Energy materials



Enhanced catalytic activity of Ni–Mo₂C/La₂O₃–ZrO₂ bifunctional catalyst for dry reforming of methane

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ABSTRACT

A series of Ni-modified Mo₂C catalysts with La₂O₃-stabilized ZrO₂ supports were synthesized via template method coupled with incipient wetness impregnation and temperature-programmed carbonization. The catalyst was tested in dry reforming of methane (DRM) reaction at the temperature range from 973 to 1173 K in a fixed-bed quartz reactor under atmospheric pressure. XRD, Raman, BET, H₂-TPD, SEM, EDS and TEM were conducted to characterize the phase constitution, the pore structure, the morphology and the crystal structure of the catalysts. Ni– Mo_2C nanoparticles of ~ 3 nm diameter were obtained for these catalysts, and the La₂O₃–ZrO₂ supports exhibited a cubic lattice structure with a sheet shape, which is believed to contain an abundant of oxygen vacancies. And the synergistic interaction between the oxygen vacancy in La-Zr-O solid solution and the Ni-Mo₂C particles could decrease the apparent activation energy of CO₂. Both of them are beneficial for accelerating DRM reaction. CH₄ conversion of the best specimen catalyst reaches 94% at 1173 K, and the catalyst maintains its stability after 100-h reaction. The superior catalytic activity of NMLZ-7.5 is attributed to the improved BET surface area (33.2 m²/g), smaller crystallites, grain boundaries and oxidation-carbonization cycle of Ni-Mo₂C.

Introduction

As low-cost and renewable energy source, H_2 -CO syngas is an important raw material for synthesis of acetic acid, methyl formate and other industrial

organic products [1–3]. Hence, carbon capture is of great interest for the storage of energy and for the decrease in anthropogenic emissions of CO₂ [4]. In the past years, the dry reforming of methane (DRM) has become an attractive process to produce H₂–CO syngas from CH₄ and CO₂ [5–8]. Compared to the

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steam reforming of methane and the partial oxidation of methane, it has two advantages: (a) The obtained syngas has a low hydrogen-to-carbon monoxide ratio, which is suitable for generating higher hydrocarbons by Fischer–Tropsch synthesis. (b) The utilization of CO_2 helps to reduce the greenhouse effects to resolve many environmental problems.

As reported, CH₄ could be dehydrogenated on active metal (Rh, Pt, Ni) particles and CO₂ could be activated on supports, when the metal was supported by lanthanum-based solids [9–14]. Materials based on oxides of zirconium (ZrO₂) are widely used for various important chemical reactions in industries due to their prominent physical-chemical properties [15]. According to the previous researches, ZrO₂ has three mixed crystal structures, including monoclinic, tetragonal and cubic [16-18]. Cubic structure is the most stable phase and can be easily obtained by doping a variety of oxides such as Y₂O₃, CeO₂ and La_2O_3 [19–23]. Moreover, the dopant is compensated by the effectively charged positive defects such as oxygen vacancies to maintain the electric neutrality [24, 25]. The lattice structure remains stable because the effective charged ions and host Zr⁴⁺ cations are in a similar size [26]. Thus, the oxygen vacancies would serve as the active sites for the surface oxygen species and boost the dissociation of CO₂ to CO [1]. Moreover, complete dehydrogenation of dissociating CH₄ could be resulted from reaction with the surface O species originated from dissociation of CO₂ or secondary H₂O product [27, 28]. Additionally, these kinds of solid solution supports could greatly improve the adsorption, activation and dissociation of CO₂ and thus accelerate the DRM reaction [29, 30]. In the case of La₂O₃-stabilized ZrO₂, lots of studies have verified that La₂O₃ has significant effects in the adsorption, activation and dissociation of CO2 due to the formation of intermediate product La₂O₂CO₃ [31–33]. Mo₂C is an excellent candidate catalyst for DRM with its high stability and activity accomplished by its oxidation-carbonization cycle [34–37]. However, Mo₂C can be easily oxidized by CO₂ at temperature above 1123 K under atmosphere pressure [38]. Yao's group [39-41] have done comprehensive research about Mo₂C in DRM, which suggested that Mo₂C performs high rate of oxidation than carbonization which leads to deactivation. And by loading Mo₂C on CNT, the obtained catalysts perform high stability within dozens of hours in DRM [40]. Previous studies have proven that Nimodified Mo₂C was highly active for DRM reaction as a dual active-site catalyst which could establish a catalytic redox cycle as follows: Mo₂C activates CO₂, then the oxygen species from CO₂ replace the carbon of Mo₂C, while Ni dissociates CH₄ and promotes the reduction of molybdenum oxides to molybdenum carbide [29, 42–45], which can maintain its high activity in long term.

Here, in this investigation, various amounts of La_2O_3 were used to stabilize the ZrO_2 supports, on which a series of Ni-Mo₂C catalysts were loaded via the template and carbonization temperature-programmed method. Ni-Mo₂C nanoparticle-of \sim 3 nm was obtained for these catalysts, and the La₂O₃-ZrO₂ supports exhibited a cubic lattice structure with a sheet shape, which is believed to contain an abundant of oxygen vacancies. The interaction between oxygen vacancies of c-La-Zr-O solutions and Ni-Mo₂C particles may lead to the formation of crystal boundary. And the oxygen vacancies may work as active sites in DRM reactions and lower its appearance activation energy. Catalytic activities of all the prepared samples were evaluated via DRM reaction. The obtained 1Ni-5Mo₂C/7.5La₂O₃-ZrO₂ catalyst shows a CH₄ conversion of 94% at 1173 K, and the catalyst maintains stable after 100-h reaction. The superior catalytic activity is attributed to the large BET surface area (33.2 m²/g), smaller crystallites, grain boundaries and oxidation-carbonization cycle of Ni-modified Mo₂C.

Experimental

Catalysts preparation

The mLa_2O_3 – ZrO_2 (m = 0, 4.5, 7.5, 11.2, 22, 30.6, 43 mol%) support was prepared via a template-assisted method. The mixture containing a tailored proportion of $ZrOCl_2$ ·8H₂O and La(NO₃)₃·6H₂O was slowly added into an aqueous solution of CTAB (cetyl trimethyl ammonium bromide), and then the ammonia was added into under stirring at 333 K until pH reached 11. The solution was kept for 12 h under the room temperature (RT), and then the precipitate was filtered and washed by deionized water and ethanol until pH 7. The obtained solid was dried at 383 K for 6 h and calcined at 1173 K for 6 h for the generation of LZ-m (mLa_2O_3 – ZrO_2) support, and then it was naturally cooled to RT.

The NiMoO x/mLa_2O_3 -ZrO₂ precursor was prepared via incipient wetness impregnation method. The aqueous solution of Ni(NiO₃)₂·6H₂O and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Ni/Mo₂C mass ratio = 1/5) was stirred and impregnated with the mLa_2O_3 -ZrO₂ support. The obtained NiMoO x/mLa_2O_3 -ZrO₂ precursor was dried at 383 K for 12 h and calcined at 1173 K for 4 h, and then it was carburized in 20 vol% CH_4/H_2 atmosphere via a temperature-programmed method which involved the following processes: Heating temperature was risen from RT to 573 K at a rate of 5 K/min, followed by increasing to 1073 K at a rate of 1 K/min, and then kept at 1073 K for 2 h. Subsequently, the obtained NMLZ-m(1Ni-5Mo₂C/ mLa_2O_3 -ZrO₂) was cooled to RT in CH₄/H₂ (20 vol%) CH₄) gas flow and passivated in a mixture of $1\% O_2/$ Ar at RT for 12 h [46].

Catalyst characterization

XRD patterns of the catalysts were conducted on the PANalytical X'Pert diffractometer (X'Pert PRO MPD, PW3040/60) with a CuKa ($\lambda = 0.154060$ nm) radiation (40 kV, 40 mA) at RT. Semiguantitative contents of different phases of supports were calculated by X'Pert Highscore Plus based on RIR method. Raman spectrum was obtained by means of LabRAM HR800-LS55 with excitation laser of 532 nm. Specific surface areas were measured on a Micromeritics ASAP-2010 apparatus, which measured the nitrogen adsorptiondesorption isotherms of catalysts at 77 K. BET (multiplot Braunauer-Emmett-Teller) method was applied to calculate the specific surface area. Pore volume and average pore size of catalysts were calculated by Barrett-Joyner-Halenda (BJH) method. H₂-TPD is conducted with Quantachrome CPB-1. The semiquantitative energy-dispersive spectrometer (EDS) analysis of NMLZ-m was carried out to investigate the elemental composition. Morphology of the catalyst was characterized by scanning electron microscope (SEM) with an S-4800 instrument at 2.0 kV and further investigated by transmission electron microscopy (TEM) on a JEM-2100 microscope. The lattice fringes and electron diffraction patterns were detected in HRTEM images according to Fourier transform and inverse Fourier transform. Concentration of gas products was detected by a gas chromatograph (GC-7890II). TG analysis is conducted with TA instrument SDT650, and tested temperature ranged from room

Catalytic activity test

DRM reaction was performed in the fixed bed with a quartz tubular reactor (4 mm inner diameter and 280 mm length). The reaction was conducted under atmospheric pressure with flowing CH_4/CO_2 (1:1 molar ratio) at a total flow rate of 40 ml/min within a temperature range between 973 and 1173 K. 0.3 g catalyst and 1.2 g quartz sand were loaded in the quartz tube supported on the quartz wool. Before the reaction, the catalyst was pre-reduced in a mixed gas flow of 20 vol% CH₄/H₂ (methane mainly as a carbon source) with a flow rate of 50 ml/min for 1 h at 1073 K. A thermocouple was set beside the center of the quartz tube to directly measure the current temperature of the bed. All the gases were controlled by mass flow meters. When the reaction became stable, they were analyzed online by the gas chromatographs (GC 7890II) equipped with a thermal conductivity detector (TCD) and a TDX-01 column for CH₄, CO₂, H₂, CO. The DRM kinetics was measured with a temperature range from 973 to 1173 K, and the reaction rates were normalized by the mass of each catalyst. The stability of catalyst was investigated for 100 h at 1173 K, 1 atm within a total flow of 40 ml/min with $CH_4/CO_2 = 1:1$.

Data analysis

The catalyst activity for DRM reaction was evaluated according to the conversions of the CH_4 , CO_2 and yields of CO, H_2 . The representative equations are given as follows:

$$X_{\text{CH}_4}(\%) = \frac{F(\text{CH}_4, \text{in}) - F(\text{CH}_4, \text{out})}{F(\text{CH}_4, \text{in})}$$

× 100,

$$X_{CO_2}(\%) = (F(CO_2, in) - F(CO_2, out))/F(CO_2, in) \times 100,$$

$$Y_{H_2}(\%) = F(H_2)/Ft(H_2) \times 100,$$

 $Y_{CO}(\%) = F(CO)/Ft(CO) \times 100,$

where F(i, in) and F(i, out) represents the inlet and outlet flow rates of the gas *i*, respectively. *Ft* is the amount of theoretical product.

Deringer

The appearance activation energy of NMLZ-m in DRM was obtained by plotting $\ln(k)$ to 1000/T, according to the Arrhenius equation: $\ln(k) = -E_a/RT + C$ [9].

Results and discussion

Characteristics of 1Ni-5Mo₂C/mLa₂O₃-ZrO₂

Figure 1a shows the XRD patterns of the calcined LZ*m* supports. XRD analysis confirms that the synthesized *m*La₂O₃–ZrO₂ could be ascribed to three crystal structures, namely (La_{0.1}Zr_{0.9})O_{1.95} (cubic and tetragonal) and cubic La₂Zr₂O₇ (c-La₂Zr₂O₇). The peaks of LZ-4.5 and LZ-7.5 at 30.2°, 35.1°, 50.4° and 59.9° correspond to the (111), (200), (220) and (311) planes of c-(La_{0.1}Zr_{0.9})O_{1.95}, while the peaks of LZ-11.2 and LZ-22, corresponding to the (101), (110), (112) and (211) planes of t-(La_{0.1}Zr_{0.9})O_{1.95}, are found at 2θ of 29.9° , 34.9° , 49.8° and 59.5° . And the peaks of LZ-30.6 and LZ-43 are found at 2θ of 28.6°, 33.2°, 47.7° and 56.6°, which correspond to the (222), (400), (440) and (622) planes of c- $La_2Zr_2O_7$. That the peaks of LZ are slightly left-shifted may be due to the crystal transition [19, 47]. And a transition of crystal structure changing with the increase in molar content of the La₂O₃ incorporated into ZrO₂ is observed as the following order as $c-(La_{0,1}Zr_{0,9})O_{1,95} \rightarrow t-(La_{0,1}Zr_{0,9}) O_{1.95} \rightarrow c-La_2Zr_2O_7$. To confirm the formation of La₂Zr₂O₇, Raman spectra of NMLZ-m have been conducted (Fig. S1). The character peak of vibration mode (E_g) of pyrochlore La₂Zr₂O₇ around 302 cm⁻¹ is observed in NMLZ-22, NMLZ-30.6 and NMLZ-43, while fluorite structure contains only F_{2g} active mode located at 494 cm⁻¹ [48]. Nevertheless, active vibration modes of ZrO₂ and La₂O₃ with slightly shift are also found [49, 50]. Thus, it is suggested that pyrochlore structure of La₂Zr₂O₇ is partly formed under 1173 K with sufficient content of La.

XRD patterns of the reduced NMLZ-*m* are shown in Fig. 1b. The peaks corresponding to (011), (-111), (111), (200), (021), (- 211), (112), (211), (022) and (220) planes of monoclinic ZrO₂ are presented in NMZ patterns. And the (- 111), (111) planes can also be observed for NMLZ-4.5 and NMLZ-7.5, while no peaks of La_2O_3 are detected, indicating that La^{3+} has well dispersed into the ZrO₂ bulk successfully [51]. The peaks of (100) and (101) planes of hexagonal Mo₂C at 34.4° and 39.4° are observed. Due to the low Ni content ($\leq 1 \text{ wt\%}$), there are no significant diffraction peaks for Ni. Meanwhile, it is clearly shown that after NiMoO x/mLa_2O_3 -ZrO₂ precursor is carburized, dramatic changes in the mass fractions of the three La-Zr-O structures occur (Table 1). Almost half of c-(La_{0.1}Zr_{0.9})O_{1.9} content in NMLZ-4.5 and NMLZ-7.5 is transformed to t- $(La_{0.1}Zr_{0.9})O_{1.95}$ crystal, and part of t-(La_{0.1}Zr_{0.9})O_{1.95} in NMLZ-11.2 and NMLZ-22 is converted to c-La₂Zr₂O₇ crystal, while NMLZ-43 has 100% support component of c-La₂Zr₂₋ O7 crystal structure. Due to lower valence state of La^{3+} cation than the host ion Zr^{4+} , a great number of oxygen vacancies are created around La atoms to maintain the neutrality of La-Zr-O lattice [25, 30].



Figure 1 XRD patterns of the calcined supports (a) and the reduced catalysts (b) with different ratios of La–Zr in support.

Catalyst/support	$c-(La_{0.1}Zr_{0.9})O_{1.95}$	$t-(La_{0.1}Zr_{0.9})O_{1.95}$	c-La ₂ Zr ₂ O ₇
LZ-4.5	97	0	3
LZ-7.5	100	0	0
LZ-11.2	0	100	0
LZ-22	0	88	12
LZ-30.6	0	17	83
LZ-43	0	0	100
NMLZ-4.5	50	47	3
NMLZ-7.5	59	37	4
NMLZ-11.2	0	78	22
NMLZ-22	0	33	67
NMLZ-30.6	0	16	84
NMLZ-43	0	0	100

 Table 1
 Semiquant(%) of La–

 Zr–O phase composition in different samples calculated by RIR method

The transition of the solid solution structure may arise by the interaction between the metal particles (Ni-Mo₂C) and oxygen vacancies of La-Zr-O, which could lead to more c-La₂Zr₂O₇ generated from both cubic and tetragonal (La_{0.1}Zr_{0.9})O_{1.95} [47, 52, 53]. For stabilized acceptor-doped metallic oxides, the dopant is always compensated by V_O according to Kröger-Vink equation: $La_2O_3 = 2La_{Zr}' + V_O'' + 3OO^{\times}$. The concentration of oxygen vacancies and lattice oxygen per unit formula depends on La/Zr ratio of each formula [54]. Thus, it is suggested that the $c-La_2Zr_2O_7$ has a higher concentration of oxygen vacancies and lattice oxygen per unit formula than that of (La_{0.1-} $Zr_{0.9}$)O_{1.95}, because that the former La/Zr ratio (1:1) is larger than the latter one (1:9). In previous studies, the oxygen vacancies are heteroatom or molecularly doped active sites in redox reactions [55] and the lattice oxygen of solid solutions has a high mobility, i.e., a high reactivity [53, 54]. This suggests that the catalytic activities could be improved with the increasing c-La₂Zr₂O₇ content.

Surface area and pore properties of all the obtained catalysts are given in Table 2. BET surface area of NMLZ-*m* decreases from 37.8 to 12.3 m²/g with the increase in La₂O₃ content. The great vary on surface

area owes to the transition of crystal structure of support components, which play an important role on pore volume and pore size. The average pore size of all materials decreased slowly from 29.2 to 22.7 nm except NMLZ-7.5, which shows that these catalysts have mesoporous structures. Besides, the pore volume decreased from 0.276 cm^3/g to 0.070 cm^3/g . In addition, the surface area of NMLZ-43 catalyst increases sharply compared to NMLZ-30.6, which may result from that the pore volume of NMLZ-43 was less blocked by forming the single phase (c-La₂₋ Zr₂O₇) in La–Zr–O structure compared to others. A H2-TPD test was conducted to investigate the surface area of Ni of reduced NMLZ-m catalysts; however, there is no H_2 desorption observed at the temperature ranging from RT to 1173 K, which may be due to that surface Ni species had been covered by coke formed during the pre-reducing process. According to the CO₂-TPO study of Ni-Mo₂C catalyst conducted by Shi et al. [35], the formed coke could be oxidized at temperature above 953 K, which suggests that the pre-formed coke would not affect the activity in DRM under studied temperature.

Typical SEM images of NMLZ-m are shown in Fig. 2. The particle size of NMLZ-4.5, NMLZ-7.5 and

Table 2 Surface area and pore
properties of NMZ and
NMLZ-m catalysts calculated
by BJH methods

Catalyst	BET surface area (m^2/g)	Pore volume (cm ³ /g)	Average pore size (nm)
NMZ	16.5	0.177	43.4
NMLZ-4.5	37.8	0.276	29.2
NMLZ-7.5	33.2	0.194	23.4
NMLZ-11.2	28.3	0.196	27.7
NMLZ-22	15.8	0.092	23.3
NMLZ-30.6	12.3	0.070	22.7
NMLZ-43	21.2	0.114	21.5



Figure 2 SEM images of NMLZ catalyst with different ratios of La–Zr in support: NMLZ-4.5 (a), NMLZ-7.5 (b), NMLZ-11.2 (c), NMLZ-22 (d), NMLZ-30.6 (e) and NMLZ-43 (f).

NMLZ-43 is more uniform compared to others. Normally, smaller crystallites with uniform size distribution have larger surface areas and more active sites [58]. Hence, NMLZ-4.5, NMLZ-7.5 and NMLZ-43 exhibit relatively high surface area, as given in Table 2. Meanwhile, high content of $c-La_2Zr_2O_7$ can be considered as a significant factor for the stability of thermal phase and sintering resistance [32, 59]. As a result, the nanoparticles of NMLZ-43 exhibit well distributions and less agglomeration by sintering (Fig. 2f) than NMLZ-11.2, NMLZ-22 and NMLZ-30.6. Elemental compositional information obtained from EDS is listed in Table 3. La and Zr compositions of each catalyst are in agreements with the standardized molar ratio designated for each support. However, the mass ratio between Ni and Mo₂C of each catalyst is smaller than the designed ratio that may be due to the inaccuracy of EDS with extremely low loading of the catalyst. In summary, the results of BET, SEM and XRD demonstrated that the NMLZ-4.5, NMLZ-7.5 and NMLZ-43 have large surface area, have smaller crystallites and contain cubic structure of La-Zr-O support.

For further investigation of lattice structures of NMLZ-4.5, NMLZ-7.5 and NMLZ-43 catalysts, the TEM images and the lattice structures of Ni–Mo₂C

nanoparticles are shown in Fig. 3. As shown clearly in Fig. 3a–c, the supports have well-organized laminar shape. The La-Zr-O structure of NMLZ-43 is further proved to be a cubic structure La₂Zr₂O₇ by HRTEM measurements (Fig. 3h), which is in consistent with the results obtained by XRD. The Ni-Mo₂C nanoparticles on NMLZ-4.5, NMLZ-7.5 and NMLZ-43 are highly uniform dispersed on the supports (Fig. 3d-f) [60]. Meanwhile, more active sites could be exposed for NMLZ-7.5 than other catalysts as it has the smallest particle size (2-3 nm). And the porous structure, which is able to support more Ni-Mo₂C nanoparticles, is found on the surface of NMLZ-7.5 with high specific surface area as BET results shown (Fig. 3e). Lattice distance of the NMLZ-7.5 particle measured from the inverse FFT image is about 2.27 and 1.74 Å (Fig. 3g), which are corresponding to the (101) and (102) plane of the hexagonal Mo₂C (2.27, 1.75 Å, PDF#01-089-3014) and consistent with the analysis of XRD. In addition, the lattice distance of 2.44 Å shown at area 1 in Fig. 3g corresponds to the (021) plane of the monoclinic NiMoO₄ (2.44 A, PDF#00-016-0291). The synergistic effect between Ni and Mo₂C particles in NiMoO₄ could improve the catalytic activity of Mo₂C significantly [52]. Furthermore, several grain boundaries

Table 3Elements contents ofNMLZ-mcatalysts analyzedby EDS

Nominal formula (molar)	Real formula (molar)	Ni loading (wt%)	Mo ₂ C loading (wt%)
4.5% La ₂ O ₃ -95.5% ZrO ₂	4.25%La ₂ O ₃ -95.75%ZrO ₂	0.71	3.53
7.5% La ₂ O ₃ -92.5% ZrO ₂	7.00%La2O3-93%ZrO2	0.89	3.33
11.2% La ₂ O ₃ -88.8% ZrO ₂	10.83%La ₂ O ₃ -89.17%ZrO ₂	0.82	3.23
22% La2O3-78% ZrO2	18.72%La ₂ O ₃ -81.28%ZrO ₂	0.79	2.74
30.6% La2O3-69.4% ZrO2	26.85%La ₂ O ₃ -73.15%ZrO ₂	0.52	3.75
43% La2O3-57% ZrO2	44.81%La ₂ O ₃ -55.19%ZrO ₂	0.82	4.40



Figure 3 TEM images for reduced NMLZ catalysts with different ratios of La–Zr in support: NMLZ-4.5 (a, d), NMLZ-7.5 (b, e) and NMLZ-43 (c, f). HRTEM images for Mo₂C particles of NMLZ-7.5

are formed in area 1 (Fig. 3g) on the crystal boundary of the particle, leading to an unstable atomic oxygen environment and always form a lot of oxygen vacancies which would absorb intermediate products with corresponding FFT and inverse FFT in area 1 (g) and $La_2Zr_2O_7$ support of NMLZ-43 in area 2 (h).

(such as O*) to enhance the yields of the syngas as well as present a grain refining effect on the catalyst nanoparticles [53].



Catalytic performance

Figure 4a, b shows the CH₄ and CO₂ conversion of each catalyst in DRM under the temperature from 973 to 1173 K. The DRM reaction of NMLZ-*m* was conducted at 1 atm and a total flow of 40 ml/min with CH₄:CO₂ = 1:1. And the equilibrium of CH₄ and CO₂ conversion is calculated with the method reported by Nikoo and Amin [61]. It can be observed that the conversion efficiency of each catalyst increases with the increase in temperature, which can be ascribed to the nature of endothermic reaction of DRM and the activation of Ni by oxidation of coke formed in prereduction. The catalytic activity increases in the order NMLZ-30.6 < NMLZ-22 < NMLZ-11.2 < NMLZ-

43 < NMLZ-4.5 < NMLZ-7.5, where NMLZ-7.5 performs the highest activity among the studied catalysts. In general, it can be noticed that the catalytic activity of NMLZ catalysts is significantly dependent on the surface area, which is coincident with the previous study [62]. The high catalytic activity of NMLZ-4.5, NMLZ-7.5 and NMLZ-43 could be attributed to their abundant porous structures found on the surface with high specific surface area as BET results shown. However, though the surface area of the NMLZ-4.5 $(37.8 \text{ m}^2/\text{g})$ is high than that of NMLZ-7.5 (33.2 m^2/g), their activities do not follow the same trend. Also, the NMLZ-11.2 possesses the surface area of 28.3 m²/g with a relative low conversion and yield, but the NMLZ-43 possesses the surface area of 21.2 m^2/g with the highest CO₂ conversion. We consider the concentration of oxygen vacancies in the catalysts as another factor for the CH_4 and CO_2 conversion in DRM reactions. As mentioned earlier, doping with more lanthanum ions will bring more oxygen vacancies. And as the XRD results shown, the content of c-La₂Zr₂O₇ phase increases with the increment in La-Zr ratio, which would be suggested to process higher concentration of oxygen vacancies and lattice oxygen per unit formula. The quantitative trend of oxygen vacancies in NMLZ-4.5 and NMLZ-7.5 meets their activities. The highest CO₂ conversion of NMLZ-43 could be attributed to the unique structure of c-La₂Zr₂O₇ that improves dispersing of active metals and high concentration of oxygen vacancies and lattice oxygen per unit formula among all the catalysts. Briefly, NMLZ-7.5 shows the best catalytic performance of all NMLZ-*m* catalysts, of which CH₄ conversion reaches 94% at 1173 K and 48% at 1023 K, which can be ascribed to the relatively large BET surface area $(33.2 \text{ m}^2/\text{g})$, smaller crystallites and several grain boundaries. And the high activity of NMLZ-43 with relatively low surface area $(21.2 \text{ m}^2/\text{g})$ may arise by its high content of La₂Zr₂O₇, which is believed to have higher concentration of oxygen vacancies.

 H_2 and CO are the primary products of DRM at the temperature range from 973 to 1173 K for all the catalysts. Figure 4c, d shows the yields of H_2 and CO, respectively. The NMZ catalyst shows a high conversion of CH_4 and CO_2 at 1123–1173 K, but its yields of H_2 and CO are lower than the theoretical production, which may be due to side reactions [63, 64]. However, the reacted CH_4 and CO_2 are almost completely converted to H_2 and CO in the DRM for NMLZ-*m* catalysts, which means that NMLZ-m shows prominent selectivity of H_2 and CO producing. This may be due to the oxygen vacancies, which are beneficial to the primary reactions, arisen from c-La–Zr–O.

The ratio of generated H₂/CO of NMLZ-m under different temperatures is shown in Fig. 4e. The ratio of H_2/CO is less than 1 in NMLZ-m under all tested temperature, which indicates that reverse water-gas shift is involved in DRM under all examined condition [7]. As the temperature increases, the value of H_2/CO increases and reaches 1 at 1173 K with NMLZ-4.5, NMLZ-7.5 and NMLZ-43 as catalyst, and the conversion of CH₄ and CO₂ is proportion to the ratio of H_2/CO . It may be because the oxidationcarbonization cycle of Mo₂C becomes the dominant reactions that consume most of the inlet CO₂ in high temperature, which is consistent with the CO₂-TPO conducted by Shi et al. [35] that suggest that Mo₂C would be oxidized in CO₂ at temperature above 1073 K.

In summary, NMLZ-7.5 shows the best catalytic performance at the temperature range from 973 to 1173 K among all the catalysts. Thus, the stability of NMLZ-7.5 catalyst was evaluated on durability test for 100 h at 1173 K as typical sample. It can be seen that the catalyst maintains stable and high activity after 100 h (Fig. 5). TG curves of NMLZ-7.5 before and after stability test are presented in Fig. 5b, in which there are a weight loss around 873 K and a steady weight increase within temperature ranging from 973 to 1273 K. The weight loss around 873 K is attributed to deposited carbon that generated during carbonization of MoO_x or pre-reducing NMLZ-m before DRM [37]. And the weight increase is owing to



Figure 4 Conversion of CH_4 (a), CO_2 (b) and yield of H_2 (c), CO (d), and ratio of H_2/CO (e) for NMLZ-*m* catalysts in DRM under different temperatures with NMLZ catalysts containing different

the oxidation of Mo_2C to MoO_x . The NMLZ-7.5 shows the same ratio of weight loss with slightly temperature shift after stability test, which indicates

ratios of La–Zr in support (reaction conditions: 973–1173 K, 1 atm, 8000 cm³/g h, total CH_4/CO_2 molar ratio = 1:1).

that there is not additional carbon deposited on the NMLZ-7.5 during DRM at 1173 K. The prominent performance of stability may be due to the oxidation–



Figure 5 The stability test of NMLZ-7.5 at 1173 K for 100 h (a) and TG curve of NMLZ-7.5 before and after stability test with a heating rate of 10 K/s (b).

carbonization cycle of Mo_2C , which maintains the carbon balance of NMLZ-7.5.

Kinetic behavior of the catalysts

To further study the effects of NMLZ-*m* on DRM, the reaction rate and the apparent activation energies are given in Table 4, and the reaction rate at equilibrium state was normalized by the mass of each catalyst. According to the Arrhenius equation [9], the apparent activation energy of dissociating CO₂ by NMLZ-7.5 and NMLZ-43 is 52.6 and 49.2 kJ/mol, respectively, which are lower than the value reported elsewhere [65, 66]. And the apparent activation energy of dissociating CH₄ by NMLZ-7.5 and NMLZ-43 at stable stage is about 116.5 and 89.5 kJ/mol which are lower than NMZ (207.4 kJ/mol) and other reported catalysts [67, 68]. This suggests that c-La–Zr–O solutions make a significant contribution to the

improvement in CO₂ dissociation. In addition, NMLZ-7.5 and NMLZ-43 have different catalytic mechanisms in DRM (Fig. 6). Obviously, the DRM includes a one-step surface reaction via NMLZ-43 at the temperature range from 973 to 1173 K due to the linear relation of Arrhenius plot and a two-step reaction via NMLZ-7.5 at different temperature ranges, which is consistent with the catalytic performance of NMLZ-7.5 and NMLZ-43. It was indicated that the catalyst with higher content of c-La₂Zr₂O₇ could decrease the apparent activation energy. The low apparent activation energy of NMLZ-43 may indicate that CH₄ is dehydrogenated not only on the metal surface, but also on the additional surface oxygen species generated by the oxygen vacancy resulting from the dissociation of the CO_2 [27]. And it is suggested that oxygen vacancies on support surface significantly contribute to DRM reaction in the way given as follows:

 Table 4 DMR reaction rate and apparent activation energies for NMLZ-m catalysts

Catalyst	Ea ^a (kJ/mol)		Rate ^b per gram of the	Rate ^b per mol of Ni	Rate ^b per mol of Mo ₂ C
	CH ₄	CO ₂	catalyst (× 10^{-5} mol/g s)	$(\times 10^{-9} \text{ s}^{-1})$	$(\times 10^{-9}$ mol/s)
7.00% La ₂ O ₃ -93% ZrO ₂	116.5	52.6	4.28	6.46	6.99
44.81% La ₂ O ₃ -55.19% ZrO ₂	89.5	49.2	4.17	5.80	8.99
NMZ	207.4	108.9	4.31	_	_

^aReaction conditions: T = 973-1173 K, P = 1 atm, $CH_4/CO_2 = 1$, F = 8000 cm³/g h

^bReaction conditions: T = 1173 K, P = 1 atm, $CH_4/CO_2 = 1$, F = 8000 cm³/g h



Figure 6 Arrhenius plot of DRM reaction with NMLZ-7.5 and NMLZ-43.

 $CO_2 + V_O^{\cdot} \to CO + O^*, \tag{1}$

 $CH_4 + O^* \to CO + H_2. \tag{2}$

Conclusion

With La-Zr-O support synthesized by template-assisted method, cubic La-Zr-O-supported Ni-Mo₂C nanocrystals with homogeneous pore size, unique sheet structure and an abundant of oxygen vacancies were prepared by incipient wetness impregnation followed by controlled temperature-programmed carbonization. Ni-Mo₂C nanoparticles with a diameter of $\sim 3 \text{ nm}$ were obtained by an appropriate calcination treatment. The synergistic interaction between oxygen vacancies of c-La-Zr-O solutions and Ni-Mo₂C particles may lead to the formation of crystal boundary. Moreover, crystal boundary on the surface of metal-support or metal-metal constructs a high-energy environment, which contributes as the active sites to DRM reaction and presents a grain refining effect on the catalyst nanoparticles. Ni-Mo₂C/c-La-Zr-O catalyst exhibits high activity, stability in the conversion of CH₄, CO₂ to H₂ and CO at high temperature. The study shows that high CH₄ conversion of 94% is reached at 1173 K and maintains stable with less than 20% deactivation after 100 h in DRM reaction for NMLZ-7.5, while CO₂ conversion can reach a highest conversion of 98% at 1173 K for NMLZ-43. The high activity and stability at 1173 K are suggested to be achieved by the oxidationcarbonization cycle of Mo₂C. The low apparent activation energy decreases by the particle size, support structure, grain boundaries and the new possible pathway caused by the oxygen vacancy.

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