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Oxidative Coupling of Methane over Mo-Sn Catalyst

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Catalyst Preparation Method

(1) Hydrothermal method without precipitant

The work in this chapter uses $Na_2SnO_3{\cdot}3H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ as precursors, referred to as the tin and molybdenum salts, respectively. The Mo-Sn catalysts were prepared by a precipitant-free hydrothermal method. The preparation process was as follows: a certain amount of tin salt was added to a polytetrafluoroethylene liner containing 100 mL of deionized water, heated in a water bath at 60 ℃, and after the powder was completely dissolved, a certain amount of molybdenum salt was weighed into the polytetrafluoroethylene liner and transferred to a homogeneous reactor after stirring, and the reaction was carried out at 120 ℃ for 24 h. The precipitate obtained by cooling was centrifuged, washed, and dried to obtain a preliminary sample of the precursor. The samples were placed in a tube furnace and roasted for 8 h at 700 ℃ under O_2 atmosphere.

The Mo-Sn catalysts prepared according to Mo/Sn molar ratios of 0:1, 1:5, 1:3, 1:2, 1:1, 2:1, and 1:0 were labeled as Sn1, Mo1Sn5, Mo1Sn3, Mo1Sn2, Mo1Sn1, Mo2Sn1, and Mo1, respectively.

(2) Ball milling method

Two different catalytic systems were prepared by the ball milling method, the first one was a molybdenum-tin catalyst with different Mo/Na_2SnO_3 by the physical mixing method of ball milling, and the second one was a tin oxide catalyst with different Na_2SnO_3/SnO_2 by the same physical mixing method of ball milling. The preparation process is as follows.

Molybdenum-tin catalyst: A certain amount of $Na_2SnO_3{\cdot}3H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were weighed according to Mo/Sn molar ratios of 0/1, 1/100, 1/50, 1/35, 1/3, 1/0, respectively, and physically mixed by ball milling; dried at 110 ℃ for 12 h; roasted at 700 ℃ under O_2 atmosphere for 8 h; obtained Na_2SnO_3, Mo1Sn100, Mo1 Sn50, Mo1 Sn35, Mo1Sn3, and MoO_3 catalysts.

Tin oxide catalysts: a certain amount of $Na_2SnO_3{\cdot}3H_2O$ and SnO_2 were weighed according to Na_2SnO_3/SnO_2 molar ratios of 1/0, 10/1, 5/1, 3/1, 1/5, and 0/1, respectively, and physically mixed by ball milling; dried at 110 ℃ for 12 h; roasted at

700 ℃ under O_2 atmosphere for 8 h; to obtain different Na_2SnO_3/SnO_2 ratio catalysts were obtained.

Catalyst performance evaluation

The experimental evaluation in this thesis was conducted on an atmospheric pressure continuous flow fixed bed reactor, and the experimental setup is shown in Figure S1. A quartz tube 500 mm long with an inner diameter of 9 mm was used as a fixed-bed reactor, and a thermocouple sleeve was installed inside the reactor to measure the temperature of the catalyst bed by a built-in thermocouple to measure the reaction temperature. A temperature control thermocouple was installed outside the reactor tube (inside the heating furnace), and the temperature of the heating furnace was controlled by an SKW-400 four-way programmable temperature controller (Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences). The feed gas consisted of CH_4, O_2 and N_2, and the flow rate of each of the three gases was controlled by a mass flow meter. The catalyst performance was evaluated as follows: CH_4, O_2 and N_2 were co-fed at a certain temperature and atmospheric pressure (N_2 was the equilibrium gas); the catalyst was filled in the middle thermostatic zone part of the reaction tube with 1 mL of catalyst (20-40 mesh) and filled with 1 mL of porcelain ring (20-40 mesh) for dilution to prevent catalyst deactivation due to massive exotherm during the reaction. The catalyst was activated in an oxygen atmosphere at a certain flow rate before the reaction at a temperature higher than the reaction temperature and lower than the roasting temperature, and then lowered to the reaction operating temperature and introduced into the raw material gas for evaluation of the experimental reaction tail gas was measured using a flow meter and the reaction products were analyzed off-line by gas chromatography.

BET characterization

Figure S2 shows the N_2 adsorption and desorption isotherms of Mo-Sn catalysts with different Mo/Sn ratios. Among them, MoO_3 and Mo2Sn1 catalysts do not show hysteresis rings, indicating that these two catalysts have larger pores or appear to be stacked; Mo1Sn1 catalyst has a nearly triangular H_2 hysteresis ring near the medium pressure region, which belongs to type IV isotherm with ink bottle-type pore structure; Mo1Sn5 and SnO_2 catalysts belong to type II isotherm, but this catalyst is a catalyst with a pore structure of flaky particles The Mo1Sn3 catalyst is a lamellar or ink bottle pore structure between the H_3 hysteresis ring of the type II isotherm and the H_2 hysteresis ring of the type IV isotherm.

Table S1 shows the weave properties of Mo-Sn catalysts with different Mo/Sn ratios. Among them, the Mo1Sn3 catalyst with the best OCM reaction performance had the largest specific surface area. Compared with the Mo1Sn3 catalyst, the other Mo-Sn catalysts with different Mo/Sn ratios have relatively small specific surface area and pore volume, and relatively larger pore size, especially the MoO_3 and Mo2Sn1 catalysts have positive small specific surface area and almost zero pore volume. The results indicate that, compared with the other Mo-Sn catalysts with different Mo/Sn ratios, the Mo1Sn3 catalyst has The larger specific surface area allows more active centers to be distributed on the catalyst surface, increasing the contact probability between the reactants and the active sites, which is one of the reasons for the improved catalytic performance of OCM.

XPS characterization

Figure S3 shows the XPS-O1 spectra of Mo-Sn catalysts with different Mo/Sn ratios, in which the peaks with binding energy around 532.5 eV are attributed to hydroxyl oxygen O_{OH}, the peaks with binding energy around 531.6 eV are considered as O_{ad} *of the* catalysts, and the peaks with binding energy around 530.5 eV are considered as O_{lat} *of the* catalysts.

Element analysis

The mass content of C, H element in the catalyst was obtained using German vario EL (Ⅲ) multifunctional automatic analyzer.

TEM characterization

Morphology of the sample was measured by a JEOL JEM-2100 transmission electron microscope (TEM) operated at 200 keV. The sample powder was dispersed in ethanol by ultrasonic for 20 min. Then, the suspension was dropped onto a carbon coated copper TEM grid (200 mesh) and dried in air before measurement.

CH_4-TPSR-MS test experiment

In order to investigate the role of adsorbed oxygen in depth, CH_4-TPSR-MS tests were designed on the Mo1Sn3 catalyst with the best catalytic performance without the participation of O_2 in the reaction conditions. Before conducting the TPSR test, the catalyst was treated with two different conditions, the first one being: the catalyst was first treated with a constant temperature of 400 °C in an Ar atmosphere to remove the chemisorbed oxygen from the catalyst surface (chemisorbed oxygen can be completely desorbed at around 300 °C), so that the methane undergoes a programmed ramp-up reaction in the presence of catalyst lattice oxygen species only, labeled as Mo1Sn3 (Ar-Ar-Ar-CH_4). The second one is: after a constant temperature of 400 °C to remove the chemisorbed oxygen from the catalyst surface in Ar atmosphere, the catalyst is treated with O_2 adsorption and programmed to warm up after Ar purging, labeled as Mo1Sn3 (Ar-O_2-Ar-CH_4). Its CH_4-TPSR-MS test results are shown in Figure 4.

Comparing the CH_4-TPSR-MS spectra of the product CO_2 under the two different treatment conditions, it was found (Figure 4) that the Mo1Sn3(Ar-O_2-Ar-CH_4) catalyst with O_2 adsorption treatment produced significantly more CO_2 than the Mo1Sn3(Ar-Ar-Ar-CH_4) without O_2 treatment when the reaction temperature was before 650 °C, and when the reaction temperature was lower than 650 °C, the adsorbed oxygen species tended to lead to the deep oxidation of methane to CO_x, and the onset temperature of CO_2 formation was lower for the Mo1Sn3(Ar-O_2-Ar-CH_4) catalyst than for the Mo1Sn3(Ar-Ar-Ar-CH_4) catalyst, indicating that the presence of adsorbed oxygen species was more likely to activate methane; comparing the two different treatment conditions for the product CH_3CH_3 CH_4-TPSR-MS spectra of the products under the two different treatment conditions revealed that the onset temperature of C2 hydrocarbon formation was lower for the Mo1Sn3(Ar-Ar-Ar-CH_4) catalyst than for the Mo1Sn3(Ar-O_2-Ar-CH_4) catalyst, and the Mo1Sn3(Ar-Ar-Ar-CH_4) catalyst formed more total C2 hydrocarbons than the Mo1Sn3(Ar-O_2-Ar-CH_4) catalysts; indicating that the adsorbed oxygen species are not favorable for the formation of the target product C2 hydrocarbons. Thus, the adsorbed oxygen species are prone to activate methane but lead to deep oxidation of reactants and products to CO_x.

Study of the three-component action of MoO_x-Na_2SnO_3-SnO_2

From the previous work, it is known that the Mo1Sn3 catalyst synthesized by hydrothermal method has a better performance with 8.6% methane conversion, 98.1% C2 hydrocarbon selectivity and further reduction of CO_x selectivity to 0.8% at 650 ℃. However, in addition to the effect of suitable lattice oxygen species and medium to strong basic sites, the XRD characterization in Fig. 1 shows that there are two variables of Mo-Sn catalysts with different Mo/Sn ratios synthesized by hydrothermal method, which are different Mo species contents and different Na_2SnO_3/SnO_2 ratios.

The reasons for being able to effectively inhibit CO_x formation may include the role of different Mo species content, the role of different Na_2SnO_3/SnO_2 ratios, or the synergistic effect of all three. elemental content of the XPS surface of the best performing Mo1Sn3 catalyst was calculated to yield a Mo/Sn of 1/35 on the catalyst surface. therefore, experiments were designed to prepare and evaluate the performance of catalysts with different Mo/Sn ratios (Mo/Sn ratios around 1/35) by controlling a single variable Na_2SnO_3/SnO_2 of 1, using the ball milling method, as shown in Table S2. A series of different Na_2SnO_3/SnO_2 catalysts were further prepared by the ball milling method under the control of a single variable Mo content of 0 and their OCM reaction performance was investigated, as shown in TableS3.

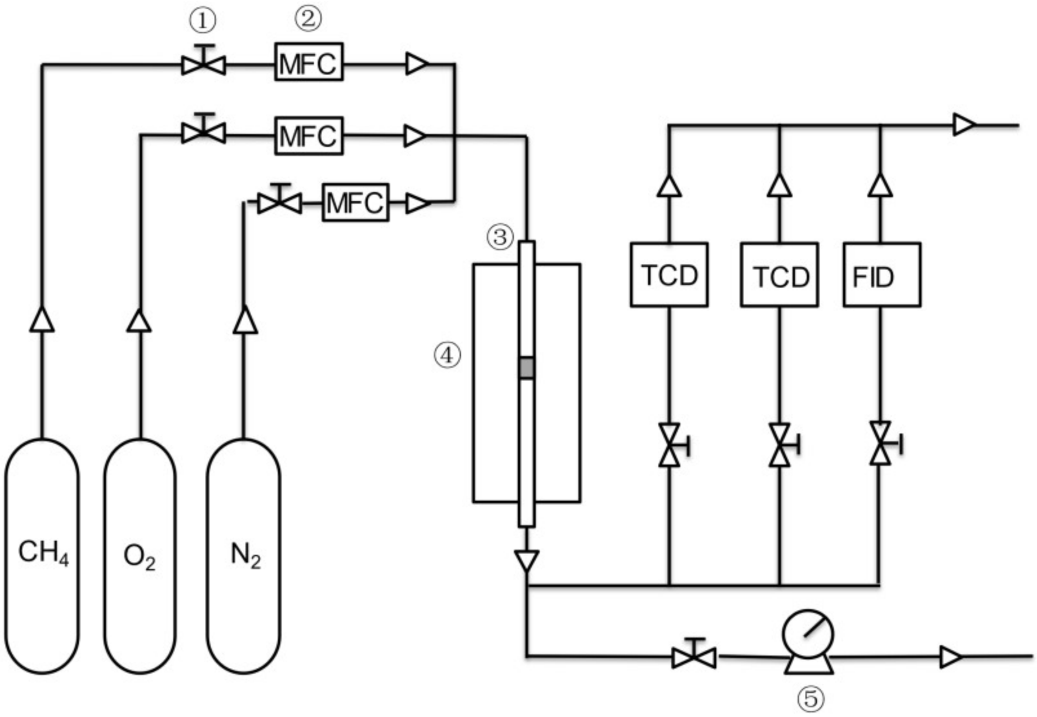
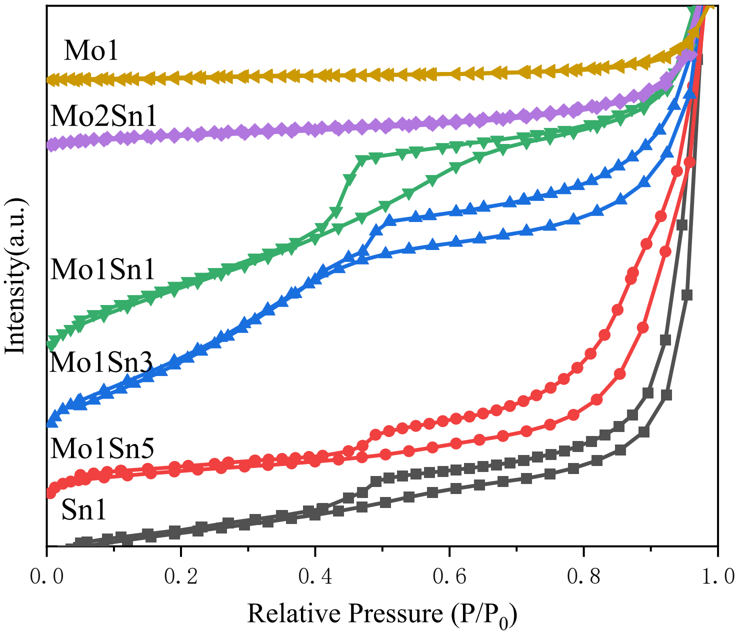


Fig. S1 Schematic diagram of the apparatus of fixed bed for CH_4 oxidation
① valve ②mass-flow controller ③reactor ④heating furnace ⑤flow-meter



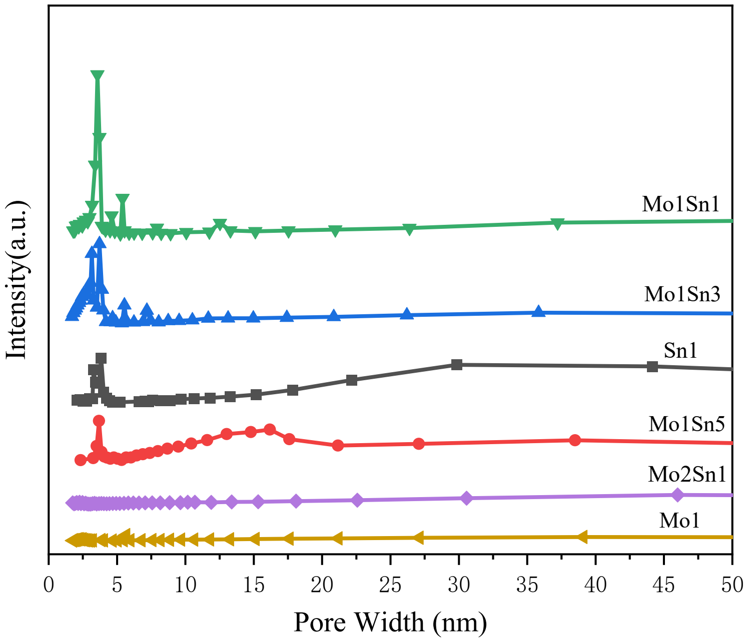


Fig. S2 N_2 adsorption-desorption isotherms and pore distribution of different Mo-Sn catalysts

Table S1 Physical properties of different Mo-Sn catalysts

Catalyst	BET specific surface area (m^2-g^{-1})	Pore volume (cm^3-g^{-1})	Average pore diameter (nm)
Sn1	10.17	0.0304	19.00
Mo1Sn5	8.82	0.0300	15.75
Mo1Sn3	27.57	0.0323	5.19
Mo1Sn1	23.94	0.0276	6.56
Mo2Sn1	4.51	0.0069	17.21
Mo1	3.58	0.0007	11.62

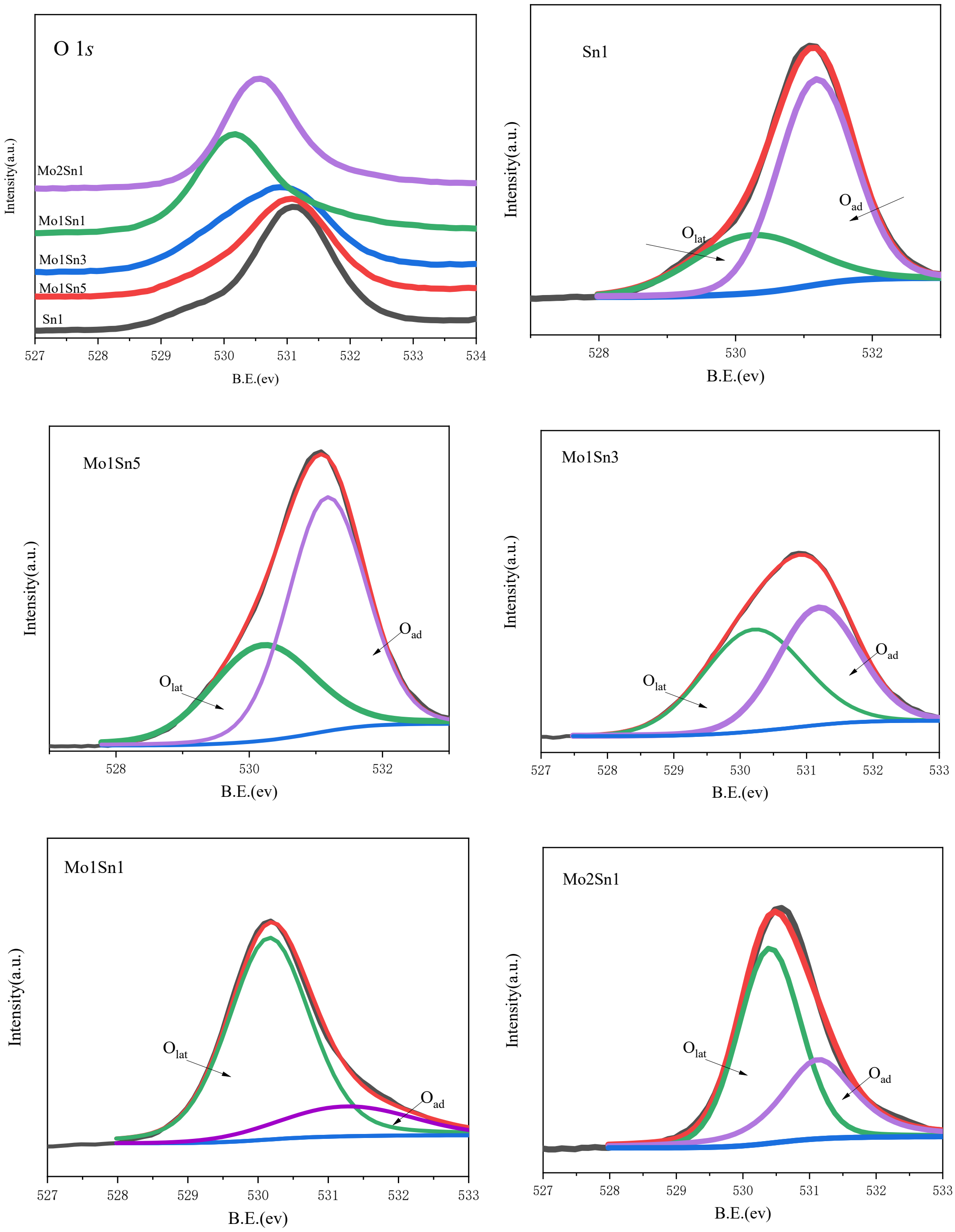


Fig. S3 The XPS-O1s spectrums of different Mo-Sn catalysts

Table S2 The XPS-O1s spectra analysis of different Mo-Sn catalysts

Catalyst	Olat	Oad	Olat/Ototal	Oad/Ototal
Mo2Sn1	530.40	531.13	0.63	0.37
Mo1Sn1	530.16	531.25	0.82	0.18
Mo1Sn3	530.20	531.18	0.52	0.48
Mo1Sn5	530.20	531.17	0.33	0.67
Sn1	530.23	531.18	0.29	0.71

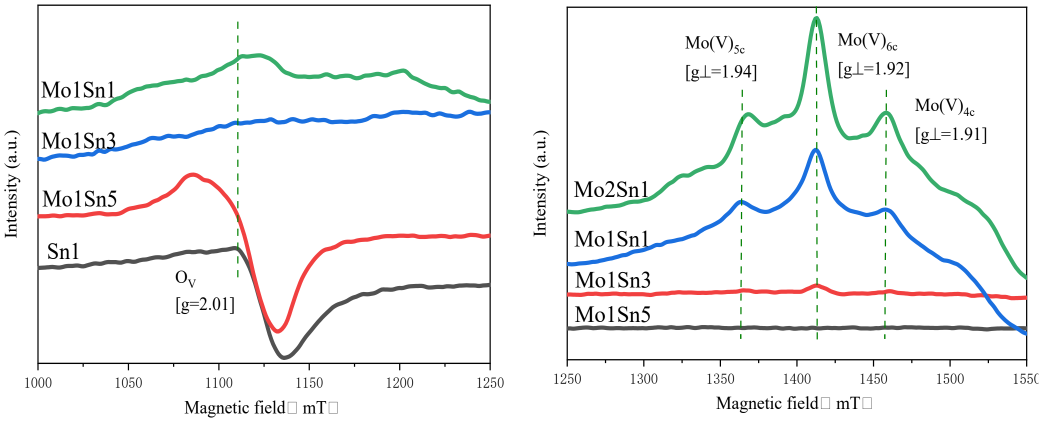


Fig. S4 Low-temperature ESR spectra of different Mo-Sn catalysts

Table S3 OCM reaction results on Mo-Sn catalyst prepared by ball milling method

Catalyst	CH_4 Conversion (%)	Cmol - Selectivity (%)							
		C_2H_6	C_2H_4	C_3H_8	C_3H_6	CO	CO_2	C2	CO_x
MoO_3	0	/							
Mo1Sn3	4.3	87.7	2.5	0.4	0	0	0.4	90.2	0.4
Mo1Sn35	5.9	81.1	2.2	0.3	0	0	6.4	83.3	6.4
Mo1Sn50	6.1	78.3	1.8	0.2	0	0	9.7	80.1	9.7
Mo1Sn100	7.2	29.4	0.8	0	0	0	69.8	30.2	69.8
SnO_2	7.7	25.3	0.8	0.1	0	0	73.8	26.1	73.8

Reaction conditions: atmospheric pressure, T_R=650 °C, CH_4:O_2:N_2=14:1:15, GHSV=10800 h^{-1}, C2: C_2H_6 and C_2H_4.

Table S4 OCM reaction results on Na_2SnO_3/SnO_2 catalyst prepared by ball milling method

Catalyst (Na_2SnO_3/SnO_2)	CH_4 Conversion (%)	Cmol - Selectivity (%)							
		C_2H_6	C_2H_4	C_3H_8	C_3H_6	CO	CO_2	C2	CO_x
1/0	7.7	25.3	0.8	0.1	0	0	73.8	26.1	73.8
10/1	9.7	32.1	1.8	0.2	0	0	65.9	33.9	65.9
5/1	9.8	38.5	2.7	0.3	0	0	58.5	41.2	58.5
3/1	10.3	28.8	2.5	0.2	0	0	68.5	31.3	68.5
1/5	9.0	33.2	2.1	0.3	0	0	64.4	35.3	64.4
0/1	9.0	7.7	0.7	0	0	26.6	65.0	8.4	91.6

Reaction conditions: atmospheric pressure, T_R=650 °C, $CH_4:O_2:N_2$=14:1:15, GHSV=10800 h^{-1}, C2: C_2H_6 and C_2H_4.

Table S5 The results of element analysis for Mo1Sn3 catalysts

Catalyst	C (%)	H (%)
[a] Mo1Sn3 Fresh	0.331	0.849
[b] Mo1Sn3 2.5 h	1.116	1.229
[c] Mo1Sn3 30 h	1.466	0.618

a- Fresh catalyst; b- the catalyst after reaction for 2.5 h; c- the catalyst after reaction for 30 h.

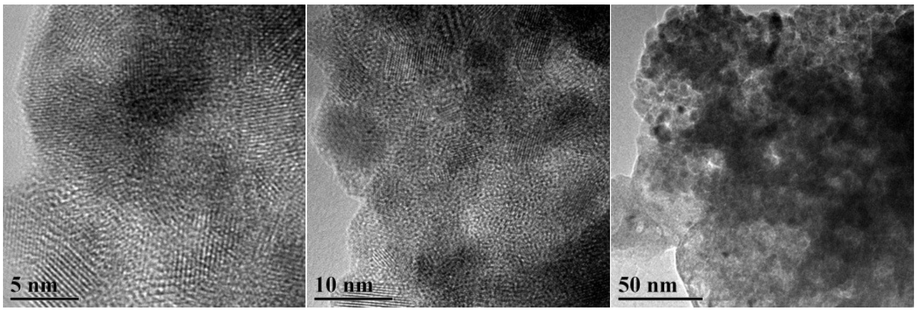


Fig. S5 The TEM images of the Mo1Sn3 catalyst.

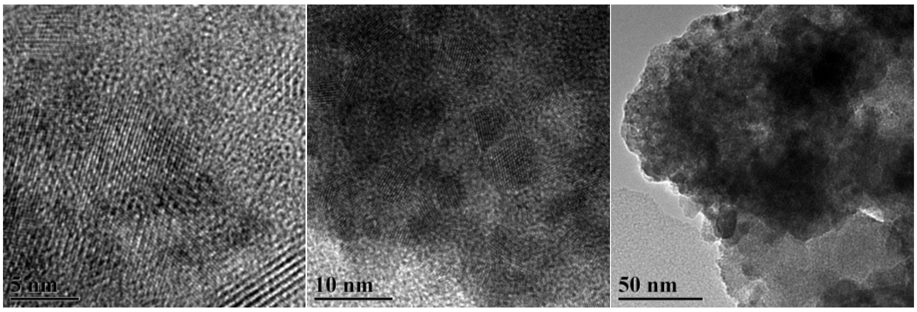


Fig. S6 The TEM images of the Mo1Sn3 catalyst after reaction for 2.5 h.

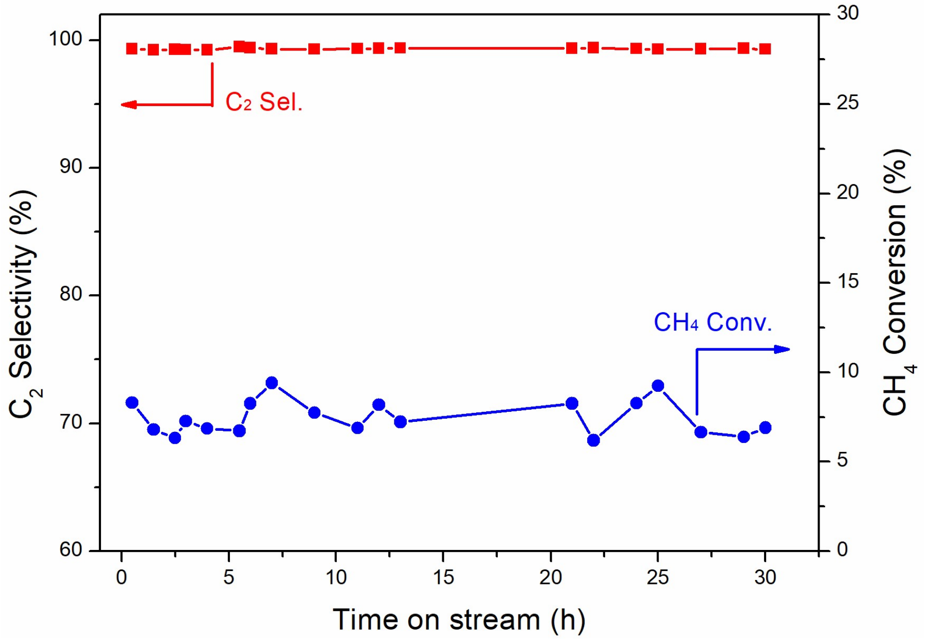


Fig. S7 Catalytic performance of OCM reaction over Mo1Sn3 catalyst during 30 h on stream under the conditions of 650 °C, atmospheric pressure, CH_4:O_2:N_2=14:1:15, GHSV=10800 h^{-1}.

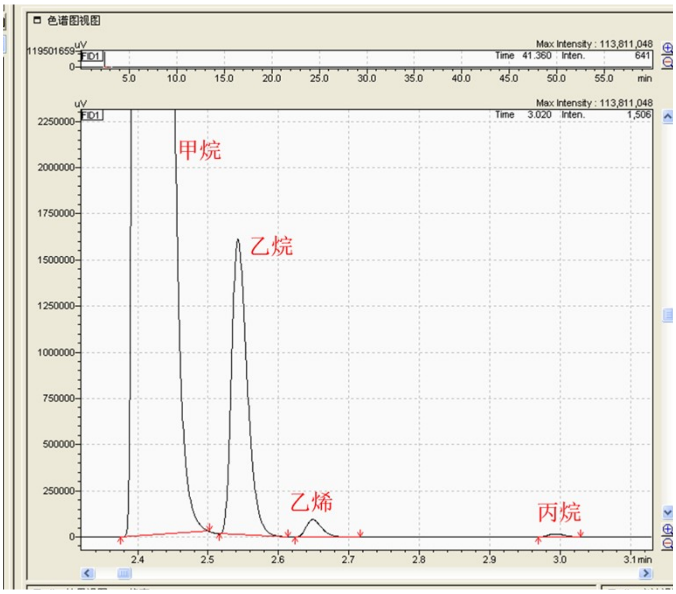


Fig. S8 The original GC spectrum of OCM reaction results over Mo1Sn3 catalyst under the conditions of 650 °C, atmospheric pressure, CH_4:O_2:N_2=14:1:15, GHSV=10800 h^{-1}.