT, the C₂ selectivity and C₂H₄ selectivity decreased and that to CO₂ increased. It indicated that excessive Mn content was certainly unfavorable for OCM catalytic

Table 1 The performance of OCM reaction over WT-supported catalysts.

Catalyst	Catalyst bed temperature (°C)	Conversion (%)	Selectivity (%)				Yield (%)	
		CH ₄	C ₂	C ₂ H ₄	CO ₂	CO	C ₂	C ₂ H ₄
WT	756.6	12.1	1.2	0.0	13.7	85.2	0.0	0
Mn/WT	760.9	16.1	11.7	4.1	73.2	9.6	1.9	0.7
Li-Mn/WT	763.4	28.2	52.5	32.2	33.2	11.8	14.8	9.1
2Li-Mn/WT	761.0	28.1	58.0	36.6	25.6	14.9	16.3	10.3
3Li-Mn/WT	758.4	25.3	60.8	37.9	21.6	15.2	15.4	9.6
Li/WT	752.3	9.8	55.3	17.9	31.7	8.5	5.4	1.7
2Li-2Mn/WT	762.9	28.6	51.3	31.7	35.8	11.0	14.7	9.1
2Li-3Mn/WT	764.9	28.3	48.5	30.0	39.5	10.1	13.7	8.5

selectivity of catalysts. This point had been addressed by Koirala *et al.*²². Compared to the WT catalyst, addition of Li significantly increased the C₂ selectivity to 55.3%, while CO_x selectivity (only 40.4%) was dramatically decreased. As Li loading in *x*Li-Mn/WT increased, C₂ selectivity and C₂H₄ selectivity increased; while CO₂ selectivity suffered an obvious decrease. It could be inferred that Li content played a significant role not only in increasing the C₂ selectivity and C₂H₄ selectivity, but also in suppressing the formation of deep oxidized CO₂. A recent study of Li/Mg catalysts also reported similar conclusions regarding the role of Li content for the OCM²³. Based on above results, it could be inferred that Li and Mn were the essential components for OCM in the solid acid WT-supported catalyst, and high catalytic performance could be obtained only when co-existence of Li and Mn were supported on WT. Co-existence of Li and Mn was essential to improve the low-temperature activity/selectivity. On 2Li-Mn/WT catalyst, the highest CH₄ conversion (28.1%) and the best C₂ selectivity (58.0%) were obtained.

3.2 Catalyst characterization

3.2.1 ICP-OES

The ICP-OES characterization was investigated for the bulk content of Li and Mn in the *x*Li-*y*Mn/WT samples, shown in Table 2. As expected, *x*Li-*y*Mn/WT exhibited the bulk Li : Mn value were in good agreement with the theoretical value. As demonstrated in Table 2, the Li/Mn atomic ratio slightly decreased after 1 h OCM reaction, indicating these catalysts were physically stable during the OCM reaction process.

3.2.2 XRD

Fig. 1 showed the XRD patterns of WT, Mn/WT, 2Li/WT and *x*Li-*y*Mn/WT catalysts, respectively. The rutile TiO₂ phase (JCPDS No. 89-4920) presented in all catalysts, only those

without Li remained anatase TiO₂ phase (JCPDS No. 89-4921). This indicated that Li promoted the anatase-to-rutile crystal structure transformation of TiO₂. It has been reported that the deep oxidation capacity of anatase TiO₂ was found to be higher than rutile phase²⁴. Thus, the Li addition hindered the deep oxidation, consistent with the experimental results (Table 1). The typical MnWO₄ phase (JCPDS No. 80-0152) was only detected for the Mn/WT. With addition Li content, a novel phase of LiMnTiO₄ (JCPDS No. 40-0975) was observed accompanied by a reduction of MnWO₄ phase. Moreover, the peaks of $2\theta = 18.6^\circ$ shifted toward lower angle with increasing Li content, which implied lattice expanding. The lattice expansion might be contributing to the replacement of the high valence state Mn species by low valence state Mn. The structure of LiMnTiO₄ was determined to be a cubic spinel phase (*Fd3m*), with Mn/Ti randomly occupying the octahedral 16d sites and Li occupying the tetrahedral 8a sites^{25,26}. In a unit cell, there are other empty octahedral sites²⁷. With increasing Li content, more Li ions would occupy the empty octahedral sites. Consequently, low valence state Mn species were formed in cubic spinel structure

Fig. 1 XRD patterns of WT-supported catalysts.**Table 2** The Li/Mn atomic ratio of *x*Li-*y*Mn/WT catalysts.

Catalyst	Li/Mn atomic ratio	
	fresh	used
Li-Mn/WT	1.01/1	0.99/1
2Li-Mn/WT	2.00/1	1.98/1
3Li-Mn/WT	3.03/1	2.96/1
2Li-2Mn/WT	1.99/2	1.98/2
2Li-3Mn/WT	1.98/3	1.91/3

Fig. 2 HRTEM images of (a) WT; (b) Mn/WT; (c) Li-Mn/WT; (d) 2Li-Mn/WT; (e) 3Li-Mn/WT; (f) Li/WT; (g) 2Li-2Mn/WT; (h) 2Li-3Mn/WT.

(LiMnTiO₄) to keep the charge balance. With increasing Mn content in 2Li- γ Mn/WT, the intensities of $2\theta = 18.6^\circ$ the diffraction peak shifted toward higher angle, which implied lattice shrinking. The lattice contraction might be owing to the stronger basicity facilitated the formation of Mn species with higher oxidation states, which was in agreement with reported by Wang *et al.*²⁸. The result indicated that the more Mn content increased the basicity of catalysts and would be further evidenced by CO₂-TPD.

3.2.3 HRTEM

Fig. 2 showed the HRTEM images of WT, Mn/WT, 2Li/WT and x Li- γ Mn/WT catalysts, respectively. Lattice spacing of 0.327 and 0.247 nm was observed from HRTEM image, matching with respectively the (110) and (101) spacing of rutile TiO₂ (JCPDS No. 89-4921). The (101) lattice plane of anatase TiO₂ ($d_{101} = 0.350$ nm) was only found in HRTEM image of WT and Mn/WT (Fig. 2a,b), which was consistent with the results of XRD analysis. For x Li- γ Mn/WT, the crystal lattice fringes of LiMnTiO₄ were 0.478, 0.296 and 0.257 nm apart, which were corresponding to the d value of (111), (220) and (311) lattice planes of cubic spinel LiMnTiO₄.

3.2.4 CO₂-TPD

Fig. 3 showed the CO₂-TPD patterns of WT, Mn/WT, 2Li/WT and x Li- γ Mn/WT catalysts, respectively. The CO₂ desorption range at around 290 °C was assigned to the weak basic sites, the desorption in the temperature range from 600 to 800 °C referred to the strong basic sites, and desorption peak above 800 °C

attributed to the very strong basic sites^{29,30}. As revealed in Fig. 3, the basicity were influenced by the Li content in the catalysts. No obvious desorption peak (>600 °C) was apparent for the 2Li/WT as it likely possessed weak basicity. As Li content in x Li-Mn/WT increased, the desorption peak (600–800 °C) shifted to lower temperature, indicated the basicity decreased. It is well known that the strong basic sites are favorable for the activation of CH₄, the basic sites with weaker strength are beneficial for improving the C₂ selectivity³¹. Consequently, the increase of Li content was unfavorable for CH₄ conversion, facilitated the selectivity to hydrocarbons. CO₂-TPD results showed Mn species formed on the catalysts are tentatively attributed to the effects of surface basicity. With the Mn content in 2Li- γ Mn/WT increased, the desorption peak shifted to higher temperature and

Fig. 3 CO₂-TPD patterns of WT-supported catalysts.

a desorption peak ($> 800\text{ }^{\circ}\text{C}$) accompanied, indicated the basicity increased. It was inferred that more Mn content could be benefited to increase the basicity, facilitated the activation of CH_4 . However, the strong basicity implied easier lead to the formation of completely oxidized CO_2 , which was unfavorable for C_2 selectivity. The CO_2 -TPD characterization profiles interpreted the OCM reaction results from the surface basicity aspect.

3.2.5 O_2 -TPD

Fig. 4 showed the O_2 -TPD patterns of WT, Mn/WT, 2Li/WT and $x\text{Li-yMn/WT}$ catalysts, respectively. As compared to the WT and 2Li/WT, the incorporation of Mn content released of surface lattice (O^{2-}), as indicated by the distinct desorption peak of oxygen above $600\text{ }^{\circ}\text{C}$. The desorption peaks of oxygen higher than $600\text{ }^{\circ}\text{C}$ were observed for all Mn-containing samples, which ascribed to the release of surface lattice oxygen (O^{2-}). However, the peaks greatly shifted to lower temperature after the introduction of Li into Mn/WT, and the phenomenon disclosed Li enhanced the mobility of the O^{2-} species. It has been widely reported that promotion O^{2-} species mobility is favorable for the activation of CH_4 ³². It was revealed by XRD that the Li content promoted the transformation of high valence state Mn species to low valence state Mn, which moderately reduction in the oxidation capacity of catalysts was available to compress the deep oxidation. Due to the optimal synergistic interaction of above factors, addition of Li increased the C_2 selectivity, while CH_4 conversion was slightly decreased. By contrast, the O_2 desorption peaks shifted gradually to higher temperature after the increase of Mn content in 2Li-yMn/WT, which indicated that the mobility of the O^{2-} species was reduced. Moreover, a new distinct desorption peak of oxygen around $800\text{ }^{\circ}\text{C}$ was appeared in high Mn content sample (2Li-2Mn/WT and 2Li-3Mn/WT), which could be attributed to the release of bulk lattice O^{2-} . It is well-known that the reduction in the mobility of the O^{2-} species was unfavorable for CH_4 conversion, while bulk lattice oxygen utilization as active species for CH_4 conversion even deep oxidation³³⁻³⁵. Due to the optimal synergistic interaction of above factors, addition of Mn slightly increased the CH_4 conversion, while C_2 selectivity was decreased. The above analyses were also consistent with the experimental results

Fig. 4 O_2 -TPD patterns of WT-supported catalysts.

Fig. 5 H_2 -TPR patterns of WT-supported catalysts.

(Table 1).

3.2.6 H_2 -TPR

Fig. 5 showed the H_2 -TPR patterns of WT, Mn/WT, 2Li/WT and $x\text{Li-yMn/WT}$ catalysts, respectively. The support WT showed two distinct reduction peaks in the regions of $700\text{--}800$ and $800\text{--}900\text{ }^{\circ}\text{C}$, respectively. The reduction at higher temperature ($700\text{--}800\text{ }^{\circ}\text{C}$ and $800\text{--}900\text{ }^{\circ}\text{C}$) could be ascribed to the reduction of tungsten cations. The H_2 -TPR patterns of Mn/WT exhibited two hydrogen reduction peaks in the regions of $600\text{--}700$ and $800\text{--}900\text{ }^{\circ}\text{C}$, respectively. The reduction peak in the temperature range from 600 to $700\text{ }^{\circ}\text{C}$ referred to the reduction of manganese cations, and reduction peak above $800\text{ }^{\circ}\text{C}$ attributed to the reduction of manganese and tungsten or the reduction of tungsten alone³⁶⁻⁴⁰. The obtained experimental result on the H_2 -TPR of Mn/WT was in good agreement with the study⁴¹ which also reported the reduction peaks of manganese and tungsten close to those observed in this study. Compared to the WT catalyst, the tungsten reduction peak of Mn/WT shifted to higher temperatures as addition of Mn content. The change in the reducibility could be due to the MnWO_4 formation. The manganese reduction peaks of $x\text{Li-yMn/WT}$ shifted to higher temperature compared to those of Mn/WT. The manganese reduction peaks shifted to higher temperature could be ascribed to the highly dispersed Li and Mn content, which had a strong interaction with the support and exists as LiMnTiO_4 . The tungsten reduction peaks of $x\text{Li-yMn/WT}$ shifted to lower temperature compared to those of Mn/WT and Li/WT, which were due to the reduction of MnWO_4 phase and Li_2WO_4 . In $x\text{Li-yMn/WT}$ system, it was particularly noted that manganese and tungsten reduction peak shifts to lower temperature with increasing Li content, suggestive of the more Li content increased the mobility of the O^{2-} species^{42,43} and facilitated the reduction of Mn. It was also seen that the increase of Mn in 2Li-yMn/WT remarkably increased in the intensity of the Mn reduction peak and reduction temperature, which was owe to Mn content increased and the mobility of the O^{2-} species decreased. Those were in good agreement with the above-mentioned XRD and O_2 -TPD results.

3.2.7 Raman

Raman spectroscopy is a highly sensitive technique for

Fig. 6 Raman spectra of WT-supported catalysts.

analyzing existing states of oxides especially with poor crystallinity. Fig. 6 showed the Raman spectra of WT, Mn/WT, 2Li/WT and x Li- y Mn/WT catalysts, respectively. It was reported that the peaks at around 138, 188, 390, 515 and 632 cm^{-1} were typical of anatase TiO_2 while the peaks at around 236, 443 and 610 cm^{-1} could be correspond to rutile TiO_2 . With the addition of Li content, a novel raman peaks of rutile TiO_2 were observed accompanied by a reduction of intensity of the raman peaks of anatase TiO_2 . This meant that the Li content dopant enhanced the anatase-to-rutile phase transformation of TiO_2 , which was in accordance with the results of XRD. A new wavenumber peak at 684 cm^{-1} , which was considered to associate with MnTiO_3 phase, was observed when the co-existence of Li and Mn were supported on WT. Wang *et al.*²⁸ reported that MnTiO_3 was beneficial to promoting of the performance for OCM at low temperature. Therefore, co-existence of Li and Mn promoted the generation of MnTiO_3 , resulting in an enhanced OCM catalytic performance of x Li- y Mn/WT catalysts (Table 1). The diffraction intensity of WO_3 (792 cm^{-1}) phase disappeared after Li or Mn content added, indicating that Li and Mn contributed to dispersing tungsten species well. Moreover, there were no obvious MnTiO_3 and WO_3 diffraction peaks were observed in XRD, which indicated that MnTiO_3 and WO_3 existed as an amorphous or highly dispersed species on the surface of catalyst.

3.2.8 XPS

XPS measurement was conducted to chemical states of the catalyst surface; the results are presented in Fig. 7 and Table S1 (in Supporting Information). Fig. 7a showed the XPS spectra of Mn $2p$ for WT, Mn/WT, 2Li/WT and x Li- y Mn/WT catalysts, respectively. The Mn $2p_{3/2}$ of all catalyst could be attributed to three peaks corresponding to three types of manganese species: Mn^{2+} (640.9 eV), Mn^{3+} (641.8 eV) and Mn^{4+} (642.5 eV)^{44,45}. It was noticeable that the $(\text{Mn}^{2+} + \text{Mn}^{3+})/\text{Mn}^{4+}$ atomic ratio increased with adding Li content (Table S1). This assignment was consistent with the characterization results from XRD (Fig. 1). It was commonly accepted that high valence state Mn species was more reactive in deep oxidation reactions due to its higher oxidation capacity than low valence state Mn species^{28,46}. High $(\text{Mn}^{2+} + \text{Mn}^{3+})/\text{Mn}^{4+}$ atomic ratio was regarded to be beneficial to catalytic performance for OCM and thereafter exhibited very high C_2 selectivity. It was noted that the results with increasing Li content were in accordance with the C_2 selectivity and $(\text{Mn}^{2+} + \text{Mn}^{3+})/\text{Mn}^{4+}$ atomic ratio. More importantly, lower basicity (CO_2 -TPD) was available to compress the deep oxidation while higher O^{2-} mobility (O_2 -TPD) was favorable for CH_4 activation. Therefore, taking into consideration the synergistic interaction of above factors, the CH_4 conversion slightly decreased with the increased of C_2 selectivity with the increasing of Li content, which was good agreement with the experimental results (Table 1). With increasing amount of Mn from 2Li-Mn/WT to 2Li-3Mn/WT, the $(\text{Mn}^{2+} + \text{Mn}^{3+})/\text{Mn}^{4+}$ atomic ratio decreased, which indicated that the deep oxidation capacity was increased. As revealed in O_2 -TPD, the mobility of the O^{2-} species reduced which was unfavorable for CH_4 conversion. Therefore, the increasing of Mn slightly increased the CH_4 conversion, while CO_2 selectivity was increased, which was consistent with we observed in this study (Table 1).

The O $1s$ XPS spectra of all catalysts were shown in Fig. 7b and Table S1. The binding energies were calibrated by using the C $1s$ peak of graphite at 284.8 eV as a standard. By assuming a single peak having 80% Gaussian plus 20% Lorentzian peak

Fig. 7 XPS spectra for (a) Mn $2p_{3/2}$ and (b) O $1s$ for WT-supported catalysts.

Fig. 8 CH₄-TPSR experiments performed on WT-supported catalysts.

shape, three peaks corresponding to different oxygen species, which could be attributed to lattice oxygen (O^{2-} , 529.6–531.0 eV), chemisorbed oxygen (O_{ads} , 531.1–532.5 eV) and carbonate groups (> 532.5 eV)^{47,48}, could be achieved. As shown in Fig. 7b and Table S1, the $O^{2-}/(O_{ads} + O^{2-})$ atomic ratio increased with increasing Li content in the catalysts. It has been widely reported that O_{ads} was the most active oxygen and highly active in oxidation reactions, the O^{2-} was responsible for abstracting hydrogen from C_2H_6 to form C_2H_4 ^{49–51}. Therefore, high $O^{2-}/(O_{ads} + O^{2-})$ atomic ratio was regarded to be beneficial to C_2H_4 selectivity while unfavorable for CH_4 conversion. The CH_4 conversion decreased with the increased of C_2H_4 selectivity with the increasing of Li content, which were in parallel to the CH_4 conversion and C_2H_4 selectivity sequence of the catalysts (Table 1). As Mn content increased, the $O^{2-}/(O_{ads} + O^{2-})$ atomic ratio decreased, which indicated that C_2H_4 selectivity decreased. As revealed in O_2 -TPD, the mobility of the O^{2-} species reduced which was unfavorable for CH_4 conversion. More importantly, the deep oxidation capacity was increased with increasing Mn content. Therefore, taking into consideration the above factor, the increasing of Mn slightly increased the CH_4 conversion, while CO_2 selectivity was drastically increased, consistent with the experimental results (Table 1).

3.2.9 CH₄-TPSR

The CH_4 -TPSR experiments on WT, Mn/WT, 2Li/WT and $xLi-yMn/WT$ catalysts were carried out. Fig. 8 showed CH_4 -TPSR profiles of WT-supported catalysts and the mass spectrum signals of C_2H_6 ($m/e = 30$), C_2H_4 ($m/e = 27$ for C_2H_4 instead of $m/e = 28$ to avoid interference caused by CO) and CO_2 ($m/e = 44$) for CH_4 -TPSR experiments on WT-supported catalysts. The

CH_4 consumption was in good agreement with the oxygen storage capacity (O_2 -TPD). The correlation of CH_4 consumption and oxygen storage capacity further testified that Mn content was the key factor for conversion of CH_4 . The CH_4 consumption occurred simultaneously as C_2H_6 , C_2H_4 and CO_2 formation appeared. This was due to the reaction of methane and oxygen species over catalysts which results in C_2H_6 , C_2H_4 and CO_2 production. Since CH_4 -TPSR experiments on WT, Mn/WT and 2Li/WT did not show any obvious mass spectrum signals of C_2H_6 and C_2H_4 , it was concluded that a kind of synergistic reaction occurs positively among Li and Mn over the $xLi-yMn/WT$ catalysts. Compared with Mn/WT catalyst, the $xLi-yMn/WT$ catalyst showed much stronger mass spectrum signals of C_2H_4 . It could be inferred that Li content altered oxygen property, which the O^{2-} content on surface enhanced; the enhancing O^{2-} content would be in favor for abstracting hydrogen from C_2H_6 to form C_2H_4 . As Mn content in 2Li- yMn/WT increased, mass spectrum signals of C_2H_6 and C_2H_4 enhanced slightly and that to the mass spectrum signals of CO_2 increased dramatically. It was thus deduced that the highly active in deep oxidation on the 2Li- yMn/WT with more Mn content was mainly a result of more O_{ads} content and bulk lattice oxygen. This was in accordance with the results of O_2 -TPD and XPS investigation.

4 Conclusions

$xLi-yMn/WT$ was a good catalyst for the OCM reaction, the reaction was found to proceed best with co-existence of Li and Mn. CH_4 conversion of 28.1% and the selectivity to C_2 of 58.0% on 2Li-Mn/WT was obtained at 750 °C. Catalysts containing

different Li and Mn content largely influenced the structures, basicity, reducibility, oxygen property, chemical states and catalytic performances of the WT-supported catalysts in the oxidative coupling of methane reaction. The improved performance was attributed to the favorable effects of Li introduction, which not only induced anatase-to-rutile crystal structure transformation of TiO₂ and reduced the basicity to suppress the formation of completely oxidized CO₂, but also increased the content of lattice oxygen (O²⁻) and reduced the high valence state Mn species to promote the selectivity to hydrocarbons. Moreover, increasing Li content of catalyst facilitated the mobility of the O²⁻ species, which triggered promotion of the activation of CH₄, thereby leading to the improvement of OCM catalytic performance. Mn was one of the key factors determining their catalytic performance for OCM, which the performance of catalyst was closely related to the Mn concentration and valence state. However, excessive Mn content was unavailable to C₂ selectivity because the higher surface basicity, more Mn⁴⁺ species and more chemisorbed oxygen content, which was favorable for the combustion of methane. In addition, co-existence of Li and Mn promoted the generation of MnTiO₃ which was important for the low-temperature performance improvement. The synergetic effect of two essential components (Li and Mn) was considered as a critical parameter for selective oxidation of methane over catalysts.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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