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Article

Surface coupling of methyl radicals for efficient low-temperature oxidative coupling of methane

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ABSTRACT

Selective coupling of methyl radicals to produce C₂ species (C₂H₄ and C₂H₆) is a key challenge for oxidative coupling of methane (OCM). In traditional OCM reaction systems, homogeneous transformation of methyl radicals in O₂-containing gases are uncontrollable, resulting in limited C₂ selectivity and yield. Herein, we demonstrate that methyl radicals generated by La₂O₃ at low reaction temperature can selectively couple on the surface of 5 wt% Na₂WO₄/SiO₂. The controllable surface coupling against overoxidation barely changes the activity of La₂O₃ but boosts the C₂ selectivity by three times and achieves a C₂ yield as high as 10.9% at bed temperature of only 570 °C. Structure-property studies suggest that Na₂WO₄ nanoclusters are the active sites for methyl radical coupling. The strong CH₃· affinity of these sites can even endow some methane combustion catalysts with OCM activity. The findings of the surface coupling of methyl radicals open a new direction to develop OCM catalyst. The bifunctional OCM catalyst system, which composes of a methane activation center and a CH₃· coupling center, may deliver promising OCM performance at reaction temperatures below the ignition temperature of C₂H₆ and C₂H₄ (~600 °C) and is therefore more controllable, safer, and certainly more attractive as an actual process.

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1. Introduction

Methane, the main constituent of the abundant natural gas and shale gas, is widely accepted as a promising alternative

resource to crude oil [1]. It is of both scientific and strong economic interest to develop processes that would convert methane to higher valued chemicals such as methanol [2], light olefins [3–5] and aromatics [6,7]. Currently, the industrial-scale

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conversion of methane adopts an indirect route which involves the intermediate manufacture of syngas and subsequent conversion to chemicals or fuels via Fischer-Tropsch or hydrogenation processes [8–12]. Although considerable progress has been achieved recently in directly converting syngas into olefins [8–10], the indirect route is energy and capital intensive which limits its widely applications, specifically in the utilization of remote and inconveniently located natural gas fields [13]. As an alternative, increasing attention has been paid to the direct conversion of methane, especially the oxidative coupling of methane (OCM) to C_2 hydrocarbons which involves only a small external energy input [14–17].

Since the pioneering work of Keller and Bhasin in the early 1980s [18], hundreds of catalytic materials composed of 68 elements have been investigated for OCM reaction [19]. Due to the high binding energy of CH_3-H bond (435 kJ mol^{-1}), oxidative coupling of methane generally proceeds at high temperatures ($\geq 700\text{ }^\circ\text{C}$) [20]. Because the high temperature process requires special materials for construction, high energy consumption and great capital input, the minimum criteria of C_2 yield for industrial application is 30% [21]. It is recognized that at high temperatures OCM follows a heterogeneous-homogeneous mechanism, which consists of a heterogeneous activation of methane at the surface of catalysts to generate methyl radicals ($CH_3\cdot$) and a subsequent homogeneous coupling of methyl radicals in the gas phase to produce C_2 species (C_2H_6 and C_2H_4) [22,23]. Because high temperature favors the desorption of methyl radicals into gas phase, the role of the traditional OCM catalysts is limited mainly to the generation of methyl radicals [24]. The uncontrollable homogeneous reaction of methyl radicals in the presence of O_2 thermodynamically favors the overoxidation to CO_2 , resulting in an upper bound of ca. 25%–28% for C_2 yield which is economically infeasible for industrial application [25]. In terms of conventional fixed-bed reactor, the possible exceeding of this limit can be obtained only if catalyst plays significant role not only in heterogeneous generation of methyl radicals but also in their subsequent transformations [14]. Unfortunately, there is no such catalyst that has been ever reported to have activity of coupling methyl radicals.

In this work, we demonstrate 5 wt% Na_2WO_4/SiO_2 as the first heterogeneous coupling catalyst for OCM reaction and systematically investigate its structure-property relationship. The activation of methane takes place over a La_2O_3 surface at relative low temperatures [26], which allows the coupling of methyl radicals proceed in a controlled manner on the surface of Na_2WO_4/SiO_2 catalyst. Such bifunctional OCM reaction system successfully separates methane activation and C–C coupling into two different active components. As a result, a C_2 yield up to 10.9% was achieved at bed temperature of $570\text{ }^\circ\text{C}$, which to the best of knowledge is the highest C_2 yield ever reported at such a low reaction temperature (Table S1). Low temperature is desirable for the commercialization of OCM [27]. It not only cuts down the energy loss and the cost of reactors, but also overcomes the limited industrial experience with catalytic processes at high temperatures [28].

2. Experimental

2.1. Synthesis of La_2O_3 nanorods

La_2O_3 nanorods were synthesized according to the literature procedure [26]. 5 mL of 25% $NH_3\cdot H_2O$ was added dropwise to 250 mL of $La(NO_3)_3$ (0.4 mol L^{-1}) solution to form a white slurry. After the slurry was vigorously stirred for 12 h, the white precipitate was obtained through centrifugation, and washed twice with water and ethanol. The precipitate was re-dispersed in 125 mL of distilled water, and then transferred into Teflon-lined autoclave to perform a hydrothermal treatment at $105\text{ }^\circ\text{C}$ for 24 h. The precipitate was separated by centrifugation, washed with ethanol for several times, and dried in vacuum oven at $25\text{ }^\circ\text{C}$ overnight. Finally, the sample was calcined at $800\text{ }^\circ\text{C}$ for 5 h before use.

2.2. Synthesis of Na_2WO_4/SiO_2

Na_2WO_4/SiO_2 was prepared by a typical impregnation method [29]. Taking 5 wt% Na_2WO_4/SiO_2 for an example, 1.00 g of silica gel was added into aqueous solution of $Na_2WO_4\cdot 2H_2O$ (0.05 g). The resulting slurry was stirred continuously at $75\text{ }^\circ\text{C}$ until dry and subsequently dried at $85\text{ }^\circ\text{C}$ overnight. Finally, the sample was calcined at $850\text{ }^\circ\text{C}$ for 5 h before use.

2.3. Characterization

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired on a Cs-corrected Titan Chemi-STEM operating at an accelerating voltage of 200 kV. Wide-angle X-ray diffraction (WXR) patterns were recorded on a Rigaku Ultimate IV with $Cu\ K\alpha$ radiation at 40 mA and 40 kV. Synchrotron-based VUV photoionization mass spectrometry (SVUV-PIMS) study was carried out at the combustion beamline of the National Synchrotron Radiation Laboratory at Hefei, China. The X-ray absorption fine structure (XAFS) spectra at W L3-edge of the samples were measured at the XAFCA beamline of Singapore Synchrotron Light Source.

2.4. Catalytic measurement

The catalytic tests were performed in a quartz fix-bed reactor tube with an inner diameter of 8 mm under atmospheric pressure. The catalyst bed was placed on quartz wool plug in the constant-temperature zone of furnace. A thermocouple well with an outer diameter of 6 mm was inserted into the quartz reactor to monitor the bed temperature and to further reduce the free space volume. CH_4 , O_2 , and N_2 in a ratio of 3:1:2.6 were cofed into the reactor through mass flow controllers. The total flow rate was 66 mL min^{-1} . The products were analyzed by an online gas chromatography equipped with an FID detector and a TCD detector. Molecular sieve 5A column Porapak N column were coupled with TCD to separate CO_2 , CH_4 , O_2 and N_2 while aluminum trioxide capillary column was coupled with FID to separate CO_2 and hydrocarbon products (CH_4 , C_2H_4 , and C_2H_6).

For testing La_2O_3 or $\text{Na}_2\text{WO}_4/\text{SiO}_2$ alone, 100 mg of catalyst was loaded. For mixed or layered experiments, 100 mg of La_2O_3 and 100 mg of $\text{Na}_2\text{WO}_4/\text{SiO}_2$ were loaded.

2.5. In situ SVUV-PIMS measurements

In situ SVUV-PIMS measurements of methyl radicals and other products were performed on the mass spectrometry beamline (BL04B) and the combustion beamline (BL03U) of the National Synchrotron Radiation Laboratory (Hefei, China) [30]. For the test of single component catalyst, 100 mg of the catalyst (10–20 mesh) was loaded. For the test of La_2O_3 -5NaWSi composite catalyst, 100 mg of La_2O_3 and 100 mg of 5wt% $\text{Na}_2\text{WO}_4/\text{SiO}_2$ (10–20 mesh) were premixed before loaded into the reactor. 75% CH_4 and 25% O_2 were cofed into the reactor with a total flow rate of 40 mL min^{-1} . The OCM reaction was operated at a total pressure of 2 Torr. After the reactions reached steady state at desired temperatures, the composition of the effluent gas was analyzed by the online SVUV-PIMS. A homemade time-of-flight mass spectrometer (TOF-MS) was used to detect the ion signals, which were amplified with a VT120C preamplifier (EG&G, ORTEC, Oak Ridge, TN) and recorded by a P7888-2 multiscaler (FAST Comtec, Germany).

2.6. DFT calculations

DFT calculations were carried out using a plane-wave-based program, Castep [31,32]. The Perdew-Burke-Ernzerhof functional was used together with the ultrasoft-core potentials [33,34]. The basis set cutoff energy was set to 330 and 370 eV for geometry optimization and post-energy evaluation. Explicitly considered electrons are H: $1s^1$, C: $2s^2 2p^2$, O: $2s^2 2p^4$, Na: $2s^2 2p^6 3s^1$, Si: $3s^2 3p^2$, and W: $5s^2 5p^6 5d^4 6s^2$.

$(\text{Na}_2\text{WO}_4)_4$ unit cell was used for the slab model without SiO_2 support. Lattice constants are $a = b = 6.458 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. The vacuum region was taken in the c -direction and set to $c = 50 \text{ \AA}$. For the models supported by SiO_2 , WO_4 tetrahedron was coupled to cristobalite (111) surface through a single W–O–Si bond. The models with different WO_4/SiO_2 ratio (density) are used to simulate different sized Na_2WO_4 . Two types of unit cells are employed. “Small model” ($\text{Si}_{12}\text{O}_{28}\text{H}_6\text{Na}_2(\text{WO}_3)_2$) corresponds to high coverage of WO_4 , and the lattice constants were $a = 7.040 \text{ \AA}$, $b = 8.534 \text{ \AA}$, $c = 30 \text{ \AA}$ (including vacuum region), $\alpha = \beta = 90^\circ$, and $\gamma = 114.3^\circ$. “Large model” ($\text{Si}_{48}\text{O}_{112}\text{H}_{30}\text{Na}_2(\text{WO}_3)_2$ and $\text{Si}_{48}\text{O}_{112}\text{H}_{26}\text{Na}_6(\text{WO}_3)_6$) corresponding to low coverage of WO_4 was built by four times (2×2) extension of small model in a - and b -directions ($a = 14.080 \text{ \AA}$, $b = 17.069 \text{ \AA}$). All the atomic coordinates were optimized, and the lattice constants were fixed to the original values. H atoms were used to encapsulate the terminal O atoms in SiO_2 unit. Chemical composition seems changing irregular among models. This is due to the formation mechanism of W–O–Si bonding. The bond is formed between O atom of WO_4 unit and HO in $\text{Si}(\text{OH})_4$ unit. Formation one W–O–Si bond reduces one OH fragment.

3. Results and discussion

3.1. OCM involving surface coupling of methyl radicals

La_2O_3 nanorod (Figs. S1 and S2), a well-known low-temperature OCM catalyst [26,35,36], was selected as the active component for methane activation. The composite catalyst, denoted as La_2O_3 -5NaWSi, was prepared by physically mixing La_2O_3 nanorods with 5 wt% $\text{Na}_2\text{WO}_4/\text{SiO}_2$ (denoted as 5NaWSi) in a mass ratio of 1. As shown in Fig. 1(b) and Table S2, La_2O_3 nanorods exhibit considerable CH_4 conversion at bed temperature (the temperature is bed temperature if not otherwise specified) of ca. 570 °C with limited selectivity to C_2 hydrocarbons, which is well consistent with the literature results [26]. Interestingly, upon combination with 5NaWSi, the C_2 selectivity is boosted from 14.37% to 33.93% with the methane conversion remaining almost unchanged ($\sim 31.3\%$). La_2O_3 -5NaWSi composite achieves a single-pass C_2 yield of 10.9% at ca. 570 °C, which to the best of our knowledge is the lowest bed temperature ever reported for 10% yield of C_2 (Table S1). In addition, La_2O_3 -5NaWSi composite also delivers very good stability in OCM reaction (Fig. 1(c)) during a 50-hour test at 570 °C and a gas hourly space velocity (GHSV) of 20000 mL $\text{h}^{-1} \text{ g}_{\text{cat}}^{-1}$. For both La_2O_3 and La_2O_3 -5NaWSi, the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ molar ratios increase with increasing temperature (Table S2), likely due to the favored ethane oxidative dehydrogenation to ethylene at high temperatures. Besides, at high C_2 selectivity, more O_2 can be used for oxidative dehydrogenation of ethane to ethylene. As a result, higher $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratios are obtained. To further verify the effect of 5NaWSi, we investigated the catalytic performances of La_2O_3 nanoparticles ($\text{La}_2\text{O}_3\text{NP}$) and $\text{La}_2\text{O}_3\text{NP}$ -5NaWSi. As shown in Table S3, although the catalytic performances of $\text{La}_2\text{O}_3\text{NP}$ and $\text{La}_2\text{O}_3\text{NP}$ -5NaWSi are not as good as those of La_2O_3 nanorods and La_2O_3 -5NaWSi (Table S2), the introduction of 5NaWSi indeed improves the C_2 selectivity and yield of $\text{La}_2\text{O}_3\text{NP}$. Besides, the improvement induced by 5NaWSi also applies to other CH_4 -to- O_2 ratios (Fig. S3).

It is important to highlight that although 5NaWSi can significantly enhance the C_2 selectivity and yield of La_2O_3 , itself is inert for OCM reaction at temperatures below 750 °C (Fig. 1(a) and Table S2). These results lead us to a hypothesis that 5NaWSi might drive the transformation of methyl radicals from gas phase to catalyst surface and selectively couple them into C_2 hydrocarbons. To test this possibility, we employed a validated synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) to detect the intermediate and products in the gas phase [37]. As shown in Fig. S4, when methane and oxygen were fed into the reactor containing La_2O_3 at 600 °C, a signal of mass-to-charge ratio (m/z) = 15 appeared at a photon energy $h\nu = 11 \text{ eV}$. Considering the ionization energy and m/z ratio, this species can be unambiguously identified to be methyl radicals ($\text{CH}_3^\bullet$). In comparison, no methyl radical was detected by SVUV-PIMS for the catalytic reaction with 5NaWSi as catalyst or without catalyst. These observations provide direct and solid experimental evidence for the formation of methyl radicals during the catalytic OCM reaction and clearly prove that the detected methyl radicals are gener-

Fig. 1. Catalytic performances of La₂O₃-5NaWSi and reference catalysts in OCM reaction. (a) C₂ yield as a function of reaction temperature; (b) CH₄ conversion, C₂ selectivity and C₂ yield at 571 ± 6 °C; (c) A stability test of La₂O₃-5NaWSi at 570 °C, CH₄:O₂:N₂ = 3:1:2.6, total gas flow rate 66 mL min⁻¹; (d) Integrated SVUV-PIMS peak intensity of gas-phase methyl radicals, ethylene and CO₂ during OCM reaction catalyzed by various catalysts at 600 °C; (e) C₂ yield as a function of reaction temperature over various catalysts (GHSV 20,000 mL h⁻¹ g_{cat}⁻¹); (f) Schematic illustration of reaction process of OCM over La₂O₃-5NaWSi.

ated by the activation of methane on the La₂O₃ catalyst surface. In addition to CH₃·, signals assigned to C₂H₄ ($m/z = 28$) could also be detected at a photon energy $h\nu = 11$ eV while signals assigned to CO₂ ($m/z = 44$) could be detected at a photon energy $h\nu = 14.5$ eV. Integrating the peak intensity of these signals ensures us to quantitatively compare the concentration of each species. As can be seen from Fig. 1(d), upon combination with 5NaWSi, the gas-phase CH₃· generated on La₂O₃ reduce, accompanied by an increasing production of C₂H₄. These results contradict to the traditional gas-phase coupling mechanism which features proportional C₂ products with the gas-phase concentration of CH₃· [37,38] and therefore lead to a conclusion that CH₃· radicals generated by La₂O₃ have been coupled on the surface of Na₂WO₄/SiO₂ to enhance the C₂ hydrocarbon production. It is noteworthy that the increase of C₂ yield upon combination with 5NaWSi is more significant at low temperatures (typically, < 650 °C) than at high temperatures (Fig. 1(a)). This is likely due to the facilitated desorption of methyl radicals into gas phase at high temperature which limits the surface coupling of CH₃· over 5NaWSi. Similarly, increasing GHSV leads to a short residence time of CH₃· on the catalyst surface. As a result, the improvement of C₂ selectivity induced by 5NaWSi is more significant at low GHSV (Fig. S5).

To further verify the transportation of CH₃· from La₂O₃ to 5NaWSi, we investigated the influence of integration manner of active components on the catalytic performance. The use of a dual-bed configuration with 5NaWSi downstream from La₂O₃ (La₂O₃||5NaWSi) provides similar CH₄ conversion but obviously increased C₂ selectivity and yield as compared with La₂O₃

(Table S2 and Fig. 1(e)), pointing to the contribution of surface coupling of CH₃· over 5NaWSi. Further increasing the proximity of La₂O₃ and 5NaWSi by a mixed-one-bed facilitates the transportation of CH₃· from La₂O₃ to 5NaWSi and therefore significantly improves the selective surface coupling of CH₃· over 5NaWSi. As a result, La₂O₃-5NaWSi (mixed one-bed) shows much higher C₂ yield than La₂O₃||5NaWSi (dual-bed). Besides, the C₂ yield could be tuned by varying the relative mass ratio of La₂O₃-to-5NaWSi (Fig. S6). Interestingly, the C₂ selectivity and yield exhibit volcano-type dependence on the La₂O₃-to-5NaWSi ratio with the optimal value achieved at 1:1, suggesting there is a balance between the generation and coupling of CH₃·. This result further supports the above hypothesis that the composite catalyst is bifunctional, and that the reaction involves intermediate transport [9]. On the other hand, once we introduce an intermediate quartz-sand bed to inhibit the transportation of CH₃· from La₂O₃ to 5NaWSi, no improvement in C₂ yield was observed over La₂O₃||Quartz||5NaWSi (layer-bed) as compared with La₂O₃||Quartz (Fig. 1(e)). These results clearly prove that the increase of C₂ yield results from the transportation of CH₃· radicals from La₂O₃ to 5NaWSi and their subsequent coupling on the surface of 5NaWSi (Fig. 1(f)). Interestingly, the transportation and surface coupling of CH₃· can even take place at a temperature as low as 500 °C if we replace La₂O₃ by Sm₂O₃, another excellent low-temperature OCM catalyst [39]. As shown in Fig. S7, the C₂ selectivity increases from 6.6% for Sm₂O₃ to 11.8% for Sm₂O₃||5NaWSi (dual-bed) at 500 °C. Moreover, due to the thermodynamic driving force [8], the coupling with 5NaWSi also slightly accelerates the CH₄ conver-

sion over Sm_2O_3 . As a result, a C_2 yield of 2.3% is achieved at 500 °C.

3.2. Structure and property of coupling site

To better understand the origin of coupling property of 5NaWSi catalyst, a series of reference samples were synthesized by the same method. The difference in C_2 yield (ΔC_2 yield) between composite catalysts and single La_2O_3 catalyst was employed as a descriptor for coupling property. As shown in Fig. 2(a) and Table S4, 5NaWSi is the only one that can improve the C_2 yield of La_2O_3 (positive ΔC_2 yield). The distinguished catalytic performance between 5NaWSi and $\text{Na}_2\text{CO}_3/\text{SiO}_2$ indicates W is a key component. Substituting Na^+ by K^+ or NH_4^+ disables the coupling of methyl radicals, suggesting Na is a critical component. Mixing La_2O_3 with $\text{Na}_2\text{WO}_4/\text{Al}_2\text{O}_3$ decreases the C_2 yield, implying SiO_2 support is also very important. Pioneer works of $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts demonstrated that the presence of Na induces the low-temperature transformation of amorphous silica into cristobalite [29,40,41]. This

result also applies to pure $\text{Na}_2\text{WO}_4/\text{SiO}_2$. As shown in Fig. 2(b), an obvious transformation of amorphous SiO_2 into cristobalite is identified in all Na^+ -containing samples ($\text{Na}_2\text{CO}_3/\text{SiO}_2$, 2NaWSi, 5NaWSi and 10NaWSi) by XRD. Once Na^+ is replaced by NH_4^+ , the transformation is inhibited, accompanied by the formation of large WO_3 crystalline. Data from literatures [42,43] indicate that there is a strong interaction between cristobalite and Na_2WO_4 . For $\text{Na}_2\text{WO}_4/\text{SiO}_2$ with different loading amounts, the interaction is different. As shown in Fig. 2(c), the configuration of all W $\text{L}_{3\text{-edge}}$ XANES spectra is similar to that of Na_2WO_4 , suggesting that all W species have a tetrahedral structure. The white line intensity, however, increases along with the decrease of Na_2WO_4 loading, indicating improved $2p_{3/2}$ to $5d$ transition probability [44] which likely results from the increased interaction between Na_2WO_4 and cristobalite. The strongest interaction between 2NaWSi and cristobalite is also evidenced by a new coordination peak in R space at about 3.4 Å (Fig. 2(d)).

The different interaction between cristobalite and Na_2WO_4 eventually changes the dispersion of Na_2WO_4 . The bright spots

Fig. 2. The structure and property of 5NaWSi. (a) The difference in C_2 yield (ΔC_2 yield) between composite catalysts and pure La_2O_3 at 570 °C; (b) XRD patterns for various catalysts; (c) The W $\text{L}_{3\text{-edge}}$ XANES spectra; (d) EXAFS-derived Fourier transforms of $\text{Na}_2\text{WO}_4/\text{SiO}_2$ with different mass loading; Catalytic performance of deep oxidation of (e) ethane and (f) ethylene ($\text{C}_2\text{H}_x/\text{O}_2/\text{N}_2 = 1:6:5$, $x = 4$ or 6 , gas flow rate 66 mL min^{-1}). The red dash lines indicate the ignition temperature at 50% conversion. HAADF-STEM images of (g) 2NaWSi, (h) 5NaWSi and (i) 10NaWSi.

shown in Fig. 2(g) suggests Na_2WO_4 is highly dispersed in 2NaWSi with sub-1 nm size (most are atomically dispersed), likely due to the strong interaction between Na_2WO_4 and cristobalite. As the loading of Na_2WO_4 increases to 5 wt%, the weakened interaction leads to the formation of tungstate clusters, which are identified by HAADF-STEM (Fig. 2(h)). Further increasing the loading to 10 wt%, Na_2WO_4 mainly exist as large particles (> 50 nm, Fig. 2(i)). Correlating these results with catalytic performances, a size effect is identified. 2 nm sized Na_2WO_4 cluster in 5NaWSi is the optimal catalyst for the coupling of CH_3 radicals.

To rationalize the experimental observations, we further performed DFT calculations to determine the coupling property of different sized Na_2WO_4 on cristobalite. The structure models were constructed according to the literature reports [29,43,45]. Tetrahedral $[\text{WO}_4]$ is grafted onto silica surface by a single W–O–Si bond (removing OH from $-\text{Si}-\text{OH}$), left three terminal O atoms for the interactions with CH_3 . The terminal O atoms in cristobalite (111) surface are saturated by hydrogen atoms. Na is introduced to maintain the neutrality. The models with different WO_4/SiO_2 ratio are used to simulate different sized Na_2WO_4 (Fig. S8). $(\text{WO}_3)_2$, $(\text{WO}_3)_6$, and $(\text{WO}_3)_8$ abbreviate $\text{Si}_{48}\text{O}_{112}\text{H}_{30}\text{Na}_2(\text{WO}_3)_2$, $\text{Si}_{48}\text{O}_{112}\text{H}_{26}\text{Na}_6(\text{WO}_3)_6$, and $[\text{Si}_{12}\text{O}_{28}\text{H}_6\text{Na}_2(\text{WO}_3)_2]_4$, respectively.

The coupling of methyl radicals on catalyst surface consists of three steps, i.e. CH_3 adsorption as the reactant, CH_3 coupling as the transition state, and C_2H_6 formation as the product. Theoretically, the adsorbed CH_3 can either react with another adsorbed CH_3 via a L-H mechanism or react with a gas-phase CH_3 via an E-R mechanism. Figs. 3(a,b) show the comparison between these two mechanisms over $(\text{WO}_3)_8$. Interestingly, the activation energy (E_a) for E-R mechanism is significantly lower than that for L-H mechanism, indicating the E-R model is thermodynamically more favorable. Similar results are also observed on other models. Therefore, we adopt the E-R mechanism in the following discussion. Interestingly, all the models exhibit considerable amount of adsorption energy (E_{ads}) of CH_3 radicals, which enable them to capture CH_3 radicals from gas phase (Figs. 3(c,d)). According to the literature [38], overoxidation reactions (initiated by $\text{CH}_3 + \text{O}_2$ reaction) in the gas phase make the major contribution to the formation of CO and CO_2 in the OCM reaction. Reducing the concentration of CH_3 in gas phase by $\text{Na}_2\text{WO}_4/\text{SiO}_2$ (Fig. 1(d)) might therefore significantly reduce the possibility of CH_3 oxidation in gas phase and improve the C_2 selectivity. On the other hand, according to the classic Sabatier principle [46], a too strong binding with reactants is also not ideal. It leads to large activation energy, excessive blocking of surface sites, and therefore low catalytic activity. As shown in Figs. 3(c) and S9, the binding between CH_3 radicals and $\text{Na}_2\text{WO}_4(111)$ surface (E_{ads} as high as 399 kJ mol^{-1}) is too strong to allow the coupling of CH_3 radicals. The activation energy (E_a) is as high as 356 kJ mol^{-1} . Grafting WO_4 on cristobalite (111) surface remarkably reduces the activation energy by destabilize the reactant. Among the models with different density of WO_4 , E_a decreases from 132, 142, to 56 kJ mol^{-1} for $(\text{WO}_3)_2$, $(\text{WO}_3)_6$, and $(\text{WO}_3)_8$ and then increases to 356 kJ mol^{-1} for $\text{Na}_2\text{WO}_4(111)$ surface. This trend on one hand sug-

gests the coupling property of Na_2WO_4 is strongly affected by the SiO_2 support, on the other hand, confirms the experimental observation that moderate concentration of Na_2WO_4 unit per SiO_2 area is optimal (Fig. 2(a)). It is important to highlight that the relative energy of TS in E-R process over $(\text{WO}_3)_8$ is negative (lower than gas phase CH_3). This result suggests that the bounded CH_3 prefers to react with another gas-phase CH_3 to form C_2H_6 rather than to desorb into the gas phase. Theoretically, if the whole reaction (adsorption and coupling) proceeds continuously and does not cool down at local minimum (LM), the TS with negative relative energy is not a significant reaction barrier [47]. It endows $(\text{WO}_3)_8$ with CH_3 coupling property. As the CH_3 concentration on the surface of $(\text{WO}_3)_8$ is very high (due to the strong CH_3 affinity), the conversion of CH_3 adsorbed on $(\text{WO}_3)_8$ will make major contribution to the C_2 productivity. In specific, when CH_3 radicals are adsorbed on Na_2WO_4 , the total electronic energy (that is, DFT calculated energy) decreases. The residual energy is converted to thermal energy such as molecular vibration. If molecular vibration is localized at the coupling site, and not dispersed. Such a vibrational energy can be reused to climb up the succeeding reaction barrier. The real situation is likely between the two ideal situations. (1) The vibrational energy can be completely (100%) reused, or (2) not be reused (0%) at all (i.e., adsorbed methyl radicals are cooled down in each LM). We don't know how

Fig. 3. DFT calculations for CH_3 coupling over various catalyst models. (a) The energy profiles; (b) the corresponding configurations for CH_3 coupling over $(\text{WO}_3)_8$ via L-H mechanism and E-R mechanisms; (c) The energy profiles for CH_3 coupling; (d) the configurations for CH_3 adsorption over various catalyst models. Other configurations are shown in Fig. S9. (e) The energy profile and (f) the corresponding configurations for the β -H elimination of W–O– CH_3 over $(\text{WO}_3)_8$. Yellow: Si, red: O, blue: W, purple: Na, gray: C, and white: H. $(\text{WO}_3)_2$, $(\text{WO}_3)_6$, and $(\text{WO}_3)_8$ abbreviate $\text{Si}_{48}\text{O}_{112}\text{H}_{30}\text{Na}_2(\text{WO}_3)_2$, $\text{Si}_{48}\text{O}_{112}\text{H}_{26}\text{Na}_6(\text{WO}_3)_6$, and $[\text{Si}_{12}\text{O}_{28}\text{H}_6\text{Na}_2(\text{WO}_3)_2]_4$, respectively.

much degree the thermal energy is maintained and can be re-used, but the agreement with experimental results justifies this interpretation. Besides, we also calculated the β -H elimination of W-O-CH₃ to produce formaldehyde (an important intermediate to generate CO_x) over (WO₃)₈. As shown in Figs. 3(e,f), the β -H elimination of W-O-CH₃ has a large reaction barrier (194 kJ mol⁻¹) and an endothermic reaction energy of 164 kJ mol⁻¹. It is therefore thermodynamically unfavorable as compared to its coupling with gas-phase CH₃ radical to produce C₂H₆. Taking all these results together, the major role of 5NaWSi is not to improve the efficiency of CH₃• coupling, but change the relative CH₃• concentration on surface and in gas-phase, which make surface coupling a major pathway for C₂ production and minimize undesired gas-phase side reactions (e.g. CH₃• + O₂ reaction).

In principle, a good coupling catalyst requires not only the ability to combine two radicals to produce ethane, but also to inhibit the over-oxidation of ethane and ethylene. To test this hypothesis, we conducted the oxidation of ethane and ethylene on various catalysts. As shown in Figs. 2(e,f), against the good catalytic performance of La₂O₃, 5NaWSi is inert for ethylene and ethane oxidation at temperatures below 700 °C. The *T*₅₀ (ignition temperature, a temperature at 50% conversion of ethane/ethylene) of 5NaWSi is even higher than the blank control. More importantly, by mixing with 5NaWSi, the oxidation of ethylene and ethane on La₂O₃ is significantly suppressed. Recently, advanced reactor concepts including chemical looping [48,49] and membrane reactor [50,51] have showed improved C₂ production performance for OCM reaction. In these reactors, the gas phase deep oxidations were minimized by separating gas phase oxygen from carbon-containing stream. Similar concept also applies to this study. The selective coupling of methyl radicals on the catalyst surface spatially separates methyl radicals and C₂ species from gas phase oxygen and therefore significantly suppresses the overoxidation. It is important to highlight that La₂O₃-5NaWSi can effectively catalyze OCM at a temperature (10.9% C₂ yield at 570 °C) below the corresponding ignition temperature of C₂H₄ and C₂H₆ (~600 °C, Figs. 2(e,f)). It is therefore more controllable, possibly safer, and certainly more attractive as an actual process.

3.3. 5NaWSi coupled with other metal oxides

Based on the knowledge of surface coupling over 5NaWSi, we then investigated the OCM performance of transition metal oxides-5NaWSi composite catalysts. As shown in Fig. 4, Cr₂O₃, MnO₂, Fe₂O₃ and Co₃O₄ are typical methane-combustion catalysts which have very limited catalytic activity towards OCM at 755 °C. Surprisingly, when these metal oxides are physically mixed with 5NaWSi, the C₂ yield is improved by 5–14 times though the CH₄ conversion remains unchanged. Specifically, Fe₂O₃-5NaWSi shows a C₂ yield of 0.92 whereas Fe₂O₃ shows zero C₂ yield. Co₃O₄-5NaWSi achieves a C₂ yield of 3.73, which is ca. 14 times as high as that of pure Co₃O₄. The constant CH₄ conversion and unprecedentedly improved C₂ yield suggest that 5NaWSi can even couple CH₃• radicals generated by methane-combustion catalysts to produce C₂ species. The en-

Fig. 4. Catalytic performance of transition metal oxides and their mixture with 5NaWSi at 755 ± 15 °C for OCM reaction. CH₄:O₂:N₂ = 3:1:2.6, total gas flow rate 66 mL min⁻¹.

dowed OCM activity by 5NaWSi catalyst further confirms its important role in methyl radical transformation, which suggests a new strategy to explore efficient OCM catalyst operated at low reaction temperature.

4. Conclusions

In summary, we have developed a bifunctional OCM catalyst system that can activate CH₄ and selectively couple CH₃• radicals over two separated catalysts. A C₂ yield as high as 10.9% is achieved at a temperature (570 °C) below the ignition temperature of C₂H₄ and C₂H₆. Similar to the bifunctional catalysis in Mo catalyzed methane dehydroaromatization [6,52,53], a tight control over both of the functional components is also of great importance to the OCM reaction. Future work will focus on the exploration of advanced catalysts that can either generate CH₃• radicals more efficiently or couple CH₃• radicals more selectively on the surface.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Surface coupling of methyl radicals for efficient low-temperature oxidative coupling of methane

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Methyl radicals generated by La_2O_3 can selectively couple on the surface of 5 wt% $\text{Na}_2\text{WO}_4/\text{SiO}_2$. The controllable surface coupling against overoxidation barely changes the activity of La_2O_3 but boosts the C_2 selectivity by three times and achieves a C_2 yield as high as 10.9% at bed temperature of only 570 °C.

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表面偶联甲基自由基实现低温高效甲烷氧化偶联

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摘要: 天然气作为一种低碳清洁能源, 其储量大, 价格低, 被认为是最有前途的石油替代资源之一。而以天然气的主要成分——甲烷为原料来生产高价值化学品被认为是石化工业中实现天然气取代石油为原料新化工路线的技术基础, 具有极为可观的社会经济价值。目前甲烷的化学利用主要采用间接转化法, 即先从甲烷制合成气, 再由合成气制备各种化工原料和油品。但该路线流程复杂, 能耗大, 生产成本低及投资大, 具有明显的局限性, 这促使着人们不断探索能量效率更高的甲烷直接转化技术。

甲烷氧化偶联(OCM)是最重要的甲烷直接转化技术之一。自1982首次报道以来, 人们开发了1000多种OCM催化剂, 涉及元素超过68种, 但C₂烃类(乙烷和乙烯)的收率普遍低于30%, 尚未实现工业化。传统研究认为, OCM反应遵循“多相-均相”催化反应机理, 甲烷在催化剂表面活化产生甲基自由基后, 在气相中进行偶联生成乙烷和乙烯等产物。由于高温下甲基自由基很容易脱附到气相, 传统的OCM催化剂一般只在甲基自由基的产生这一步发挥作用。而随后在气相中发生的甲基自由基均相反应并不受催化剂控制, 在热力学驱动下, 会倾向于深度氧化生成CO₂等副产物, 因此OCM反应中C₂的收率上限为25%–28%。理论上来说, 只有当催化剂能够在甲基自由基偶联这一步发挥作用时, C₂物种的收率才可能打破上限, 但目前尚未有催化剂实现甲基自由基可控表面偶联。

本文提出并证实5wt% Na₂WO₄/SiO₂(5NaWSi)具有催化甲基自由基表面偶联的能力。在低温下, 5NaWSi本身对于OCM没有催化活性, 但是它的加入能够显著提高La₂O₃催化剂的C₂选择性, 进而提高C₂收率, 使其在570 °C的低温下即可达到10.9%的C₂收率。在La₂O₃和5NaWSi之间加入一层甲基自由基淬灭剂——石英砂, 这种提升作用随即消失, 表明甲基自由基在5NaWSi上的表面偶联可能是C₂选择性和收率提升的主要原因。本文进一步采用同步辐射光电质谱技术原位检测了反应过程中的自由基中间体, 结果发现, La₂O₃表面产生的甲基自由基确实可以在5NaWSi表面进行偶联, 进而提高C₂的选择性和收率。通过对5NaWSi的组成和结构进行分析, 发现5NaWSi中的Na₂WO₄纳米团簇可能是甲基自由基偶联的活性位点, 该位点不仅具有很强的甲基自由基吸附能力, 为甲基自由基表面偶联提供机会, 同时不会深度氧化C₂物种, 有效地提高了C₂选择性。以此为基础建立理论模型, 我们通过DFT计算对甲基自由基在5NaWSi表面的偶联机制进行了研究。结果表明, 5NaWSi对甲基自由基具有很强的吸附能力, 而吸附后的甲基自由基更倾向于偶联生成C₂产物, 而不是β-H消除生成HCHO等副产物, 表明5NaWSi确实是很好的甲基自由基表面偶联催化剂。甲基自由基表面偶联的证实为OCM催化剂的开发开辟了新方向。从双功能催化剂设计的角度出发, 将OCM反应分解成甲烷活化和甲基自由基偶联这两个部分, 并分别针对这两个部分来筛选和优化催化剂, 将有望突破C₂收率上限, 进而推进OCM的工业化进程。

关键词: 甲烷氧化偶联; 双功能催化; 甲基自由基; 表面偶联; La₂O₃; Na₂WO₄/SiO₂

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