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The effect of reg	generation period on the selectivity of synthesis gas
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Abstract

Chemical looping partial oxidation of CH₄ is a promising method to produce syngas with suitable H₂/CO ratio, and avoiding risk of explosion and expensive air separation plant. However, regeneration of reduced OCs by O₂ usually leads to the enrichment of surface electrophilic O²⁻ or O⁻ species thus the CO₂ formation and the decrease in total CO selectivity. In this work, it was found that CO selectivity of BaFe₃Al₉O₁₉ hexaaluminate (BF₃A) OC was greatly improved from 58% to 83% by tuning regeneration period with CH₄ conversion of 86%, H₂/CO ratio of 2, syngas yield of 4.2 mmol/g without significant carbon deposition. This resulted from the decrease of regeneration time (from 15 min to 4.2 min) leading to the decline in Fe³⁺ in Al(1), Al(2) and Al(3) sites (Fe¹, Fe² and Fe³) active for combustion of CH₄, and the increase in reduced Fe^{2+} to Fe^0 responsible for the partial oxidation of CH_4 . Consequently, the amount of CO₂ decreased while that of CO increased significantly. In addition, un-oxidized surface Fe⁰ resulted from shorter regeneration period (5 min and 4.2 min) acted as catalysts for dry reforming of CH₄ and CO₂ at the beginning of reaction, which also contributed to the increase of CO formation for these two samples.

Key words: CH₄ conversion; Chemical looping partial oxidation; The improvement of syngas; Regeneration period; Ba-hexaaluminate

1. Introduction

The conversion of methane as the main component of natural gas and shale gas to high value-added chemicals is getting more economically attractive since crude oils have become depleted and natural gas has been more available due to the discovery of shale gas reservoirs.^{1, 2} Currently, methane is industrially transformed to chemicals and fuels through the indirect route, e.g. it is converted to syngas (CO+H₂) and then the syngas is used as feedstock for the production of methanol, and liquid fuels by Fischer-Tropsch synthesis.^{3, 4} Three representative pathways to reform methane to form syngas are steam reforming (SR, equation 1),⁵ dry reforming (DR, equation 2)⁶ and partial oxidation (PO, equation 3).⁷

$$CH_4 + H_2O \rightarrow CO + 3H_2, \Delta H^{\circ}_{298K} = 206 \text{ kJ mol}^{-1}$$
 (1)

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \Delta H^{\circ}_{298K} = 247 \text{ kJ mol}^{-1}$$
 (2)

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2, \Delta H^{\circ}_{298K} = -36 \text{ kJ mol}^{-1}$$
 (3)

The H₂/CO ratio for SR and DR is 3 and 1, respectively, which is not suitable for the downstream process such as methanol production and Fischer-Tropsch synthesis.⁸ Moreover, these two reactions are endothermic and energy intensive. In comparison, PO is mildly exothermic and its H₂/CO ratio is favourable for the downstream process for the production of chemicals.⁹ Unfortunately, this reaction has to require a costly air separation to supply pure oxygen and has risk of explosion because of mixing methane and oxygen, which hamper the industrial implementation of this route.¹⁰ Thus, a novel technique for the conversion of methane to syngas with suitable H₂/CO ratio, and avoiding risk of explosion and expensive air separation plant is highly desired.

Chemical looping partial oxidation (CLPOx) was proposed to overcome these drawbacks above by a two-step method for the production of syngas using lattice oxygen of oxygen carriers (OC).¹¹⁻¹⁶ In this process, CH_4 is reacted with lattice oxygen to form CO and H_2 and then the reduced OC is re-oxidized by air. Lattice oxygen is used to react with CH_4 instead of gaseous oxygen, which allows considerable cost savings without air separation unit and avoids risk of explosion.

Excellent performance of OC with high CH₄ conversion, syngas selectivity, good redox stability and carbon-resistance is of great importance to the realization of this process. Various studies have been contributed to improving syngas selectivity based on the development of novel OC materials.¹⁷⁻²³ Shafiefarhood et al.²⁴ designed a Fe₂O₃@La_{0.8}Sr_{0.2}FeO_{3.5} core-shell redox catalysts for CLPOx of methane in order to avoid the direct contact of CH₄ and Fe₂O₃, which significantly increased the selectivity of CO. Mishra et al.²⁵ found that BaMnO₃ showed higher syngas selectivity than CaMnO₃ did, which was because CaMnO₃ contains significantly higher amounts of loosely bound oxygen species that were highly active for the formation of CO₂. Chen et al.²⁶ reported that syngas yield of Ni-promoted WO₃/Al₂O₃ could be substantially increased by about 2.7-fold in comparison with its unmodified counterpart, which was attributed to that surface-grafted nickel species could effectively activate methane molecules and catalyze the partial oxidation reaction. The studies above focus on the effect of the modification of OC materials on the syngas selectivity.

Besides the variation of OCs, oxidation atmosphere in the re-oxidation process also influences the syngas selectivity in the reduction step greatly.²⁷ More et al.²⁸ found that compared with air oxidation, CO₂ as oxidants could keep Ni in its metallic state which catalyzed the gasification of carbon deposited on Ni thus leading to the increase of syngas selectivity. Zhu et al.²⁹ also discovered that the syngas selectivity of LaFe₃Al₉O₁₉ hexaaluminate OC was much higher when using CO₂ as oxidants than that using O₂. This resulted from that CO₂ could selectively regenerate Fe³⁺-O₅(Tr) and Fe³⁺-O₄(Th) sites which were highly active for the CH₄ partial oxidation to syngas. H₂O as a soft oxidant used to recover OCs was also reported to be able to increase the syngas selectivity in the reduction step. Neal et al.³⁰ used a low concentration of steam (2%) to regenerate iron species to FeO, which avoided the initially complete oxidation reaction of CH₄ resulting in the increase of CO selectivity. Compared with these weak oxidants, using air/oxygen to replenish OCs can usually completely regenerate their structure due to the strong oxidization. Moreover, this process is mildly exothermic, which is highly energy efficient. However, regeneration Page 5 of 37

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of OCs by O_2 as strong oxidants usually results in the enrichment of surface electrophilic O^{2-} and O^{-} species which was highly active for the CO_2 formation, thereby the total CO selectivity decreases. Thus, it is highly desired to enhance the selectivity of syngas when using O_2 as regeneration agent for CLPOx of CH₄.

In our previous work, BaFe₃Al₉O₁₉ hexaaluminate OC exhibited high activity for complete oxidation of CH₄ due to significant CO₂ formation in the initial of reduction reaction leading to low syngas selectivity.^{31, 32} In this paper, its CO selectivity could be greatly enhanced from 58% to 83% by tuning regeneration period with CH₄ conversion of 86%, H₂/CO of 2 without significant increase in amount of carbon deposited. The effect of regeneration period on the micro-structure of OCs was studied in detail by a series of characterization techniques such as HRTEM and ⁵⁷Fe Mössbauer spectroscopy. Then the underlying reason for the improvement of CO selectivity was revealed.

2. Experimental

2.1 OCs preparation

BaFe₃Al₉O₁₉ (denoted as BF₃A) hexaaluminate OC was synthesized by the two-step method proposed by Huang et al.^{33, 34} The first step was to prepare BF₃A precursor, 0.52 g of Ba(NO₃)₂, 6.75 g of Al(NO₃)₃·9H₂O and 2.42 g of Fe(NO₃)₃·9H₂O were dissolved in 52 ml of N,N-dimethylacetamide (DMAC) under stirring overnight at room temperature, and then poured into 15.98 g of NH₃·H₂O and 58.5 ml of DMAC mixed solution under stirring for 0.5 h to form the precursor precipitate. The precipitate was filtered and washed with ethanol for three times. The second step was the resin coating process wherein the precipitate was dispersed in 280 ml of ethanol under ultrasonic treatment for 0.5h and then were added into 17.62 g of resorcinol, 19.46 g of formaldehyde and 8.57g of NH₃·H₂O step by step. After that, the mixture was further treated by ultrasonic for 1 h. Subsequently, the precipitate was filtered, washed with ethanol one time and then dried at 120 °C overnight. Finally, the sample was calcined in argon atmosphere until the temperature reached 1200 °C and then the gas switched to air in high-temperature tube furnace for 6 h.

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For nitric acid washing experiment, a certain amount of OCs was added to nitric acid with the concentration of 1 mol/L and vigorous stirred at room temperature for 3 h. Then, the mixed solution was filtered, washed with ultrapure water for 3 times and dried in an oven at 120 °C overnight.

2.2 OCs characterization

The X-ray diffraction (XRD) patterns were obtained to analyze the crystal phase composition before and after cycling using a PANalytical X'Pert-Pro powder X-ray diffractometer (U=40 KV, I=40 mA) with Cu K_{α} monochromatized radiation (λ =0.15418nm), and the diffraction angle (2 θ) was scanned from 10° to 80°.

The morphology of the hexaaluminates was studied by scanning electron microscopy (SEM) on a JEOL JSM-7800F electron microscope.

Scanning transmission electron microscopy (STEM) and elemental mapping were performed using a field-emission transmission electron microscope (JEOL JEM-2100F). The samples were dispersed in ethanol and then dropped onto a carbon-coated 300-mesh copper grid and dried in an oven.

The ⁵⁷Fe Mössbauer spectra were recorded at room temperature with a spectrometer working in constant acceleration mode with the ⁵⁷Co γ -quantum source in Rh matrix. The powder samples were used approximately 10mg/cm² of natural iron. During preparation of BF₃A OC, 0.02 g ⁵⁷Fe/g Fe was added to improve the signal-to-noise of samples. All spectra were fitted by the MossWinn package and the isomer shifts (IS) were given relative to the centroid of α -Fe at room temperature.

2.3 OCs reactivity evaluation

The performance of as-prepared BF₃A and that after regeneration for different time for CLPOx of CH₄ was investigated in a U-shape quartz fixed bed reactor under atmospheric pressure. OC (0.2g) with a particle size of 20-40 mesh was placed in a quartz tube and a K-type thermocouple was used to monitor the reaction temperature. Prior to each measurement, pure He (50 ml/min) was flowed to the reactor from room temperature to 900 °C to remove the possible impurities on the OC. When the reaction temperature reached 900 °C, the reactions between 5% CH₄ and 5% O₂ were switched Page 7 of 37

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and the total gas flow was kept to 15ml/min. Helium (He) was used as the carrier gas to prevent mixing between methane and gas-phase oxygen. The reduction time was 8 min and the oxidation time was 15min, 6min, 5min and 4.2min. The product components were analyzed by a quadruple mass spectrometer system (InProcess Instruments GAM 200). The mass spectrometer signals were calibrated accurately before the experiment using the calibration gas with known composition. Blank experiment using inert silica with the same void volume at identical conditions suggested low contribution of gas-phase reactions (<2% methane conversion of gas-phase reaction).

The conversion of CH₄ (X), the product selectivity (S), the ratio of H₂/CO (R) and the amount of CO₂ (n_{CO_2}) and CO formation (n_{CO}) in mmol/g during the reduction process were defined as followed:

$$X = \frac{F_{red} \times \int_{0}^{0} y_{CO_2} + y_{CO} dt + V_C}{F_{red} \times y_{CH_{4,in}} \times t} \times 100$$
(1)

$$S_{CO_2} = \frac{F_{red} \times \int_{0}^{t} y_{CO_2} dt}{F_{red} \times \int_{0}^{t} (y_{CO_2} + y_{CO}) dt + V_C} \times 100$$

(2)

t

t

$$S_{CO} = \frac{F_{red} \times \int_{0}^{t} y_{CO} dt}{F_{red} \times \int_{0}^{t} (y_{CO_2} + y_{CO}) dt + V_C} \times 100$$

$$E_{red} \times \int_{0}^{t} (0.5 \times y_{CO}) dt + V_C \qquad (3)$$

$$S_{H_{2}} = \frac{F_{red} \times \int_{0}^{t} 0.5 \times y_{H_{2}} dt}{F_{red} \times \int_{0}^{t} (y_{CO_{2}} + y_{CO}) dt + V_{C}} \times 100$$

$$R = \frac{F_{red} \times \int_{0}^{t} y_{H_{2}} dt}{F_{red} \times \int_{0}^{t} y_{co} dt}$$
(4)
(5)

$$n_{CO2} = \frac{F_{red} \times \int_{0}^{t} y_{co2} dt}{24.4 \times W_{oc}}$$
(6)
$$n_{CO} = \frac{F_{red} \times \int_{0}^{t} y_{co} dt}{24.4 \times W_{oc}}$$
(7)

Where F_{red} is the total volume flow rate of the effluent gas in ml/s, $y_{CH_{4,in}}$, y_{H_2} , y_{CO_2} and y_{CO} are the volume fraction of CH₄ in the inlet gas, and that of H₂, CO₂ and CO in the effluent gas in the reduction step, respectively, W_{OC} is the initial weight of OC in the bed in g, and V_C is the volume of carbon produced in ml which is calculated as:

$$V_{C} = F_{ox} \times \int_{0}^{t} y_{CO_{2,ox}} + y_{CO_{0,ox}} dt$$
(8)

Where F_{ox} is the total volume flow rate of the effluent in ml/s, $y_{CO_{2,ox}}$ and $y_{CO_{2,ox}}$ are the volume fraction of CO₂ and CO in the effluent gas in the re-oxidation step.

The yield of synthesis gas $n(2H_2 + CO)$ was calculated as:

$$n(2H_2 + CO) = \frac{F_{red} \times \int_{0}^{t} (2 \times y_{H_2} + y_{co}) dt}{24.4 \times W_{oc}}$$
(9)

3. Results and discussion

3.1 Reactivity test and structure characterization of BF₃A-x OCs

3.1.1 The effect of regeneration period on the performance of BF₃A OC

Fig. 1 presents the kinetic curves of BF_3A OC in the reduction process after re-oxidation for different time (denoted as BF_3A -x, x indicated oxidation time). It could be seen that CO_2 formation significantly declined with the reduction of regeneration period from 15 min to 4.2 min (Fig. S1(a)). In addition, CO formed earlier after regeneration for shorter period (Fig. S1(b)). For example, it was about 112 s when CO began to form for BF_3A -15 while it decreased to 88 s for BF_3A -6. For

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 BF_3A-5 and $BF_3A-4.2$, CO formed at the beginning of reduction reaction, indicating that CO formation increased with the shortening regeneration period. The results above presented that CO_2 formation significantly decreased while CO increased after regeneration for shorter time.

The amount of CO₂ and CO formed for BF₃A-x is given in Table 1. It could be seen that the former reached as high as 0.38 mmol/g for BF₃A-15 and it decreased with the regeneration time. For BF₃A-4.2, it was only 0.12 mmol/g, about decreased by 3 times. On the other hand, the amount of CO increased from 0.62 mmol/g for BF₃A-15 to 0.83 mmol/g for BF₃A-4.2 with the decrease of regeneration time. The decrease of amount of CO₂ and increase of that of CO formation resulted in the CO selectivity markedly increasing from 58% to 83% with the decrease of regeneration time (Fig. 2a). Despite the regeneration time decreased by almost 4 times, CH₄ conversion, H_2/CO ratio and the amount of carbon deposited changed a little (Fig. 2(b, c, d)), indicating that active species in BF₃A OC for partial oxidation of CH₄ was still recovered. The stability of BF₃A-x during multiple redox cycles was shown in Fig. 3. Their performance was almost constant during 20 redox cycles even though the regeneration time decreased to 4.2 min with CH₄ conversion of 86%, CO selectivity of 87%, H₂/CO ratio of 2 and syngas productivity of 4.2 mmol/g, indicating that good redox stability of BF₃A OC could be maintained even if re-oxidation time decreased by 4 times. It was generally accepted that the enrichment of surface electrophilic O²⁻ or O⁻ species by regeneration of O₂ led to the CO₂ formation in the initial period of reaction thus the decrease of total CO selectivity.35, 36 In the present work, svngas selectivity could be significantly improved due to the decrease of CO₂ and increase of CO formation by tuning regeneration period of O₂.

3.1.2 X-ray diffraction patterns of BF₃A-x OCs

Fig. 4 shows X-ray diffraction (XRD) patterns of BF₃A OC before reaction and after different regeneration time. For fresh BF₃A OC, the diffraction peaks attributed to β -Al₂O₃ phase and MP-type hexaaluminate (JCPDS No. 1-84-1788) were observed. After re-oxidation, the MP-type hexaaluminate for all the samples was transformed completely to β -Al₂O₃ phase, which was in line with the results of our previous

work $^{31, 32}$ In addition, all the diffractogram after re-oxidation shifted to a lower 20 values compared with that of fresh BF₃A and the shifting extent became larger with the decrease of regeneration time (Fig. 4(b)). Meanwhile, the cell parameters of BF₃A after oxidation for shorter time were larger (Table 2), suggesting that the decrease of regeneration time caused that more Fe ions in lower oxidation state could not be oxidized. It was worthwhile to note that diffraction peaks associated with Fe⁰ (JCPDS No. 1-1262) were observed besides β -Al₂O₃ phase for BF₃A-5 and BF₃A-4.2 and its intensity for BF₃A-5 was lower than that for BF₃A-4.2. This could be also confirmed by HRTEM results wherein some sphere particles with size of about 50-100 nm only composed of Fe without Ba, Al and O element were clearly observed on the surface of plate-like hexaaluminates for these two samples (Fig. 5 (a and b)). This should result from shorter regeneration period leading to that Fe⁰ formed in the reduction step was not oxidized in the re-oxidization step. Combined with our results of reactivity test that syngas formed at the beginning of reduction reaction for BF₃A-5 and BF₃A-4.2 (Fig. 1 and Fig. S1(b)), this might be associated with these Fe^0 species resulted from shorter regeneration time.

3.1.3 SEM characterization of BF₃A-x OCs

SEM images of BF_3A -x OCs are presented in Fig. 6. The morphology of BF_3A after regeneration remained unchanged compared with fresh sample still showing typically plate-like hexaaluminate crystallites even though the re-oxidization time decreased by about 4 times, indicating that hexaaluminate structure could be also recovered after regeneration for shorter time.

3.1.4 ⁵⁷Fe Mössbauer spectroscopy of BF₃A-x OCs

Fig. 7 shows ⁵⁷Fe Mössbauer spectroscopy of BF₃A-x and the corresponding parameters are listed in Table 3. For BF₃A-15, two magnetic sextets were observed. One with IS of 0.27 mm/s, QS of 0 mm/s and hyperfine field of 486 KOe was attributed to Fe³⁺ in Al(3) sites (Fe³) in β -Al₂O₃ phase while the other one with IS of 0.47 mm/s, QS of 0.55 mm/s and hyperfine field of 385 KOe was associated with Fe³⁺ in Al(1) sites (Fe¹).²⁴ Their relative area (A) was 16% and 25%, respectively. In addition, two doublets with IS of 0.25 mm/s and 0.7 mm/s were attributed to Fe³⁺ in

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Al(2) sites (Fe²) (48%) and Fe²⁺ (5%), respectively.³⁷⁻⁴⁰ With the decrease of regeneration time to 6 min, the amount of Fe³ and Fe² did not change but that of Fe¹ decreased to 12%, which resulted in the amount of Fe²⁺ increasing to 18%. Further decreasing regeneration time to 5 min, the amount of Fe³ remained unchanged but Fe¹ completely disappeared and that of Fe² decreased to 44% causing that of Fe²⁺ further increased to 32%. Moreover, a new sextet with IS of -0.05 mm/s, QS of -0.08 mm/s and magnetic field of 331 KOe was seen which was associated with Fe^{0,41,42} suggesting that the decrease in regeneration time resulted in that not only Fe²⁺ but also Fe⁰ could not be re-oxidized to Fe³⁺. For BF₃A-4.2, the amount of Fe³ also decreased besides that of Fe^2 further decreasing to 25% as well as that of Fe^{2+} and Fe^0 increasing to 47% and 18%, respectively. ⁵⁷Fe Mössbauer spectroscopy results presented that the shortening of regeneration period caused that Fe¹, Fe² and Fe³ could not be recovered, which led to the decrease of their amount and the increase of that of Fe^{2+} and Fe^{0} . Considering the results of reactivity test, it could be inferred that the decline of CO₂ formation might originate from the decrease of Fe¹, Fe² and Fe³ while increase of CO amount might be due to the enhancement of Fe^{2+} and Fe^{0} .

3.2 Discussion

Our reactivity test results demonstrated that CO selectivity of BF_3A OC in the reduction step increased with the shortening of regeneration period, which resulted from the decrease in amount of CO_2 and the increase in that of CO formation. In the following section, the underlying reason why CO selectivity increased would be uncovered.

3.2.1 The reason for decrease of CO₂ formation for BF₃A-x

⁵⁷Fe Mössbauer spectroscopy of BF₃A-15 and BF₃A-6 after reduction time of 105s and 75s (denoted as BF₃A-15-R and BF₃A-6-R) when no CO formation was observed (Fig. 1(a, b)) was carried out and the results are shown in Fig. S2 and corresponding parameters are listed in Table S1. For BF₃A-15-R and BF₃A-6-R, both Fe³ and Fe¹ completely disappeared and that of Fe² decreased from 54% to 44% compared with BF₃A-15 and BF₃A-6 (Table 4). This result indicated that all of Fe³, Fe¹ and Fe² were responsible for CO₂ formation. The correlation between the total amount of these three crystallographic sites and that of CO_2 formation during reduction reaction is shown in Fig. 8. It could be clearly seen that the amount of CO_2 formation decreased with the total that of Fe³, Fe¹ and Fe², which demonstrated that shortening of regeneration time led to the significant decline in amount of high activity for CH₄ combustion of Fe³, Fe¹ and Fe², thereby the CO₂ formation decreased during reduction reaction.

3.2.2 Active species for syngas formation for BF₃A-x

Our reactivity test results showed that curves of CO concentration differed greatly after regeneration for different time (Fig. S1(b)). For BF₃A-15 and BF₃A-6, CO concentration increased significantly after a fixed reaction time, which was denoted as reaction *i* (Fig. S3). For BF₃A-5 and BF₃A-4.2, small amount of CO could be detected at the beginning of reaction besides reaction *i*, which was denoted as reaction *ii* (Fig. S3). The amount of CO formed in these two reactions was given in Table S2. In the following section, we would identify the active sites for these two reactions separately.

In order to determine active species for reaction *i*, ⁵⁷Fe Mössbauer spectroscopy of deeper reduction (480 s) for these four samples (denoted as BF₃A-x-Re) was performed (Fig. S4 and Table S3). For BF₃A-15-Re, the amount of Fe² decreased from 44% to 18% compared with BF₃A-15-R (Table 4), which was responsible for CO₂ formation during deeper reduction (after reaction time of 105 s) since Fe² was active for combustion of CH₄ as discussed in the last section. In addition, Fe⁰ appeared and its amount reached 18%, which was due to the reduction of Fe²⁺, indicating that the reduction of Fe²⁺ to Fe⁰ contributed to CO formation in reaction *i* ($CH_4 + Fe^{2+} \rightarrow CO + 2H_2 + Fe^0$). Further decreasing regeneration time to 6 min, the amount of Fe⁰ increased to 19% (Table 4 and S3) resulted from enhanced reduction of Fe²⁺, which led to the increase in the amount of CO from 0.62 mmol/g to 0.69 mmol/g (Table S2). For BF₃A-5-Re and BF₃A-4.2-Re, the amount of Fe⁰ further increased by 20% (28%-8%) and 22% (40%-18%) compared with BF₃A-5 and BF₃A-4.2 (Table 4 and S3), resulting in the increase of CO formation to 0.72 mmol/g and 0.78 mmol/g,

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respectively. In order to correlate amount of reduced Fe^{2+} and reactivity, the amount of CO formed in reaction *i* was given in Fig. 9. It could be clearly observed that CO increased with the reduction of Fe^{2+} to Fe^{0} , indicating that the decline of regeneration time led to the enhancement of reduction of Fe^{2+} to Fe^{0} , which was responsible for increased CO formation in reaction *i*. For BF₃A-5 and BF₃A-4.2, small amount of CO formed at the beginning of reaction

(reaction *ii*). TEM results indicated that Fe⁰ nanoparticles were clearly observed on the surface on these two OCs. These Fe⁰ particles might catalyze the dry reforming of CH₄ and CO₂ formed.^{43.45} In order to confirm this, we used nitric acid (1 mol/L) to remove these Fe⁰ particles on the surface at room temperature and then examined if the syngas would form at the beginning of reaction. The X-ray diffraction patterns of BF₃A-5 and BF₃A-4.2 after nitric acid washing showed that the diffraction peaks of Fe⁰ could hardly be detected (Fig. S5). In addition, ⁵⁷Fe Mössbauer spectroscopy of these two samples presented that no subspectra attributed to Fe⁰ could be observed (Fig. S6 and Table S4), indicating that Fe⁰ particles were successfully removed on the surface of these two samples. Moreover, syngas indeed could not be detected for the samples after nitric acid washing (Fig. 10), which gave solid evidence that these Fe⁰ particles resulted from shorter regeneration period acted as catalysts for the dry reforming of CH₄ and CO₂ leading to syngas formation (reaction *ii*: $CH_4 + CO_2 \xrightarrow{Fe^0} 2CO + 2H_2$) in the initial of reaction for BF₃A-5 and BF₃A-4.2.

According to the discussion above, manipulating regeneration time led to the remarkable drop of Fe¹, Fe² and Fe³, highly active for CH₄ combustion, and increase in the amount of reduced Fe²⁺ to Fe⁰, responsible for the partial oxidation of CH₄. As a result, CO₂ decreased and CO formation increased significantly. Specially, for BF₃A-5 and BF₃A-4.2, appearance of Fe⁰ catalyzed the dry reforming of CH₄ and CO₂ at the beginning of reaction, which also contributed to the increase of CO formation. This provided a possible strategy to decrease CO₂ formation in the initial of reaction due to the surface electrophilic oxygen species when OCs were regenerated by O₂ thus increasing CO selectivity.

4. Conclusions

In this work, the effect of regeneration period on the syngas selectivity of BF₃A OC was investigated. It was for the first time found that tuning regeneration period could remarkably increase its CO selectivity from 58% to 83% with CH₄ conversion of 86%, H₂/CO ratio of 2, syngas yield of 4.2 mmol/g without evident carbon deposition, which was due to significant decline of CO₂ and increase of CO formation. The decrease of regeneration time resulted in decline of Fe¹, Fe² and Fe³ which exhibited high activity for combustion of CH4 thus CO2 formation, and the enhancement of reduced Fe²⁺ to Fe⁰ which was responsible for the partial oxidation of CH₄ thus the increase of CO formation. Specially, for BF₃A-5 and BF₃A-4.2, un-oxidized Fe⁰ formed in the reduction step due to shorter regeneration period catalyzed dry reforming of CH₄ and CO₂ leading to small amount of CO formation in the initial of reaction, which provided the possibility to decrease the amount of CO₂ at the beginning of reaction resulted from surface electrophilic O²⁻ or O⁻ species if reduced OCs were regenerated by O₂ thus the increase of CO selectivity. The present work proposes a novel method to enhance the syngas selectivity based on the manipulation of regeneration period.

Supporting Information. Additional experimental results of the performance and characterization of catalysts including Figures S1– S6 and Tables S1–S4

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Figure 1 The kinetic curves of reduction process for BF_3A -x hexaaluminate OC (a) BF_3A -15, (b) BF_3A -6, (c) BF_3A -5 and (d) BF_3A -4.2



Figure 2 CO and CO₂ selectivity (a), CH₄ conversion (b), H₂/CO ratio (c) and C yield (d) of BF₃A-x

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Figure 3 Performances of BF_3A -x during multiple redox cycles, CH_4 conversion (a), CO_2 selectivity (b), CO selectivity (c), H_2 selectivity (d), H_2/CO ratio (e) and synthesis gas yield (f)





Figure 4 X-ray diffraction patterns of fresh BF₃A and BF₃A-x, (a) 10-80° and (b) $30-40^{\circ}$





Figure 5 STEM images of (a) BF_3A -5, (b) BF_3A -4.2, EDS elemental mapping and line scans results of BF_3A -5 and BF_3A -4.2



Figure 6 SEM images of BF₃A-15 (a), BF₃A-6 (b), BF₃A-5 (c) and BF₃A-4.2 (d)





Figure 8 Correlation between the percentage of $Fe^3+Fe^1+Fe^2$, and the amount of CO_2 over BF_3A -x OCs



Figure 9 Correlation between the percentage of reduced Fe^{2+} to Fe^{0} and the amount of CO formation in reaction *i* over BF_3A -x OCs



Figure 10 The kinetic curves of reduction process for BF_3A-5 (a) and $BF_3A-4.2$ (b) after nitric acid washing

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Table 1 The amount of CO ₂ and CO over BF ₃ A-x OCs							
Samples	CO_2 (mmol/g)	CO (mmol/g)					
BF ₃ A-15	0.38	0.62					
BF ₃ A-6	0.32	0.69					
BF ₃ A-5	0.20	0.76					
BF ₃ A-4.2	0.12	0.83					

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Table 2 Cell	parameters of BF ₃ A-x OCs
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Samples	$a_0=b_0$ (Å)					
	β -Al ₂ O ₃	MP				
BF ₃ A	5.625	5.7322				
BF ₃ A-15	5.6354	-				
BF ₃ A-6	5.6354	-				
BF ₃ A-5	5.6425	-				
BF ₃ A-4.2	5.6444	-				

OC	IS ^a	QS^b	Hc	$A^d(\%)$	Assignment	Lattice oxyger
	(mm/s)	(mm/s)	(KOe)			(mmol/g)
BF ₃ A-15	0.25	0.84	-	54	Fe ²	
	0.47	0.55	385	25	Fe ¹	
	0.27	0	486	16	Fe ³	1.67 ^e
	0.70	1.30	-	5	Fe ²⁺	0.18^{f}
BF ₃ A-6	0.27	0.82	-	54	Fe ²	
	0.47	0.60	428	12	Fe ¹	
	0.31	-0.01	493	16	Fe ³	1.44 ^e
	0.92	1.25	-	18	Fe ²⁺	0.63 ^f
BF ₃ A-5	0.27	0.83	-	44	Fe ²	
	0.31	-0.03	484	16	Fe ³	1.05 ^e
	0.85	1.32	-	32	Fe ²⁺	1.13 ^f
	-0.05	-0.08	331	8	Fe ⁰	
BF ₃ A-4.2	0.26	0.75	-	25	Fe ²	
	0.41	-0.25	487	10	Fe ³	0.62 ^e
	0.90	1.25	-	47	Fe ²⁺	1.65 ^f
	0	0	330	18	Fe ⁰	

om temperature ⁵⁷Fe Mössh Table 3 Ro . fDE A

^bQuadrupole splitting;

^cMagnetic field

^dRelative area

eLattice oxygen coordinated with Fe³, Fe¹ and Fe², calculated as

 $\frac{1}{M} \times 3 \times \frac{A(Fe^3 + Fe^2 + Fe^1)}{100} \times 0.5$, where M indicated molar weight of BF₃A

^fLattice oxygen coordinated with Fe²⁺, calculated as $\frac{1}{M} \times 3 \times \frac{A(Fe^{2+})}{100}$

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Table 4 (Comparison	of the	amount	of I	Fe	species	in	samples	after	reduction	for
different t	ime										

Samples	A (%) ^a						
	Fe ³	Fe ¹	Fe ²	Fe ²⁺	Fe ⁰		
BF ₃ A-15	16	25	54	5	0		
BF ₃ A-15-R	0	0	44	56	0		
BF ₃ A-15-Re	0	0	18	64	18		
BF ₃ A-6	16	12	54	18	0		
BF ₃ A-6-R	0	0	44	56	0		
BF ₃ A-6-Re	0	0	19	62	19		
BF ₃ A-5	16	0	44	32	8		
BF ₃ A-5-Re	0	0	15	57	28		
BF ₃ A-4.2	10	0	25	47	18		
BF ₃ A-4.2-Re	0	0	15	45	40		

^aRelative area

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