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Article

Chemical looping partial oxidation over FeWO_x/SiO₂ catalysts

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ARTICLE INFO

Article history:

Received 30 September 2019

Accepted 6 November 2019

Published 5 July 2020

Keywords:

Fe-W alloy

Methane activation

Lattice oxygen diffusion

Phase segregation

Ion oxidation rate

ABSTRACT

This paper describes the design of a FeWO_x-based oxygen carrier for the chemical partial oxidation of methane (CLPOM). Thermodynamic screening and kinetic analyses both forecast the FeWO_x-based oxygen carrier as a promising candidate for the production of syngas. The total methane conversion and syngas yield can be dramatically increased with this catalyst compared to the case with the unmodified WO₃/SiO₂, thereby enabling CLPOM with 62% methane conversion, 93% CO gas-phase selectivity, 94% H₂ selectivity, and a 2.4 H₂/CO ratio. The catalyst has the advantages of high availability of lattice oxygen to oxidize carbonaceous intermediates in time, together with the formation of an Fe-W alloy to promote the surface reaction. Consequently, it demonstrates excellent catalytic performance with no catalyst deactivation at 900 °C and 1 atm. The excellent structural stability plays an essential role in CLPOM. As revealed via XPS and ICP, the phase segregation has not been observed due to the strong interaction between Fe and W, which resulted in the formation of the Fe-W alloy during the reduction processes and the match between the ion oxidation rates of the Fe and W ions in the oxidation stage. The results provide fundamental information on the reaction mechanism of FeWO_x/SiO₂, and present it as a promising candidate for CLPOM.

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1. Introduction

The extraction of shale gas, which is composed mostly of methane, has increased drastically in recent years, and its growth is predicted to be stable over the coming decades [1,2]. Methane is cheap and abundant on Earth, and its conversion and utilization into valuable chemicals and liquid fuels via syngas, an intermediate mixture of carbon monoxide and H₂, have attracted great attention [3,4].

Steam reforming of methane (SRM), autothermal reforming (ATR), and partial oxidation of methane (POM) are three rep-

resentative pathways to methane reforming [5].

The SRM reaction, as shown in Equation (1), is endothermic and requires a complicated reactor design with external heating to sustain the operation temperature. Both POM and ATR in Equation (2) are exothermic, and oxygen, which is expensive, is used to partially oxidize methane. The explosive issue arises because of the mixing of methane and oxygen in the POM process as well [6].

To overcome the above problems, chemical looping partial

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This work was supported by the National Key R&D Program of China (2016YFB0600901), the National Natural Science Foundation of China (51761145012, 21525626, U1663224), and the Program of Introducing Talents of Discipline to Universities (B06006). We also acknowledge the financial support from China National Petroleum Corporation for this research.

DOI: 10.1016/S1872-2067(20)63544-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 7, July 2020

oxidation of methane (CLPOM) has been developed. This approach includes two main steps [7]:

In the first step, CH_4 is partially oxidized by the lattice oxygen from the metal oxide, and the metal oxide is reduced. In the second step, the consumed lattice oxygen in the metal oxide is fully recovered by oxidization, for example, in air. CH_4 and air are injected separately; consequently, an explosion can be avoided and the air separation process can be eliminated.

Since metal oxides play a crucial role in the CLPOM, substantial research efforts have been devoted to the design and development of efficient oxygen carriers, which have high oxygen-carrying capacities, high selectivities toward syngas, and excellent redox reactivities [8]. Metal oxides such as nickel oxides [9–11], copper oxides [12], ferrite oxides [8,13–15], and tungsten oxides [16] have been applied in CLPOM and have shown great potential.

Ni-based oxygen carriers have been widely used and found to be one of the most promising candidates, due to their substantially high reactivity and the subsequently appreciable catalytic reforming activity of metal Ni [17]. Nevertheless, the reduced Ni dramatically promotes methane decomposition, which leads to serious carbon deposition and deactivation of the redox catalysts [18–20]. Fe-based oxides are much cheaper than nickel oxides and nontoxic; thus, they have been studied extensively as alternative oxygen carriers [21–24]. However, owing to their lower reactivity toward methane than nickel oxides and the severe sintering under high reaction temperatures, a support material such as Al_2O_3 and SiO_2 is required, which overcomes these drawbacks by increasing the dispersion of oxygen carriers and minimizing the crystalline size of the iron oxides [5,25–28]. Cerium oxide is another widely used redox catalyst, which exhibits excellent performance due to the high lattice oxygen transfer rate in the POM toward syngas [29]. However, due to its limited oxygen-carrying capacity, it is not suitable for large scale applications [30–32].

There are several challenges associated with selecting a suitable oxygen carrier for CLPOM. On the one hand, carbon deposition, which is caused by slow lattice oxygen activation and diffusion kinetics, leads to the deactivation of the oxygen carrier. Several strategies have been proposed for overcoming this problem. Muller *et al.* [33] provided insights into the reduction pathways of the Cu-promoted and unpromoted oxygen carriers and the different oxidation states of iron oxides using *in situ* XANES. They proposed that metallic Cu, which readily segregates from the spinel structure under reduction conditions, can promote the reduction rate of $\text{FeO} \rightarrow \text{Fe}^0$, indicating the availability of more lattice oxygen. Li *et al.* [13] investigated the underlying mechanisms of POM over $\text{Fe}_2\text{O}_3/\text{LSF}$ redox catalyst, indicating that the mixed conductive support enables facile O^{2-} transport to and from the iron oxide to participate in the surface redox reactions. DFT calculations revealed the role of oxygen vacancy concentrations in modulating the oxygen diffusion rate. Specifically, a high oxygen vacancy concentration can lead to a low oxygen diffusion energy barrier and oxidize the carbon deposition in time [34].

On the other hand, the structure changes of oxygen carriers, which occurred in the redox process, not only affected the catalytic performance but also had a significant effect on the structural stability [35,36]. Thus, the minimization of the structural change of the oxygen carrier during the redox processes is another challenge. To overcome the high attrition rate of oxygen carriers, which is caused by morphological changes, Fan *et al.* [37] confined active metal oxide in an Al-based skeleton to obtain a low-cost oxygen carrier and achieved exceptional chemical and physical stability over 3000 redox cycles under high pressure and temperature conditions. Xiao *et al.* [38] studied a CoFeAlO_x spinel solution as an oxygen carrier for CLHP, indicating that the control of the exsolution process could lead to the formation of confined particles in the interface, which would significantly improve the redox performance under high a temperature condition. Wu *et al.* [35] utilized SrTiO_3 as a model perovskite to investigate the impact from the reconstruction of surface and subsurface monolayers on methane oxidation and presented a direct connection between the composition of the subsurface layers and the performance of the catalyst for CH_4 activation.

Tungsten oxides, due to their highly tunable composition and physical stability, have attracted extensive attention in various applications, including chemical looping reforming technologies. Metallic W shows the highest anti-sintering potential among all the reported metals due to its high melting point (above 3400 °C). Based on thermodynamic analysis (Fig. 1), tungsten oxides show high syngas selectivity over 90%, which is appropriate for the CLPOM process. W-based oxygen carriers can provide great resistance to sintering while allowing sufficient redox cycles. However, the major drawbacks of W-based oxygen carriers are their low reducibility and methane reactivity, which limit their application in the CLPOM process.

In this work, a novel FeWO_x -based oxygen carrier material was designed and synthesized to overcome the above-described challenges. Thermodynamic screening and CH_4 -pulse were used to investigate the redox performance of $\text{FeWO}_x/\text{SiO}_2$. CH_4 temperature-programmed reduction (CH_4 -TPR) and H_2 temperature-programmed reduction (H_2 -TPR) were performed to study the association between methane activation and the lattice oxygen diffusion. X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP) analyses were carried out to explore the phase stability of the FeWO_x -based oxygen carrier material. The CLPOM reaction mechanism of $\text{FeWO}_x/\text{SiO}_2$ is specifically discussed in combination with experimental characterizations.

2. Experimental

2.1. Preparation of catalysts

$\text{Fe}_y\text{WO}_x/\text{SiO}_2$ oxygen carrier particles were prepared by impregnation. The loading of WO_3 was fixed to 40 wt% for all the samples used in this study. The atomic ratios between Fe and W were tuned to be 0, 0.5, 1, and 2 by varying the amount of Fe, and the resulting samples were denoted as $y = 0, 0.5, 1$, and 2,

Fig. 1. Thermodynamic analysis of methane partial oxidation reactions and selected redox materials.

respectively. The required amounts of ammonium metatungstate (99.0%, J&K Chemicals Co., Ltd.) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.0%, Aladdin biological technology Co., Ltd.) were dissolved in a moderate amount of deionized water. Thereafter, the mixed solution was added dropwise to SiO_2 (99.8%, Aladdin biological technology Co., Ltd.) under continuous vibration, which was followed by ultrasonication for 1 h. Subsequently, the resultant mixture was dried at 80 °C for 24 h, ground to powder, and calcined at 900 °C for 4 h at a heating rate of 5 °C/min in ambient air. $\text{Fe}_2\text{O}_3/\text{SiO}_2$ with the same amount of Fe as $\text{FeWO}_x/\text{SiO}_2$ was prepared by a similar procedure as described above with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and SiO_2 . FeWO_x was prepared by sol-gel with the same Fe:W atom ratio as that of $\text{FeWO}_x/\text{SiO}_2$. Stoichiometry quantities of the starting materials were dissolved in deionized water under continuous stirring to form a homogeneous solution. Gelation precursors were achieved by maintaining the stirred solution at 80 °C to induce evaporation of the solvents. The resulting gelation precursors were exposed to heat of 120 °C for 12 h to evolve the organic components. Afterward, the obtained powder was calcined at 900 °C for 4 h to form the FeWO_x . The Fe-W/ SiO_2 alloy was synthesized by the reduction of $\text{FeWO}_x/\text{SiO}_2$ under H_2 flow at 900 °C for 4 h.

2.2. Catalytic activity tests

The gas-solid reaction of CLPOM was carried out under atmospheric pressure in a fixed-bed reactor system. Typically, 1.2 g of the oxygen carrier with particle sizes between 20 and 40 mesh was mixed with 1 mL of inert silica; afterward, the mixture was placed in a quartz tube with an internal diameter of 8 mm. Successive CLPOM cycle tests were conducted at 900 °C. The oxygen carrier was reduced using methane (10% CH_4/N_2 , 60 mL/min) for 8 min. Thereafter, it was oxidized using air (21% O_2/N_2 , 54 mL/min) for 15 min for regeneration. Between reduction and reoxidation, a N_2 purge (54 mL/min) was inserted to prevent the mixing of CH_4 and air during the two half steps for 15 min. Such a $\text{CH}_4\text{-N}_2\text{-air-N}_2$ process was denoted as one CH_4/air redox cycle. The stability test was carried out over

$\text{Fe}_2\text{O}_3/\text{SiO}_2$ and $\text{Fe}_y\text{WO}_x/\text{SiO}_2$ ($y = 0, 0.5, 1, 2$) for 10 continuous redox cycles. A total of 50 continuous CH_4/air cycles were performed for $\text{FeWO}_x/\text{SiO}_2$ to further evaluate its stability. The outlet gases including CH_4 , H_2 , CO , CO_2 , and N_2 were collected after condensation by a cold trap and analyzed using a gas chromatograph (GC2060, Shanghai Ruimin Instrument) on-line. The gas chromatograph was equipped with a thermal conductivity detector and two columns, including a TDX-01 column, followed by a 5A molecular sieve column. Blank experiments using inert silica with the same void volume were performed under identical conditions and demonstrated a low contribution of the gas-phase reaction (1.7% methane conversion of the gas-phase reaction) in the current work.

The CH_4 conversion (5), the selectivities of H_2 (6), CO_2 (7), CO (8), and the H_2/CO (9) ratio during the reduction step are calculated by the following equations:

$$X_{\text{CH}_4} = (f_{\text{CH}_4,\text{in}} - f_{\text{CH}_4,\text{out}}) / f_{\text{CH}_4,\text{in}} \quad (5)$$

$$S_{\text{H}_2} = f_{\text{H}_2,\text{out}} / 2(f_{\text{CH}_4,\text{in}} - f_{\text{CH}_4,\text{out}}) \quad (6)$$

$$S_{\text{CO}_2} = f_{\text{CO}_2,\text{out}} / (f_{\text{CH}_4,\text{in}} - f_{\text{CH}_4,\text{out}}) \quad (7)$$

$$S_{\text{CO}} = f_{\text{CO},\text{out}} / (f_{\text{CH}_4,\text{in}} - f_{\text{CH}_4,\text{out}}) \quad (8)$$

$$S_{\text{CO-gas phase}} = f_{\text{CO},\text{out}} / (f_{\text{CO},\text{out}} + f_{\text{CO}_2,\text{out}}) \quad (9)$$

$$R_{\text{H}_2/\text{CO}} = f_{\text{H}_2,\text{out}} / f_{\text{CO},\text{out}} \quad (10)$$

2.3. Characterization

The textural properties of the catalysts were measured through N_2 adsorption-desorption at -196 °C using a Micromeritics Tristar 3000 analyzer. All the samples were pre-treated at 300 °C for 4 h before the tests. The specific surface areas were calculated based on the N_2 isotherms and the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method.

The elemental components of the catalysts were evaluated by ICP optical emission spectroscopy (ICP-OES) (VISTA-MPX, Varian) at a high frequency emission power of 1.5 kW and a plasma airflow of 15.0 L/min ($\lambda_{\text{Ni}} = 216.56$ nm, $\lambda_{\text{Al}} = 396.16$ nm, $\lambda_{\text{Cu}} = 324.76$ nm, $\lambda_{\text{Co}} = 238.89$ nm, $\lambda_{\text{Pt}} = 265.95$ nm). The samples were dissolved in a mixed solution consisting of hydrochloric acid, nitric acid, and hydrofluoric acid.

X-ray powder diffraction (XRD) patterns were recorded with 2θ values between 20° and 80° . A Rigaku C/max-2500 diffractometer with graphite filtered Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$) was used, and the scan speed was $8^\circ/\text{min}$.

H₂-TPR was measured on a Micromeritics Autochem II 2920 instrument. Typically, 50 mg of the catalysts was pretreated under Ar stream at 300°C for 1 h and thereafter cooled to 100°C . H₂ (10 vol%) in Ar (30 mL/min) was introduced to analyze the samples, and the temperature was ramped from 100 to 900°C at $10^\circ\text{C}/\text{min}$.

The Raman spectra were recorded with a 532 nm Ar ion laser beam using a Renishaw via reflex Raman spectrometer under ambient condition. The samples were dried at 100°C for 2 h before measurements.

The UV-vis spectra in the range of 200–800 nm were recorded for FeWO_x/SiO₂ and WO₃/SiO₂ with BaSO₄ as a blank reference on a Shimadzu UV-2550 spectrophotometer.

Transmission electron microscopy (TEM) was carried out on a JEM-2100F transmission electron microscope under a working voltage of 100 kV, which was equipped with an energy-dispersive X-ray spectroscopy (EDS) detector for elemental analysis.

XPS analysis was performed with a PerkinElmer PHI 1600 ESCA system with Mg K_α 1253.6 eV radiation as the excitation source. The samples were mounted on the specimen holder using a double-sided adhesive tape, and the spectra were collected in steps of 0.15 eV.

CH₄-TPR was carried out on a Micromeritics Autochem II 2920 instrument, which was equipped with a Hiden QIC-20 mass spectrometer. A portion (100 mg) of the oxygen carrier was pretreated at 300°C for 1 h and subsequently cooled to 100°C under an Ar stream. The analysis was carried out from 100 to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a mixture of 10 vol% CH₄ in Ar (30 mL/min). CO₂, CO, H₂, H₂O, and CH₄ were detected instantaneously by mass spectrometry (MS).

CH₄ pulse reactions were performed using the same apparatus as that of CH₄-TPR. A portion (100 mg) of the sample was tested at 300°C for 1 h under flowing pure Ar gas (30 mL/min), and afterward, the temperature was increased to 900°C at a rate of $10^\circ\text{C}/\text{min}$. Subsequently, the pulses of CH₄ (0.5082 mL) were admitted to the reactor, and the gas was analyzed using an online mass spectrometer after each pulse.

The temperature-programmed oxidation (TPO) profiles of the spent catalysts were obtained using the same procedures as described for TPR. Typically, the samples were pretreated at 300°C for 0.5 h under an Ar stream and subsequently cooled to 100°C . Finally, the TPO analysis was performed at a ramping rate of $10^\circ\text{C}/\text{min}$ from 100°C to the required temperature under a 10 mol% O₂-He stream (50 mL/min), and the MS signal was recorded continuously.

3. Results and discussion

3.1. Thermodynamic screening

From the point of view of thermodynamics, the redox material can be considered as an oxygen “source” in the methane

reduction step and an oxygen “sink” in the air oxidation step [39]. Thus, a high equilibrium oxygen partial pressure (PO₂) for a redox pair such as Fe₂O₃/Fe₃O₄ can guarantee a complete conversion of methane but lead to the overoxidation of syngas to CO₂ and H₂O. In contrast, the redox pairs with relatively low PO₂ values such as WO₂/W will result in low methane conversion. Partial oxidation, conversely, monotonically appreciates at intermediate PO₂ values. The blue area in Fig. 1 represents the high-performance region for syngas production, where the methane conversion is near 100% and the equilibrium yield of syngas is over 90%. The relationship among the Gibbs free energy of the reaction, equilibrium syngas yield, and equilibrium PO₂ at various temperatures is illustrated in Fig. 1. As can be seen, the equilibrium PO₂ of the WO₂/WO₃ redox pair deviates from the ideal (high performance) region for CLPOM. Unlike monometallic oxides, mixed metal oxides could offer more superior thermodynamic properties toward partial oxidation. When the reaction temperature is set as high as 900°C , it can be seen from Fig. 1, that FeWO₄ can achieve a high methane conversion, and also provide excellent syngas selectivity (details in Supporting Information). This theoretical analysis justifies the selection of iron and tungsten composite oxides as oxygen carriers for the CLPOM process, and their performance can be verified in the following experimental studies.

3.2. Textural properties of fresh oxygen carriers

Fig. 2(A) shows the XRD patterns of the calcined Fe₂O₃/SiO₂ and Fe_yWO_x/SiO₂ ($y = 0, 0.5, 1, 2$). A stoichiometric rhombohedral Fe₂O₃ phase (JCPDS89-8104) appeared in the diffraction patterns of Fe₂O₃/SiO₂. For WO₃/SiO₂, the peaks in the diffractogram are attributed to the monoclinic WO₃ phase (JCPDS20-1324). The Fe₂WO_x/SiO₂ sample displays reflection only from Fe₂WO₆ (JCPDS70-2024). The results suggest that due to the strong interaction between Fe cations and WO₃, the generation of Fe₂WO₆ under the calcination condition is considerably easy.

Fig. 2(B) shows the XRD patterns of Fe₂O₃/SiO₂ and Fe_yWO_x/SiO₂ ($y = 0, 0.5, 1, 2$) after one redox cycle. They are dramatically different from those of the calcined oxygen carriers. The FeWO_x/SiO₂ sample displays only reflections from the monoclinic FeWO₄ phase (JCPDS85-1354), indicating that the pure crystallinity could be obtained under the reaction condition when the atomic ratio between Fe and W is 1. While for Fe_yWO_x/SiO₂ ($y = 0.5$ and 2), the excess W or Fe ions would exist in the form of WO₃ or Fe₂O₃, respectively.

To further investigate the structures for different oxygen carriers after the first redox cycle, Raman measurements (Fig. 2(C)) were performed. For the WO₃/SiO₂ sample, the two Raman peaks at 715 and 807 cm^{-1} are assigned to the W=O modes. The peaks at 260 and 330 cm^{-1} are due to the bending vibration of the W–O–W modes, which are characteristics of monoclinic WO₃ [16]. For Fe₂O₃/SiO₂, the peaks at 225 cm^{-1} are due to the bending vibration of the A_{1g} modes, and the peaks at 291, 399, 499, and 609 cm^{-1} are due to the bending vibration of the E_g mode of α -Fe₂O₃ [40,41]. For FeWO_x/SiO₂, the vibration peaks at 132, 215, 270, 349, 683, and 875 cm^{-1} are due to the

Fig. 2. XRD patterns of (A) calcined oxygen carriers and (B) oxygen carriers after the first cycle; (C) Raman spectra of oxygen carriers after the first cycle; (D) XRD patterns of oxygen carriers after 10 cycles. (a) FeWO_x, (b) WO₃/SiO₂, (c) Fe_{0.5}WO_x/SiO₂, (d) FeWO_x/SiO₂, (e) Fe₂WO_x/SiO₂, (f) Fe₂O₃/SiO₂.

bending vibration of the Fe–O–W modes [42]. This indicates the doping of Fe²⁺ into the lattice of WO₃ and the formation of FeWO₄. The Fe–O–W bond may modulate the activity of lattice oxygen and result in different performances of FeWO_x/SiO₂ compared with those of WO₃/SiO₂ and Fe₂O₃/SiO₂.

XPS was also conducted to further identify the chemical states of FeWO_x/SiO₂ after the first redox cycle. Fig. 4(C) shows the detailed XPS spectra of the Fe 2p core level for FeWO_x/SiO₂. The peaks correspond to the typical binding energies of the Fe²⁺ oxidation states (centered at 710.7 eV) [10]. Based on the thermodynamic analysis in Fig. 1, the phase transition from Fe₂O₃ to Fe₃O₄ is prone to full oxidation, while the partial oxidation is more favored during the reduction of FeO to Fe. Thus, the Fe²⁺ state in FeWO_x/SiO₂ is beneficial for CLPOM toward syngas. As for the detailed XPS spectra of the W 4f core level, the peaks can be classified into the typical binding energies of W⁶⁺ oxidation states (centered at 35.2 eV) [16]. The high-resolution XPS spectra of O 1s is shown in Fig. S8; the peaks are fitted with three subpeaks at 530.4 eV (labeled as OI), 532.0 eV (labeled as OII), and 534.0 eV (labeled as OIII) [15]. The OI peak is characteristic of the lattice oxygen in FeWO_x/SiO₂, while the OII and OIII peaks are respectively attributed to the oxygen defects and/or adsorbed –OH in water and C–O in CO₃²⁻. The aforementioned results indicate that FeWO₄ is a more favorable phase under the reaction condition, which can also be seen in the Fe–O–W phase diagram in Fig. S7. All the characterizations in the following discussions use the catalyst after one redox cycle of the fresh catalyst.

The average crystallite sizes of FeWO₄ calculated from the Scherrer equation and the surface area of oxygen carriers

based on BET characterization are reported in Table S2. All the oxygen carriers have surface areas around 50 m²/g, and their crystalline sizes were about 20 nm.

TEM was used to investigate the morphology of the selected FeWO_x/SiO₂ sample as shown in Fig. S1. The particles with a d spacing of 0.38 nm were associated with the (011) FeWO₄ facet (JCPDS 20-1324) [43]. The EDS mappings in Fig. S2 demonstrated that Fe and W are uniformly dispersed on the SiO₂ support, which may contribute to the excellent structural stability.

3.3. Redox performance and stability

The above oxygen carriers were applied for the partial oxidation of methane. Fig. 3(A) shows the CH₄ conversion, H₂ selectivity, CO gas-phase selectivity, and H₂/CO ratio. The corresponding conversion, CO selectivity (78%), H₂ selectivity, and H₂/CO ratio with the consideration of carbon deposition are shown in Fig. S3. Compared to the case with WO₃/SiO₂, the methane conversion dramatically increased and the selectivity toward CO and H₂ maintained a relatively stable value with Fe_yWO_x/SiO₂. A significant increase can be seen in the selectivity of syngas for FeWO_x/SiO₂ with the minimal appearance of full oxidation products (CO₂, H₂O) in comparison to the case with Fe₂O₃/SiO₂. Although Fe₂WO_x/SiO₂ has the highest methane conversion, the H₂/CO ratio is much higher than those of other oxygen carriers. This may be due to the reduction of excess iron oxide, which might lead to serious methane cracking. For Fe_{0.5}WO_x/SiO₂, the remaining WO₃ displays a considerably low methane conversion due to its low activity. For FeWO_x, the

Fig. 3. In the first cycle: (A) CH₄ conversion, CO gas phase selectivity, H₂ selectivity, and average H₂/CO ratio, (B) surface rate and syngas yield from methane oxidation at 900 °C. During 10 cycles: (C) CH₄ conversion, (D) H₂ selectivity, (E) CO gas phase selectivity, and (F) H₂/CO ratio from methane oxidation at 900 °C.

methane conversion was much lower and the H₂/CO ratio was higher compared with those of FeWO_x/SiO₂, which is attributable to the large crystalline size of FeWO₄ (39.8 nm) without the dispersion effect of SiO₂, as shown in Fig. S4. FeWO_x/SiO₂ shows both the second-highest methane surface reaction rate and the highest syngas yield with appropriate H₂/CO (2.4), as seen from Fig. 3(B); thus, it is more suitable for the POM.

The results of the CH₄ isothermal reaction with various oxygen carriers are presented in Fig. S5. In general, there are four consecutive reaction regions appearing as the reaction proceeds. In the beginning, surface oxygen species are highly active, which leads to the complete oxidation of methane (region I). As the surface oxygen species are gradually consumed, the bulk oxygen species could diffuse to the surface and result in the POM to CO and H₂ (region III). There is also a transition region (region II) between region I and region III. When oxygen species are further consumed, the cracking of methane dominates (region IV). For WO₃/SiO₂, the ability to activate methane is poor. For Fe₂O₃/SiO₂, there is a relatively long time for region I and region II, indicating that the main products are CO₂ and H₂O, which is consistent with the thermodynamic analysis that Fe₂O₃ tends to induce full oxidation. FeWO_x/SiO₂ has a long partial oxidation time and a high methane conversion, which implies a relatively high syngas yield. The formation of carbon deposition is adverse for CLPOM, because it not only leads to great changes of the structure over oxygen carriers but also results in the oxidation of deposited carbon, which gives off more heat, causing severe sintering. Above all, FeWO_x/SiO₂ is more promising for partial oxidation; it can help avoid the formation of large amounts of carbon deposition and improve the catalytic performance of redox processes significantly.

To further investigate the stability for the CLPOM process, continuous redox tests at 900 °C were performed over all the samples for 10 cycles, as shown in Figs. 3(C–F). With the addition of Fe and formation of FeWO₄, the conversion of methane increased significantly. As for Fe₂WO_x/SiO₂, the selectivity of H₂ and the H₂/CO ratio increased continuously, indicating that methane cracking occurred during the redox processes because of the excess Fe₂O₃. For Fe₂O₃/SiO₂, the products were mainly CO₂ and H₂O from the complete oxidation of methane, and the conversion of methane was reduced rapidly because iron oxides are prone to sintering at high temperatures. FeWO_x/SiO₂ could retain the high methane activation capacity, and also exhibited remarkable lattice oxygen donation ability over long-term redox cycles. To further confirm the stability of FeWO_x/SiO₂, an extended stability test for 50 cycles was performed. As shown in Fig. S6, the selectivity of both H₂ and CO was stable above 95%. There was a slight decrease (<5%) in methane conversion. The results show that the oxygen carrier maintained a good catalytic performance through 50 redox cycles.

3.4. Textural properties of spent oxygen carriers

The specific structural changes of Fe₂O₃/SiO₂ and Fe_yWO_x/SiO₂ ($y = 0, 0.5, 1, 2$) after 10 cycles are shown in Fig. 2(D). All the crystalline phases were recovered to the same as the fresh oxygen carriers, demonstrating the reversible structural change during the redox processes. Table S2 shows a comparison of the textural properties of the fresh and spent oxygen carriers. FeWO_x/SiO₂ demonstrated minimal variation in particle size and surface area before and after 10 cycles, reflecting

an effective resistance toward thermal sintering during the harsh high-temperature redox operation. We also characterized the structural changes of oxygen carriers after 50 cycles using EDS-Mapping. As shown in Fig. S7, Fe and W elements were still dispersed in a relatively uniform state on SiO_2 without noticeable phase segregation. The experimental results show that $\text{FeWO}_x/\text{SiO}_2$ is chemically and physically stable and well suited for CLPOM.

To analyze the carbon deposition on the oxygen carrier during the reduction stage, O_2 -TPO analysis of the oxygen carriers after 8 min methane reduction was carried out. In general, two kinds of deposited carbons exist from CH_4 pyrolysis, including amorphous carbon and graphite carbon. It is commonly believed that the carbon oxidized above 400°C is graphite carbon, which is difficult to eliminate in the oxidation process. In the reduction processes, graphite carbon might be continuously deposited on the catalyst and cover the surface active sites, leading to catalyst deactivation. Conversely, the carbon oxidized below 400°C is amorphous carbon, which can be oxidized with ease and has little adverse effect on stability. As shown in Fig. S8, $\text{FeWO}_x/\text{SiO}_2$ shows both types of carbon deposition centering at 306 and 470°C , which moves toward low-temperature zones relative to other oxygen carriers. For others, the carbon deposition type is mainly graphite carbon. $\text{FeWO}_x/\text{SiO}_2$ has a relatively high methane conversion but with the lowest carbon deposition rate based on the peak area as a semi-quantitative evaluation. The results suggest that the lat-

tice oxygen activation and transfer capacity might be enhanced in $\text{FeWO}_x/\text{SiO}_2$, which can help immediately remove the carbon intermediates.

3.5. Structural stability

The structural changes during the reduction of $\text{FeWO}_x/\text{SiO}_2$ could provide important information for understanding the overall CLPOM process. Fig. 3(A) presents XRD diffraction patterns over fresh and methane activated samples at different reduction times. FeWO_4 is reduced to Fe-W alloy in one-step, which is consistent with the Fe-O-W phase diagram in Fig. S9. As the reduction progresses, phase segregation would occur to form the metal Fe and W after 8 min. With deep reduction (15 min), the metal would be carbonized to form corresponding metal carbide, which is detrimental to the CLPOM process. The suitable reduction degree for oxygen carriers is key to maintaining stability, and in this study, the methane reduction time is set to 8 min for optimum performance.

XPS was carried out to further identify the chemical state of $\text{FeWO}_x/\text{SiO}_2$ after methane reduction and confirm the existence of the Fe-W alloy. Fig. 4(C) shows the high-resolution XPS spectra of Fe $2p$, which was ascribed to Fe $2p_{3/2}$ and $2p_{1/2}$, respectively, and the peaks can be deconvoluted into two pairs centering at 710.7 and 706.3 eV, corresponding to the typical binding energies of two Fe oxidation states: Fe^{2+} and Fe. As for the XPS spectra of W $4f$, shown in Fig. 4(D), the peaks are fitted

Fig. 4. (A) XRD patterns of $\text{FeWO}_x/\text{SiO}_2$ at different times on CH_4 stream at 900°C ; (B) XRD patterns of $\text{FeWO}_x/\text{SiO}_2$ at different times on O_2 stream at 900°C ; (C) XPS Fe $2p$ and (D) W $4f$ spectra of $\text{FeWO}_x/\text{SiO}_2$ oxygen carrier. (a) Fresh, (b) after the first reduction.

Fig. 5. CH₄ pulses at 900 °C over (A) WO₃/SiO₂, (B) FeWO_x/SiO₂, and (C) Fe₂O₃/SiO₂. (a) CO₂, (b) H₂O, (c) CH₄, (d) CO, (e) H₂.

with two subpeaks at 35.2 and 31.4 eV, which can be assigned to W⁶⁺ and W, respectively. The decrease in FeWO₄ and the increase in the surface absorbed oxygen (OII) during the reduction (Fig. S10) demonstrated that the reaction boundary was fixed on the surface of the oxygen carrier particle. The standard binding energies with the resultant binding energies of metal Fe and W after the reduction are compared. The binding energy of metal Fe shifts from 706.8 to 706.3 eV, and that of metal W shifts from 31.0 to 31.4 eV. According to the electronegativity principle, there is a strong interaction between metal Fe and W, resulting in the formation of the Fe-W alloy.

A CH₄ pulse experiment was performed to gain insights into the effect of the Fe-W alloy on the methane surface reaction microkinetics, as shown in Fig. 5. FeWO_x/SiO₂ exhibited much higher H₂ and CO mass signal intensities compared to that for CH₄, which may be ascribed to the surface kinetics promotion effect of the Fe-W alloy. The Fe-W alloy, as shown in Fig. S12 [43–45], and WO₃ were compared to further study the effect. Compared to WO₃, the Fe-W alloy has a lower initial methane activation temperature and a stronger methane activation capacity estimated from the slope of the H₂ curve, which can reflect the H₂ generation rate according to the results of CH₄-TPR, as shown in Fig. S13. O₂-TPO was performed to measure the carbon deposition of these two samples, which are reduced for 30 min under CH₄ flow at 750 °C, and the results are shown in Fig. S14. As for WO₃/SiO₂, there is almost no carbon deposition, which indicates that the activation of methane rarely occurred under this reaction condition. Nevertheless, the amount of carbon deposition produced by the cracking of methane for

Fe-W alloy was significantly higher. Therefore, the Fe-W alloy can facilitate the methane surface activation at a lower temperature compared to WO₃.

ICP characterizations were also conducted on oxygen carriers at different reduction times. Table 1 shows a comparison of the results of XPS and ICP, indicating that during the reduction reaction, the atomic ratio of Fe and W on the surface is almost the same as that in the bulk phase. Therefore, the formation of the Fe-W alloy, and the strong interaction between Fe and W contribute to restraining the phase segregation.

The utilization of air as the oxidizing agent could regenerate the lattice oxygen of the oxygen carrier and burn off carbon deposition, simultaneously. Such a process is strongly exothermic, which would lead to serious sintering of oxygen carriers. In addition, the high partial oxygen pressure would induce the diffusion of metal ions to the surface and result in phase segregation [46]. Thus, it is important to study the structure change of oxygen carriers during the oxidation process.

As shown in Fig. 4(B), the structural transformation during the oxidation process of FeWO_x/SiO₂ is mainly a reversible change of the reduction process. The Fe-W alloy and remaining W were oxidized to FeWO₄ in one-step. The peak of the Fe-W alloy gradually weakened and completely disappeared after 15 min. XPS was performed aiming to further identify the chemical state of FeWO_x/SiO₂ after 1 redox cycle, shown in Fig. S15. The results show that the structure of FeWO_x/SiO₂ after 1 cycle is virtually the same as that of the fresh catalyst, indicating its outstanding structural stability.

Both the XPS and ICP data over the oxygen carriers at dif-

Table 1

XPS and ICP-derived characteristics of FeWO_x/SiO₂ oxygen carriers at different reduction times and different oxidation times.

	Time (min)	XPS					ICP		
		Fe (%)	W (%)	O (%)	Si (%)	Fe:W	Fe (ppm)	W (ppm)	Fe:W
Reduction	Fresh	1.2	1.2	69.5	28.1	1:1	25.1	79.1	1:1
	4	1.0	0.9	69.1	29.0	1:0.9	25.2	79.1	1:1
	8	1.1	1.0	68.9	29.0	1:0.9	25.2	79.2	1:1
	12	2.2	2.1	67.0	28.6	1:1	25.2	78.9	1:1
Oxidation	2	2.6	2.5	72.1	22.8	1:1	25.1	79.2	1:1
	6	1.0	1.9	72.6	23.5	1:1	25.2	79.1	1:1
	10	1.4	1.4	70.0	27.2	1:1	25.1	79.3	1:1
	15	1.6	1.6	70.3	26.5	1:1	25.1	78.1	1:1

Fig. 6. STEM-EDX-mapping of $\text{FeWO}_x/\text{SiO}_2$ oxygen carrier after 10 cycles.

ferent oxidation times are presented in Table 1. The atomic ratio of Fe to W on the surface for $\text{FeWO}_x/\text{SiO}_2$ is nearly equal to the results obtained by ICP, which are the bulk composition of Fe and W. Therefore, during the oxidation process, no phase segregation occurred as well. For bimetallic alloys, the oxidation rate of the corresponding metal is a key factor when considering the structural stability of the oxygen carrier during the oxidation process. If the oxidation rate of the two metals differs significantly, phase segregation would occur, such as the case of the Fe-Ni system [47]. According to Fan *et al.* [47], the ion oxidation rate can be defined as the ion diffusion rate under the oxygen condition. Thus, the oxidation rate is further analyzed based on the interruption kinetic technique [48–52]. The specific calculation method is shown in Supporting Information. In

$\text{FeWO}_x/\text{SiO}_2$, the oxidation rate of Fe is $1.25 \times 10^{-4} \text{ cm}^2/\text{s}$, which is similar to the oxidation rate of W ($1.26 \times 10^{-4} \text{ cm}^2/\text{s}$). Therefore, Fe and W could be oxidized simultaneously to avoid phase segregation and guarantee the structural stability.

EDS-mapping was carried out on $\text{FeWO}_x/\text{SiO}_2$ after 10 cycles to identify the elemental distribution. As shown in Fig. 6, Fe and W were distributed homogeneously on SiO_2 . This indicates that the effect of redox treatment on the crystal structure of $\text{FeWO}_x/\text{SiO}_2$ sample is not significant. As reported in the previous literature [46], Fe tends to migrate to the surface during oxidation due to the induction of high oxygen partial pressure and can lead to the irreversible structural change of the oxygen carriers. $\text{FeWO}_x/\text{SiO}_2$ shows excellent structural stability. The formation of the Fe-W alloy with strong interaction between Fe and W together with the matching of the ion oxidation rates for the Fe-W alloy under air condition contributes to the elimination of phase segregation and the maintenance of structural stability during the redox cycles.

3.6. Lattice oxygen activation and diffusion

The activity test shown in Fig. 3 indicates that the methane conversion can be enhanced rapidly with the gradual addition of Fe, implying that the introduction of Fe ions into WO_3 may weaken the W-O bond and release more lattice oxygen to the surface to participate in CLPOM. To gain more insights, the reduction performances of various samples were evaluated by H_2 -TPR, as shown in Fig. 7(F). WO_3/SiO_2 exhibited three major reduction peaks [16]. The first peak at 610°C corresponded to the reduction of WO_3 - $\text{WO}_{2.72}$. The reduction of $\text{WO}_{2.72}$ - WO_2 occurred at about 695°C , and the reduction of WO_2 -W occurred

Fig. 7. CH_4 -TPR mass spectra of (A) $\text{Fe}_2\text{O}_3/\text{SiO}_2$, (B) $\text{Fe}_2\text{WO}_x/\text{SiO}_2$, (C) $\text{FeWO}_x/\text{SiO}_2$, (D) $\text{Fe}_{0.5}\text{WO}_x/\text{SiO}_2$, and (E) WO_3/SiO_2 ; (F) H_2 -TPR profiles of fresh oxygen carriers.

at over 900 °C. There are also three peaks for $\text{Fe}_2\text{O}_3/\text{SiO}_2$, which are around 450, 640, and above 900 °C, corresponding to the reduction of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4\text{--FeO}$, and FeO--Fe , respectively [22]. For $\text{FeWO}_x/\text{SiO}_2$, the initial reduction peak corresponding to the reduction of $\text{WO}_3\text{--WO}_{2.72}$ moves from 610 to 545 °C compared to the case for WO_3/SiO_2 due to the influence of Fe^{2+} on the W–O bond, and the initial state of the Fe ions are confined in Fe^{2+} in comparison to the case with $\text{Fe}_2\text{O}_3/\text{SiO}_2$. The results indicate that the W–O bond in FeWO_4 is more active than that in WO_3 , and the Fe–O bond is more selective to syngas compared with Fe_2O_3 . Therefore, more available lattice oxygen would be released to participate in the partial oxidation instead of complete oxidation, which is consistent with the thermodynamic analysis in Fig. 1. For $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and WO_3/SiO_2 , the lattice oxygen released with the first reduction peaks contributes to the full oxidation region ($\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and $\text{WO}_3\text{--WO}_{2.72}$), and the subsequent reduction peaks can be assigned to the partial oxidation region. For $\text{FeWO}_x/\text{SiO}_2$, the partial oxidation tends to occur nearly in the entire temperature range. Table S3 shows a comparison of the peak areas in the temperature range, which belong to the partial oxidation, and $\text{FeWO}_x/\text{SiO}_2$ has the largest amount of available lattice oxygen, providing a guarantee for prolonged catalytic activity toward CLPOM.

To further illustrate the reduction behaviors of oxygen carriers under a CH_4 flowing environment, the $\text{CH}_4\text{--TPR}$ mass spectra over $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and $\text{Fe}_y\text{WO}_x/\text{SiO}_2$ ($y = 0, 0.5, 1, 2$) are presented in Figs. 7(A–E). The evolution peaks of CO via the oxidation of carbon intermediates with the lattice oxygen diffused from oxygen carriers shift toward lower temperatures from 810 °C for WO_3/SiO_2 to 730 °C for $\text{FeWO}_x/\text{SiO}_2$, and the initial activation temperature of CH_4 moves from 750 to 710 °C, indicating a relatively high lattice oxygen activity in $\text{FeWO}_x/\text{SiO}_2$. These results can be due to the reduced activation energies for CLPOM and improved catalyst activity. It can be seen that the H_2 from methane activation and dehydrogenation was produced earlier than CO. According to Li *et al.* [13], the oxygen evolution was the rate-determining step in the POM via a transient pulse injection approach over Fe-based mixed metal oxide. Thus, based on the above two points, the diffusion of the lattice oxygen is potentially the rate-determining step during the methane reduction process over $\text{FeWO}_x/\text{SiO}_2$. If the dissociation rate of methane is overly high, while the lattice oxygen cannot be supplied immediately, the carbon deposition will form and accumulate. On the contrary, if the surface oxygen is abundant and active, the total oxidation of methane to generate CO_2 and H_2O could be dominant. To a certain extent, the initial evolution temperature difference between H_2 and carbon monoxide reflects the capacity of lattice oxygen activation and diffusion relevant to that of carbon deposition from methane cracking. As shown in Fig. 7(C), the initial peak temperatures at which H_2 and CO evolved were almost the same for $\text{FeWO}_x/\text{SiO}_2$, indicating that they were produced merely simultaneously. The fraction of H_2 and CO tailed up with a constant ratio close to 2. Therefore, it has an outstanding oxygen activation and diffusion capacity and can oxidize the carbon intermediate immediately, which accounts for its good catalytic stability. $\text{FeWO}_x/\text{SiO}_2$ also has better oxygen vacancy formation ca-

Fig. 8. Proposed reaction scheme of CLPOM over $\text{FeWO}_x/\text{SiO}_2$ oxygen carriers.

capacity compared with WO_3/SiO_2 as can be seen from the UV-vis reflectance spectra in Fig. S17 [16]. The increasing concentration of the oxygen vacancies can lower the oxygen migration barrier and facilitate the migration of bulk lattice oxygen to the catalyst surface toward syngas production.

Therefore, the potential reaction mechanism and structural change of $\text{FeWO}_x/\text{SiO}_2$ in the CLPOM process can be proposed, as shown in Fig. 8. In the methane conversion step, $\text{FeWO}_x/\text{SiO}_2$ is gradually reduced to form Fe–W alloy in one-step; the capacity of lattice oxygen activation and diffusion is strong enough to oxidize the carbon deposition immediately. In the air regeneration step, the reduced oxygen carrier is oxidized to form FeWO_4 . Therefore, the oxygen carrier structure swings reversibly between FeWO_4 and the Fe–W alloy and exhibits excellent structural stability. All the above results present $\text{FeWO}_x/\text{SiO}_2$ as a very promising candidate for CLPOM.

4. Conclusions

This study investigates $\text{Fe}_y\text{WO}_x/\text{SiO}_2$ redox catalysts for POM under a cyclic redox CLPOM scheme. The main phase existing under the reaction condition is FeWO_4 . This oxygen carrier does not only have an outstanding methane conversion and an appropriate syngas selectivity but also excellent structural stability. Combining the results of $\text{CH}_4\text{--TPR}$, $\text{O}_2\text{--TPO}$, CH_4 pulse, and $\text{H}_2\text{--TPR}$, the main reasons for the remarkable catalytic performance of the oxygen carrier were established as the conspicuous lattice oxygen activation and diffusion capacity. Consequently, it can react with the carbon intermediates in time and facilitate the methane surface activation due to the formation of Fe–W alloys during the reduction process. The results of XPS and ICP indicate that the outstanding structural stability during 50 redox cycles can be mainly attributed to the strong interaction between Fe and W, as evidenced in the formation of their alloy, and the matching of Fe and W ion oxidation rates for the Fe–W alloy. The findings can offer mechanistic insights into $\text{Fe}_y\text{WO}_x/\text{SiO}_2$ for CLPOM and provide promising redox catalysts for this potentially advantageous process.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1140–1151 doi: 10.1016/S1872-2067(20)63544-6

Chemical looping partial oxidation over $\text{FeWO}_x/\text{SiO}_2$ catalysts

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This paper describes the remarkable catalytic performance of $\text{FeWO}_x/\text{SiO}_2$ due to the promoted methane surface reaction kinetics and the enhanced lattice oxygen activation and diffusion capacity.

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基于FeWO_x/SiO₂载氧体的甲烷化学链部分氧化反应

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摘要: 甲烷具有价格低廉且储量丰富的优点, 因此将甲烷转化为合成气(一种H₂:CO为2的混合物), 从而进一步合成有价值的化学品和液体燃料引起了人们的极大关注. 化学链甲烷部分氧化(CLPOM)技术能避免甲烷与空气直接接触而引起爆炸的危险, 可以降低后续对合成气与氮气分离操作所带来的费用, 因此日益受到关注. CLPOM过程主要分为两步: 第一步, CH₄被载氧体所携带的氧部分氧化, 载氧体被还原; 第二步, 利用氧化剂(例如空气)将被还原的载氧体再氧化恢复. 因此, 载氧体在CLPOM过程中起到至关重要的作用. 载氧体的选择主要存在两个问题: (1)甲烷被活化所产生含碳产物的能力与晶格氧的给氧能力不匹配所带来的严重碳沉积; (2)金属离子间扩散速率不匹配而造成载氧体在氧化还原过程中结构的不可逆变化. 基于上述两个问题, 本文设计了FeWO_x/SiO₂载氧体用于CLPOM. 与未改性的WO₃/SiO₂载氧体相比, 甲烷的转化率和合成气的收率都有显著提高. FeWO_x/SiO₂在900 °C、1 atm反应条件下表现出62%的甲烷转化率、93%的CO气相选择性、94%的H₂选择性和2.4的H₂/CO比值, 同时在50个循环中表现出优异的催化活性和稳定性. 本工作利用CH₄脉冲反应研究了FeWO_x/SiO₂的甲烷表面反应过程; 采用CH₄-TPR和H₂-TPR相结合探究了甲烷活化速率与晶格氧扩散速率之间的关系; 通过XPS和XRD对FeWO_x/SiO₂在氧化还原过程中的结构稳定性进行了探讨. 综合上述实验结果, 对FeWO_x/SiO₂应用于CLPOM的反应机理进行了阐述.

H₂-TPR结果表明, 在FeWO_x/SiO₂中, 相较于Fe₂O₃/SiO₂, Fe-O的活性受到抑制, 使其更倾向于与甲烷发生部分氧化反应; 相较于WO₃/SiO₂, W-O的活性得到明显提升, 因此更多的晶格氧可以参与到部分氧化反应中来氧化积碳, 从而使合成气收率大幅度提升. 从CH₄-TPR结果可以看出, 对于FeWO_x/SiO₂, CO与H₂的生成温度最接近, 意味着晶格氧的传输速率较快并且能够与甲烷活化产生含碳中间物种的速率相匹配, 将其及时氧化生成CO, 避免由于积碳造成的催化剂失活.

结合XPS和XRD结果可以得出, 在甲烷还原过程中, FeWO_x经历一步还原形成Fe-W合金, 由于其间存在强相互作用, 因而抑制了还原过程中催化剂相分离现象的发生. 同时, 根据铁钨离子在空气条件下扩散速率的公式计算可以得出, 其相近的离子氧化速率也保证了在氧化过程中催化剂结构的稳定性. 本工作为进一步构建用于甲烷化学链部分氧化制合成气的复合金属氧化物载氧体提供了研究思路.

关键词: Fe-W合金; 甲烷活化; 晶格氧扩散; 相分离; 离子氧化速率

收稿日期: 2019-09-30. 接受日期: 2019-11-06. 出版日期: 2020-07-05.

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基金来源: 国家重点研发计划(2016YFB0600901); 国家自然科学基金(51761145012, 21525626, U1663224); 高等学校学科创新引智计划(B06006).

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