

Preparation of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ solid solution and its catalytic performance for oxidation of CH_4 and CO

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Abstract A series of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ ($0 < x \leq 0.5$) catalysts were prepared by the co-precipitation method, and their catalytic performances were investigated for the total oxidation of CO and CH_4 as model reactions. X-ray diffraction (XRD) and Raman spectroscopy results show that $\text{Ce}_{1-x}\text{Fe}_x\text{O}_{2-\delta}$ solid solutions are formed with $x \leq 0.2$. $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ solid solution presents superior catalytic performance for CH_4 and CO oxidation, while $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ with $x > 0.2$ shows less active for CO and CH_4 oxidation. The results of H_2 -temperature programmed reduction (H_2 -TPR), CH_4 -temperature programmed surface reaction (CH_4 -TPSR) and CO-TPSR reveal that, the surface oxygen of catalyst is relevant to CO oxidation, which was promoted by the oxygen vacancies formed in Ce–Fe–O solid solution, while the easier lattice oxygen migration property and the favorable reducibility of the catalysts is responsible for the promoted catalytic performance for CH_4 oxidation.

Introduction

The catalytic combustion of methane and CO oxidation has been studied extensively in recent decades owing to the energy utilization and environmental requirements. For the total oxidation of methane and CO oxidation, the supported noble metal catalysts present an excellent activity [1, 2]. However, the noble metal catalysts are not fully satisfactory owing to the high price and scarce resources. Recently, the ceria-based catalysts have drawn much attention as a

substitute or part substitute for the noble metal catalysts owing to their low cost and good performance for the oxidation reaction [3, 4]. Ceria (CeO_2) has been widely used as a promoter of the catalysts or an oxidation catalyst because of its unique redox property and high oxygen storage capacity [4, 5]. The important role of ceria in the catalytic oxidation reactions is the generation and participation of surface oxygen species and anionic vacancies in the catalytic reactions [6].

It is well known that the redox property and the lattice oxygen mobility of CeO_2 can be profoundly improved by the substitution of Ce^{4+} with other trivalent ions (Pr^{3+} and Tb^{3+}) or smaller homovalent ions (Zr^{4+}) [7, 8]. Given the effects of trivalent ion and smaller size on the structure and properties of ceria, considerable scientific interest is focused on introducing Fe^{3+} ions into the ceria lattice [9]. It was found that Fe substitution of Ce in CeO_2 can distort the sublattice oxygen to promote an activation of lattice oxygen, which is responsible for the better CO oxidation [10]. It has been reported that the mesoporous Ce–Fe mixed oxides present good performance for total oxidation of methane owing to a generation of oxygen vacancies and moderate pore sizes [11]. As an oxygen carrier, the CeO_2 – Fe_2O_3 complex oxides can directly transform methane to synthesis gas by using the lattice oxygen [12]. Li et al. [13] also reported that the chemical interaction between surface iron sites and the Ce–Fe solid solution strongly enhances the reducibility of the Ce–Fe–O materials, and methane tends to be activated on the surface iron sites as the carbonaceous species and hydrogen.

For the CH_4 combustion or CO oxidation, whether the Ce–Fe–O solid solution behaves better performance than the CeO_2 – Fe_2O_3 complex oxide, was reported relatively rarely. Moreover, the influence of Ce–Fe–O solid solution formation on the redox property of CeO_2 – Fe_2O_3 complex

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oxide and the active sites of the Ce–Fe–O solid solution catalyst for methane catalytic combustion and CO oxidation need be illuminated further.

In this paper, the Ce–Fe–O solid solutions were prepared by the co-precipitation method, and their structure and catalytic properties for the CH₄ and CO oxidation were evaluated. The effect of the iron concentration on the properties of the solid solutions has been studied in detail. The difference of the properties between the Ce–Fe–O solid solution and its complex oxides has been discussed based upon the results of structural, redox properties and the catalytic performance.

Experimental

Catalyst preparation

Ce_{1-x}Fe_xO₂ ($x = 0-0.5$, atomic percent) composite oxides were prepared by the co-precipitation method [9]. Ce(NO₃)₃·6H₂O (0.03 mol) and Fe(NO₃)₃·9H₂O (0–0.015 mol) were solved in de-ionized water. The synthesis solution above and 10 wt% ammonia aqueous solution were simultaneously added drop by drop to a precipitating batch containing 200 mL de-ionized water under stirring. After the pH value of synthesis solution reached 8–9, it was heated to 70 °C under stirring and kept for 4 h. Subsequently, the precipitates were filtered and washed with successive de-ionized water, dried at 110 °C overnight and calcined at 600 °C for 4 h in air. After calcination, the solid powder was pressed and crushed to 40–60 mesh. The pure CeO₂ and Fe₂O₃ were prepared by similar procedures described above.

Catalyst characterization

The powder X-ray diffraction (XRD) patterns were performed on a Rigaku D/max 2250VB/PC diffractometer (Rigaku, Japan) with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The N₂ adsorption–desorption isotherms were measured at 77 K with a NOVA 4200e Surface Area and Pore Size Analyzer. Before measurements, the samples were out-gassed at 180 °C under vacuum for 4 h. The surface areas of samples were calculated by the Brumauer–Emmett–Teller (BET) method. The Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a CCD detector at ambient temperature and moisture-free conditions. The emission line at 514.5 nm from an Ar⁺ ion laser (Spectra Physics) was focused, analyzing spot about 0.01 cm, on the sample under the microscope. The Fourier transform infrared (FT-IR) absorption spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer with 32 scans at an effective resolution of 4 cm⁻¹. The sample to

be measured was ground with KBr and pressed into thin wafer for analysis.

H₂-temperature-programmed reduction (H₂-TPR) of samples was conducted with a thermo-conductivity detector (TCD). 50 mg sample was loaded in the U-shaped quartz tube reactor. 10% H₂/N₂ mixture gas of 45 mL min⁻¹ was used at ambient pressure and the heating rate was 10 °C min⁻¹. CH₄-temperature-programmed surface reaction (CH₄-TPSR) and CO-TPSR of samples were performed in a quartz micro-reactor. 100 mg catalyst in the reactor was pretreated at 500 °C for 30 min in 50 mL min⁻¹ 20% O₂/He mixture gas. After the sample was cooled to the room temperature, the sample was heated from the room temperature to 750 °C in 50 mL min⁻¹ of 1% CH₄/He (or 2% CO/He) at a heating rate of 10 °C min⁻¹. The outlet gas was analyzed by a quadrupole mass spectrometer (INFICON Transpector 2). The signals of CH₄, CO, CO₂ were recorded at the $m/z = 15, 28$ and 44 , respectively.

Testing of catalytic activity

The catalytic activity of the Ce_{1-x}Fe_xO₂ catalyst for CO (or CH₄) oxidation was tested in a quartz tube microreactor with 100 mg catalyst at atmospheric pressure. The feed gas was consisted of 1% CO and 10% O₂ (or 1% CH₄ and 4% O₂) balanced by Ar. The flow rate was 50 mL min⁻¹, and space velocity (SV) was 30000 mL g⁻¹ h⁻¹. The reactants and products were analyzed online by gas chromatograph (GC) equipped with TCD.

Results and discussion

Textural and structural properties

The XRD patterns of Ce_{1-x}Fe_xO₂ mixed oxides are shown in Fig. 1. For Ce_{1-x}Fe_xO₂, only diffraction peaks of cubic ceria are observed as $x \leq 0.2$, and with an increase in Fe content ($x > 0.2$) the α -Fe₂O₃ diffraction peaks appear just. After adding Fe in CeO₂, the CeO₂ (111) peak shifts toward higher diffraction angles and the lattice parameters of ceria decrease from 0.5377 to 0.5332 nm (Table 1), which indicates that the Ce_{1-x}Fe_xO_{2- δ} solid solution has been formed after smaller size Fe³⁺ (0.64 Å) substitutes for Ce⁴⁺ (0.97 Å) inside the cubic phase CeO₂ structure [14], and the oxygen vacancies in CeO₂ tend to be formed owing to the charge balance. F. J. Pérez-Alonso et al. [9] also reported that cubic ceria-like (Fe in CeO₂) and hematite-like (Ce in Fe₂O₃) solid solutions can be formed when Fe content is high ($\text{Fe}/(\text{Ce} + \text{Fe}) \geq 0.5$) in the samples calcined at 300 °C, and the cubic ceria-like solid solution structure would be destroyed, after calcination at higher temperature (such as 500 °C).

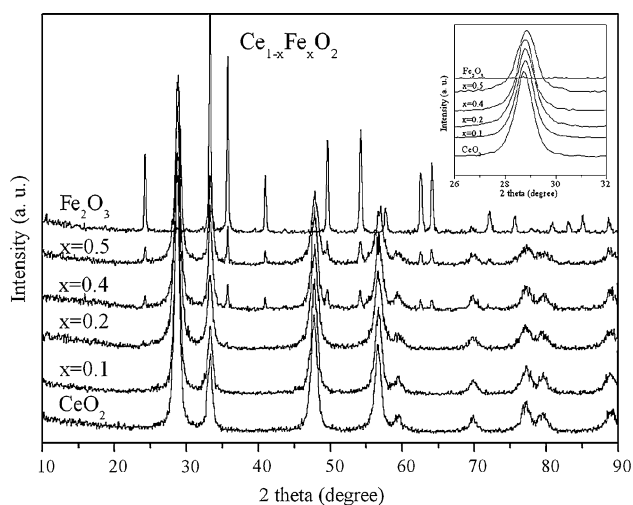


Fig. 1 XRD patterns of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ catalysts

The BET surface areas of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ mixed oxides are shown in Table 1. It is found that the surface area increases obviously with the introduction of Fe in CeO_2 . However further increase in the Fe content from 0.1 to 0.5 leads to the decrease of its BET surface area from 63.6 to 18.3 $\text{m}^2 \text{g}^{-1}$.

Figure 2 shows the Raman spectra of all samples. For all $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ samples, a broad band with relatively high intensity at $\sim 465 \text{ cm}^{-1}$ and a weak band at 1180 cm^{-1} are observed, which are ascribed to the F_{2g} vibration mode and primary A_{1g} asymmetry of CeO_2 , respectively [15], indicating the existence of cubic CeO_2 structure. The band at $\sim 600 \text{ cm}^{-1}$ is linked to lattice defects resulted from the produced oxygen vacancies in the ceria fluorite structure [16]. With the Fe addition in CeO_2 , the band ascribed to the F_{2g} mode of CeO_2 shifts slightly to lower wave number region as shown in the enlarged graphic in Fig. 2, which should be attributed to the formation of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ solid solution with Fe ion replacing Ce ion in CeO_2 lattice, and the nanosized sample in current study [17]. The Fe_2O_3 sample exists the characteristic peaks of $\alpha\text{-Fe}_2\text{O}_3$: A_{1g} at 500 cm^{-1} , E_g at 407 and 612 cm^{-1} , and second harmonic

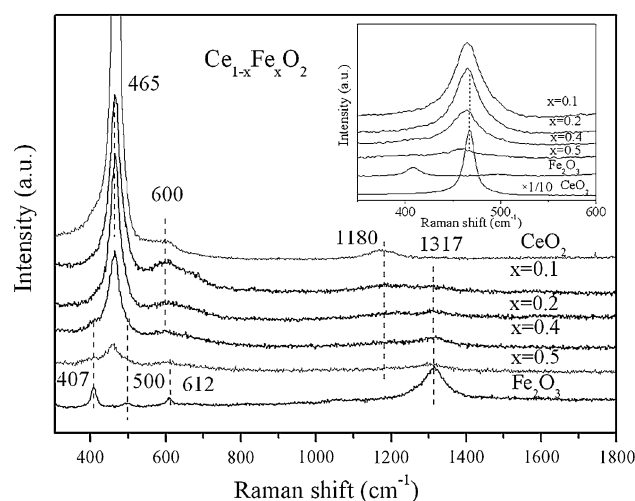


Fig. 2 Raman spectra of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ catalysts

vibration at 1317 cm^{-1} [18]. With an increase in Fe content, the intensity of band at 1317 cm^{-1} enhances obviously, and the band at 1194 cm^{-1} decreases conversely, indicating the formation of $\alpha\text{-Fe}_2\text{O}_3$ on the surface of solid solution. Therefore correlated with XRD results, it shows that only a small part of Fe^{3+} ($x < 0.2$) can be incorporated into the ceria lattice, resulting in the oxygen vacancy formation; with an increase of Fe content in $\text{CeO}_2\text{-Fe}_2\text{O}_3$ sample, $\alpha\text{-Fe}_2\text{O}_3$ has been formed in the sample.

Catalytic performances for CH_4 and CO oxidation

The catalytic performances of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ for CH_4 and CO oxidation are shown in Fig. 3 and the corresponding light-off temperatures are listed in Table 1. In the CH_4 catalytic combustion reaction, CH_4 can be totally oxidized to CO_2 and H_2O , and the catalyst activity is improved obviously because of an addition of Fe in CeO_2 . When $x = 0.1$, the sample exhibits superior activity, the reaction temperature of 50% CH_4 conversion (T_{50}) is $484 \text{ }^\circ\text{C}$. While further increasing Fe amount from 0.1 to 0.5 gradually leads to the

Table 1 BET surface areas, lattice constants, and performances of the catalysts for the oxidations of CH_4 and CO

Catalyst	S_{BET} (m^2/g)	Lattice constant (nm) ^a	Oxidation of CO		Oxidation of methane	
			T_{10} ($^\circ\text{C}$) ^b	T_{50} ($^\circ\text{C}$) ^b	T_{10} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)
CeO_2	33.2	0.5377	284	365	511	615
$\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$	63.6	0.5365	125	188	410	484
$\text{Ce}_{0.8}\text{Fe}_{0.2}\text{O}_2$	44.4	0.5361	138	204	425	497
$\text{Ce}_{0.6}\text{Fe}_{0.4}\text{O}_2$	31.1	0.5358	159	214	428	512
$\text{Ce}_{0.5}\text{Fe}_{0.5}\text{O}_2$	18.3	0.5352	182	247	449	543
Fe_2O_3	9.4	—	220	277	426	499

^a Calculated from the line broadening of the (111) reflection of CeO_2 by the Scherrer equation

^b Reaction temperature of 10 and 50% conversion

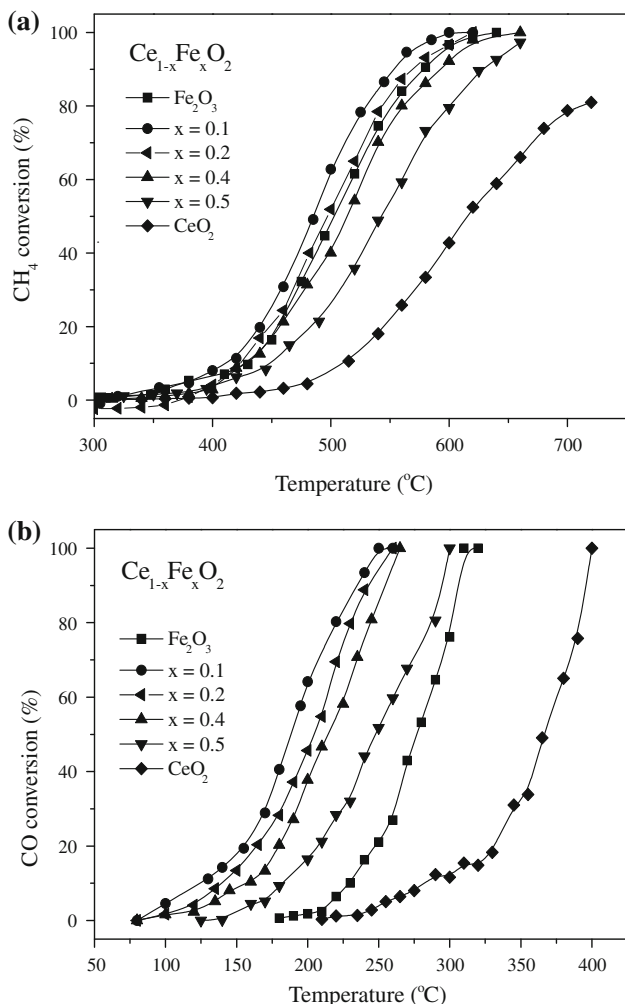
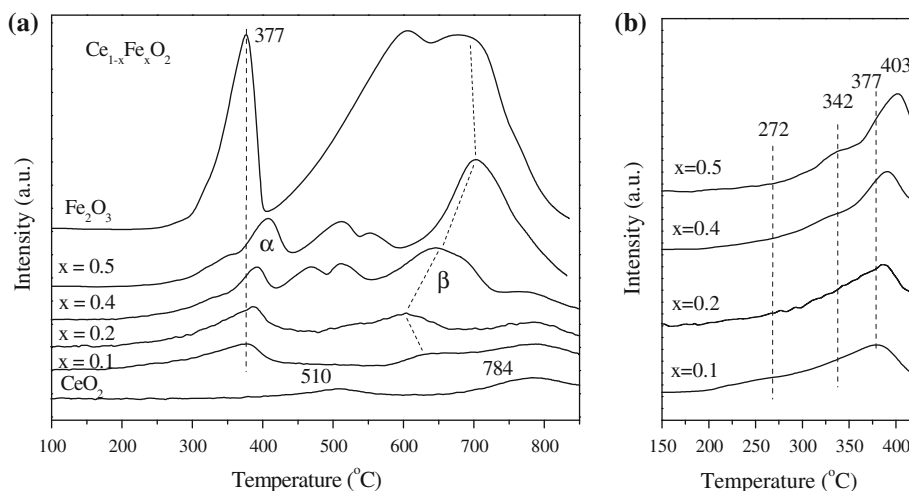


Fig. 3 Light-off curves of the CH₄ (a) and CO (b) oxidation over Ce_{1-x}Fe_xO₂ catalysts

decrease of the catalytic activity. It should be noted that pure Fe₂O₃ shows good performance, almost comparable to the performance of Ce_{0.2}Fe_{0.8}O₂. Bulk iron oxide has been

Fig. 4 H₂-TPR profiles of Ce_{1-x}Fe_xO₂ catalysts



studied as an alternative catalyst for CH₄ combustion, because of its good activity [19]. For CO oxidation, the presence of Fe in ceria can obviously improve the catalytic activity, when $x = 0.1$, Ce_{0.9}Fe_{0.1}O₂ catalyst exhibits superior catalytic activity, such as $T_{10} = 125$ °C and $T_{50} = 188$ °C. However, its activity decreases with an increase of Fe content in the sample. Pure CeO₂ and Fe₂O₃ show poor activity for CO oxidation.

The results above show that Ce_{0.9}Fe_{0.1}O₂ solid solution has an excellent activity for CH₄ and CO oxidation, and changing Fe content in Ce_{1-x}Fe_xO₂ can affect obviously its catalytic activity. Meanwhile, pure Fe₂O₃ exhibits better catalytic performance than pure CeO₂ in the CH₄ oxidation and CO, especially for the deep oxidation of CH₄.

H₂-TPR testing

The H₂-TPR profiles of CeO₂, Fe₂O₃, and Ce_{1-x}Fe_xO₂ mixed oxides are shown in Fig. 4. For Fe₂O₃, there is a sharper peak at 377 °C and a broad band at ~650 °C with two overlapping peaks, which are corresponding to the reduction of hematite (Fe₂O₃) to magnetite (Fe₃O₄) and magnetite to Fe⁰, respectively [20]. In the H₂-TPR profile of CeO₂, two peaks are observed at ~510 and 784 °C, which should be assigned to the reduction of surface and bulk oxygen, respectively [21]. For Ce_{1-x}Fe_xO₂ mixed oxides, more complex TPR profiles are obtained, involving more reduction peaks [14]. In the H₂-TPR profiles of Ce_{1-x}Fe_xO₂ ($x \leq 0.2$) solid solution samples, α peak at 350–400 °C is attributed to the reduction of Fe³⁺ inside Ce–Fe–O solid solution and β peak at 600–650 °C should be ascribed to the reduction of Fe²⁺, and the peak at >700 °C should be because of the reduction of bulk Ce⁴⁺. With an increase in Fe amount ($x > 0.2$), two additional peaks appear between α and β peaks, which should be assigned to the reduction of aggregated Fe₂O₃ on the sample surface. The rise of reduction temperature of α and

β peaks may be explained by the decreased oxygen vacancy in CeO_2 as shown in Raman spectra, resulting in the low reducibility of ceria. As shown in Fig. 4b, the low temperature reduction peaks at <380 °C should be attributed to the reduction of surface oxygen species [22], which shift to higher temperature with an increase of Fe amount in the samples. Moreover, the larger intensity of the peaks at <380 °C in $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ sample supports the fact that more oxygen species could adsorb on the samples because of larger surface area.

In order to evaluate the redox property of the mixed oxides, after H_2 -TPR run, the sample was re-oxidized at 600 °C in O_2 (20 mL min^{-1}) for 0.5 h, then H_2 -TPR of sample was carried out again. The H_2 -TPR profiles of CeO_2 , Fe_2O_3 , $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ and $\text{Ce}_{0.5}\text{Fe}_{0.5}\text{O}_2$ for continuously two times are plotted in Fig. 5. After one cycle of reduction–oxidation, Fe_2O_3 exhibits two small reduction peaks at 505 and 625 °C in the TPR profiles, and the high-temperature peak disappears after two cycles of reduction–oxidation. For pure CeO_2 , three TPR curves are almost the same, which shows that the redox property of CeO_2 is not affected by the treatment of reduction–oxidation and the large reduction peak at >800 °C should be ascribed to the consumption of H_2 by bulk oxygen in CeO_2 [23].

After repeated reduction/oxidation, the low temperature reduction peak of $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ solid solution is located at ~ 465 °C, and that of $\text{Ce}_{0.5}\text{Fe}_{0.5}\text{O}_2$ is at ~ 540 °C. For the pure Fe_2O_3 and CeO_2 , the low temperature reduction peaks are located at higher temperature of ~ 505 and ~ 540 °C, respectively. It can be found that $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ has lower temperature reduction peak after the cycle of reduction/oxidation, which indicates the formation of Ce–Fe–O solid

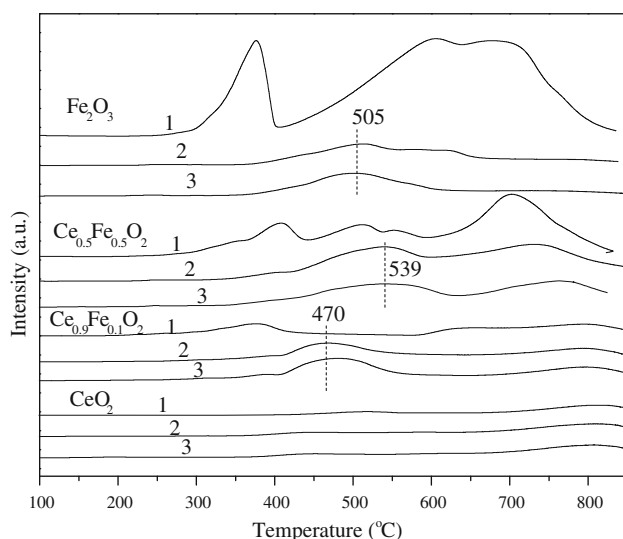


Fig. 5 H_2 -TPR profiles of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ (1) fresh, (2) after one cycle of reduction/re-oxidation and (3) after two cycles of reduction/re-oxidation

solution by Fe incorporating the CeO_2 lattice can improve the oxygen ability of the sample, resulting in better redox property of the $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ sample. Furthermore, the reduction peak area at ~ 465 °C of $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ solid solution is larger than that at ~ 505 °C of Fe_2O_3 . Based on the XRD results, it is suggested that for the sample with high Fe content, Fe_2O_3 remained on the surface would debase the reducibility of catalyst. Therefore, it could be concluded that the facile redox property and the lattice oxygen mobility of CeO_2 can be profoundly enhanced by the formation of Ce–Fe–O solid solution with proper amount of Fe doped into CeO_2 .

CO-TPSR and CH_4 -TPSR testing

CO-TPSR-MS and CH_4 -TPSR-MS testing over pure CeO_2 , Fe_2O_3 and $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ were carried out after the samples were pretreated in 20% O_2 at 500 °C for 1 h, and the results are shown in Fig. 6. It shows from Fig. 6 that CO and CH_4 consumption is accompanied by CO_2 formation.

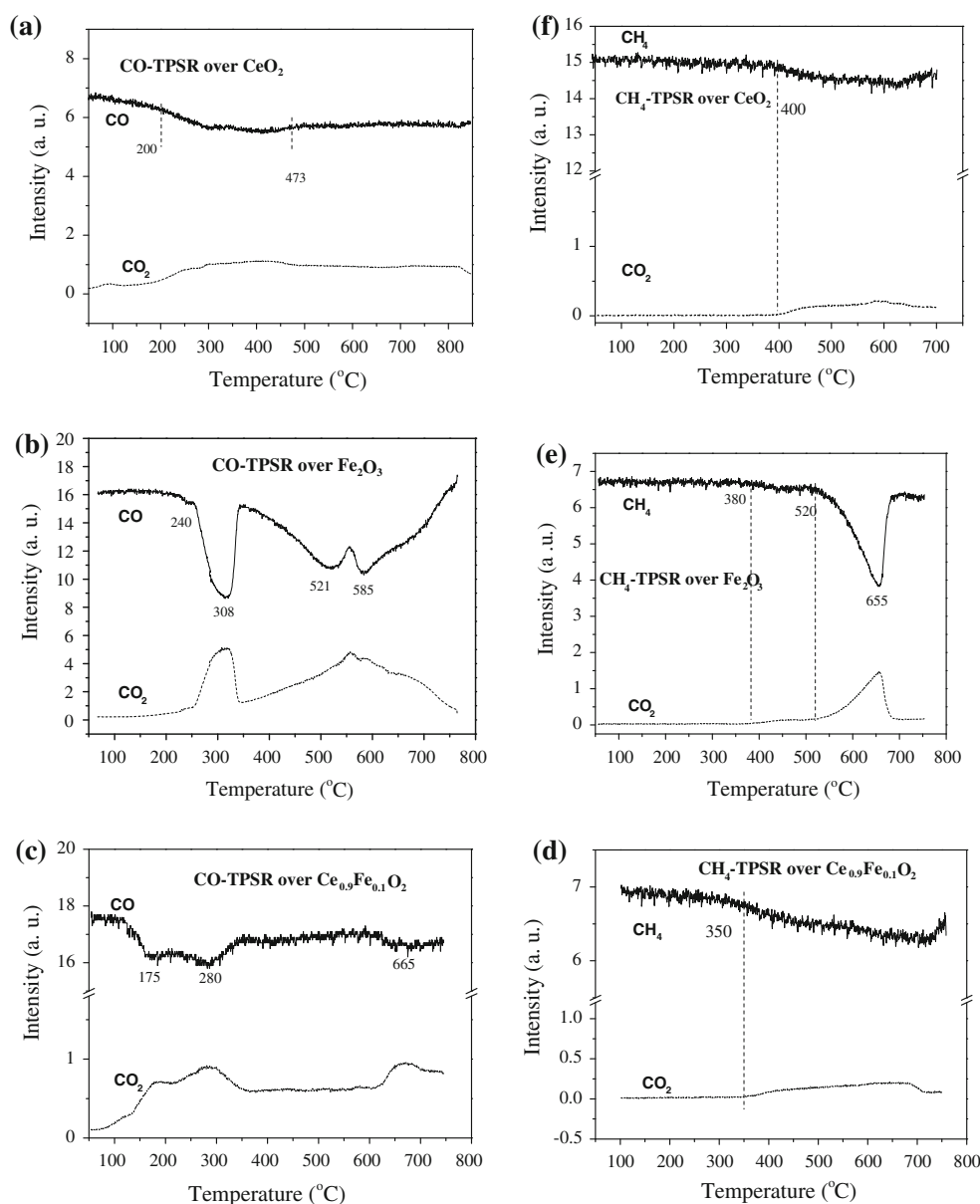
For the CO-TPSR profiles, over CeO_2 , small amount of CO_2 are formed at 200–500 °C (Fig. 6a) and over Fe_2O_3 , the oxidation of CO occurs at 250–350 °C, with the top temperature of CO_2 forming at 308 °C (Fig. 6b); over the $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ solid solution, there are two consumption peaks of CO with the top temperatures of 175 and 280 °C (Fig. 6c). Relating to the T_{50} results of CO oxidation in Table 1, T_{50} is resemble to the top temperature of low temperature reduction peak in the CO-TPSR profiles of $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ and Fe_2O_3 ; however, a weak broad plateau of CO_2 formation of CeO_2 is observed, with T_{50} of CO oxidation located in the middle of this plateau. Combined with the TPR results, it should be suggested that the CO consumption peaks of $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$, Fe_2O_3 and CeO_2 should be ascribed to the reduction of surface oxygen species including the absorbed oxygen and surface lattice oxygen.

The CH_4 -TPSR profile of CeO_2 is similar to that of $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ solid solution, and there is a weak broad plateau of CO_2 desorption at 400–650 °C in the former and in the latter at 350–700 °C. It is indicated that the doping of Fe in CeO_2 promotes its lattice oxygen mobility and makes the oxygen reduction facile, resulting in the benefiting of CH_4 oxidation. In the CH_4 -TPSR profile of Fe_2O_3 , two CH_4 consumption peaks are observed, with very weak at 380–520 °C and at 655 °C, respectively. Relating to the T_{50} (499 °C) of CH_4 oxidation over Fe_2O_3 , the first weak peak is contributed to the activity of Fe_2O_3 for the oxidation of CH_4 .

Discussion about the catalytic activity of Ce–Fe–O solid solution

Compared with the pure CeO_2 , Fe_2O_3 and CeO_2 – Fe_2O_3 mixed oxide with high Fe content, the Ce–Fe–O solid

Fig. 6 CO-TPSR-MS (a, b, c) and CH₄-TPSR-MS (d, e, f) profiles over CeO₂, Fe₂O₃ and Ce_{0.9}Fe_{0.1}O₂



solution shows better catalytic activity for the CH₄ and CO oxidation. The formation of Ce–Fe–O solid solution can increase obviously the surface area of ceria, and promote the redox property of the sample. With further increase of the Fe content in Ce_{1-x}Fe_xO₂ ($x > 0.2$), the redox property and the surface area of catalyst decline severely, resulting in activity decrease for the oxidation reaction. The density functional theory (DFT) calculations [10] showed that the oxygen sublattice was highly distorted in Fe doped CeO₂ which led to formation of long and short M–O (M = Fe, Ce) bonds, and the presence of longer oxygen bonds could improve an activation of lattice oxygen. As shown in XRD and Raman results, only a small part of Fe³⁺ ($x < 0.2$) in Ce_{1-x}Fe_xO₂ sample can be incorporated into the ceria lattice to form a solid solution. As $x > 0.2$, part of Fe in the

form of iron oxide would aggregate on the sample surface and block the oxygen activation of M–O bond, resulting in a decrease in the redox property. Moreover, the iron oxide formed on the sample surface would lower the surface area, which would also debase the activity of the catalysts.

It is well-known that, an increase of the oxygen storage capacity and bulk oxygen mobility of ceria-based catalysts can effectively promote hydrocarbons oxidation reactions [24], and the surface oxygen is benefit to CO oxidation over CeO₂ related catalysts [25]. Therefore, the improving performance of Ce–Fe–O solid solution for the CH₄ oxidation should be because of the promoted oxygen mobility and the facile redox property of the Ce–Fe–O solid solution. The H₂-TPR and CO-TPSR results reveal that more surface oxygen species (including the adsorbed oxygen and

active sublattice oxygen) induced by the oxygen vacancy formation and the distorted lattice oxygen for the Ce–Fe–O solid solution, would contribute to the CO oxidation.

Conclusions

The Ce–Fe–O solid solution was prepared successfully by the simultaneous precipitation method. The concentration of Fe in the $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ sample affects remarkably on the formation of the solid solution and its catalytic performance. As $x < 0.2$, the Ce–Fe–O solid solution can be obtained; as $x > 0.2$, part of Fe is incorporated into CeO_2 lattice and the rest leaves in the form of iron oxide on the surface of sample. The $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$ solid solution exhibits superior catalytic activity for the CH_4 and CO oxidation. With an increase of Fe amount in the sample, its catalytic activity declines gradually. The formation of Ce–Fe–O solid solution obviously enhances the redox property and increases the surface areas, which should contribute to CH_4 oxidation. And the more surface oxygen species formed in the solid solution are propitious to CO oxidation.

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