A facile synthesis of CuCe and CuCeFe mixed-oxide catalysts by solution combustion method for catalytic methane combustion

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Abstract. In this research, the solution combustion method was used to synthesize non-noble catalysts including copper-cerium (CuCe) and copper-cerium-iron (CuCeFe) mixed-oxides for catalytic combustion of methane. The effects of Cu contents (5, 10 and 15 wt%) and Fe addition were investigated. The synthesized catalysts were characterized by XRD, N₂-physisorption, and H₂-TPR. The results showed that increasing Cu content exceeds 10 wt% for a series of CuCe catalyst, leading to a collapse textural structure and formation of larger CuO phase. It resulted in the substantial drop of the catalytic activity for methane combustion. Furthermore, incorporation of Fe into Cu-Ce mixed oxides causes the formation of Fe₂O₃ and Ce-Fe-O solid solution, stabilizing the textural properties, enhancing the oxygen vacancies and oxygen mobility. The superior catalyst was 15CuCeFe because it revealed the highest methane conversion at 500 °C and relatively high conversion at a lower temperature. It can be seen that solution combustion is a facile method to prepare the mixed-oxide catalysts and incorporating the metal promoters. The Cu, Ce and Fe metals play a significant role in catalytic methane combustion not only enhancing reactants (methane and oxygen) activation but also improving the physical properties.

1. Introduction

Methane is high abundance because it is a major component in natural gas, methane hydrate, and biogas. The latter is also accounted as renewable energy which many countries try to increase the utilization portion. Methane is generally used as heat-generating fuel due to its abundance, low cost, and higher H/C ratio suggests lower CO₂ emissions [1]. However, conventional methane combustion is operated at high temperature, which causes environmental problems due to the emitting of low-concentration of unburned methane and the formation of NOₓ at high combustion-temperature [2]. Therefore, catalytic combustion of methane has been widely garnered attention because it could solve those mentioned problems such as lower combustion-temperature, enhancing thermal efficiency and inhibiting NOₓ emission [1,2].

Noble metals such as Pt and Pd catalysts have been proven to be high activity for catalytic methane combustion. However, the high cost, low availability and low thermal stability limited their wide applications. It is widely accepted that the reducibility and oxygen vacancy concentration of the oxide catalyst significantly affects the catalytic activity for methane combustion [3]. Therefore, non-noble metal oxides have been potentially interest because of the cheaper and their excellent oxygen storage capacity and oxygen mobility. CeO₂ catalyst is widely studied for the oxidation reactions such as CO
oxidation, volatile organic compounds oxidation, and etc. owing to its excellent properties for the reactions such as redox properties, high oxygen storage capacity, high oxygen mobility, and ability to stabilize highly-dispersed metal on its surface [4]. However, CeO₂ suffers from low thermal stability, therefore, many researchers have been developed the CeO₂ catalyst by incorporating metal promoters. CuO-CeO₂ demonstrated better thermal stability due to its strong Cu-O-Ce interaction which also plays an important role in the hydrocarbons activation [5]. Furthermore, Fe promoter also enhancing oxygen vacancies and mobility and stabilizing the porous structure by the formation of Ce-O-Fe solid solution [6,7]. Hence, the tri-metal oxides catalysts may suit for the catalytic methane combustion. Solution combustion is a facile method to produce mixed metal oxides in one-pot because of the mixing of precursors in aqueous solution allows the formation of porous nanoparticle powders with uniform composition, rapid, eco-friendly (water as solvent) and scalable for the industry [8].

In this research, we used the solution combustion method to synthesize non-noble catalysts including copper-cerium (CuCe) and copper-cerium-iron (CuCeFe) mixed-oxide catalysts for catalytic combustion of methane. The effects of copper content (5, 10 and 15 wt%) and Fe promoter were studied. The catalysts were characterized by XRD, N₂ physisorption, and H₂-TPR. It is found that solution combustion is a facile method for synthesizing Ce-Fe-O solid solution, stabilizing textural properties, oxygen properties, and hence catalytic combustion of methane.

2. Experimental

2.1. Catalyst preparation.
First, desired amount of Cu(II) nitrate trihydrate, Ce(III) nitrate hexahydrate, Fe(III) nitrate nonahydrate, and urea were dissolved in 15 ml of deionized water with a fuel/oxidizer ratio of 1. Then, the solution was stirred until a clear solution was obtained and transferred to a preheated open-muffle furnace at 400 °C to induce self-sustained combustion. After that, the combustion powder was crushed and further calcined at 550 °C for 3 h with a heating rate of 10 °C/min. Two series of catalysts were prepared and assigned as xCuCe and xCuCeFe (Ce: Fe = 0.44: 0.56 molar ratio), where x is the copper content in weight percent (5, 10 and 15 wt%) of the sample.

2.2. Catalyst characterization.
The XRD measurement was used to determine the bulk crystalline phases of catalysts. The XRD patterns were recorded by Shimadzu XRD-7000 in the range 20 from 10° to 80° with Cu - Kα using the conditions of 30 kV and 20 mA. The crystallite sizes were determined from XRD data using the Scherer equation. Nitrogen physisorption was used to determine the BET surface area, the average pore size diameter and the pore volume of the catalyst using Micrometritrics ASAP 2010. The catalysts were firstly pre-treated in a helium gas flow of 50 ml/min at 180 °C for 3 h. After cooled down to the ambient temperature, the weight of the dried sample was recorded. The volume of N₂ was measured at different partial pressure of N₂ at -196 °C. Temperature-programmed reduction of H₂ (H₂-TPR) was used to examine the reducibility of catalysts using a Micrometritrics Auto Chem 2910 instrument. Approximately, 100 mg of catalyst was placed in a U-shape quartz reactor. The catalyst was pre-treated in a nitrogen flow rate of 30 ml/min at 150 °C for 1 h with a heating rate of 10 °C/min. Then, the system was cooled down to 100 °C. The TPR profile was recorded in 30ml/min of 10% H₂/N₂ atmosphere from 100 °C to 800 °C with a ramp rate of 10 °C/min and held at 800 °C for 1 h. During the reduction process, the produced-water in the process was trapped by the liquid nitrogen.

2.3. Catalytic methane combustion.
The catalytic methane combustion reaction was carried out in a stainless steel tube with outside diameter 6.35 mm and tubular flow reactor at ambient pressure. Approximately, 100 mg of catalyst was packed at the middle of the reactor tube between two quartz wool layers, which was inside a muffle furnace. The flow rate of the gas reaction was 1% CH₄, 20% O₂ in Ar balance and operating temperature ranging from 300 °C to 500 °C. First, the catalyst was preheated at 300 °C in Ar flow for 30 min with a heating rate of 5 °C/min. After that, Ar flow was switched to the reaction gas before heated to 500 °C with a similar ramp rate. The product gases were analyzed by gas chromatography
equipped with TCD (The conductivity detector) with Molecular Sieve 5-A and Porapak Q columns. The catalytic activity is expressed in terms of %methane conversion.

3. Results and discussion

3.1. Physical properties.

The XRD patterns of all catalysts (figure 1) showed the peaks at 28.3°, 32.8°, 47.3°, and 56.2°, corresponding to the face-centered cubic (FCC) fluorite type oxide structure of CeO$_2$. For a series of CuCe catalyst, the characteristic peaks at 35.5° and 38.7° which are specified to CuO (002) and CuO (111) planes (JCPDS 34-394) which appeared only for 10 and 15CuCe samples. This indicated that the CuO phase highly dispersed on CeO$_2$ for 5CuCe but the agglomeration of CuO occurred when increasing the Cu content to 10 and 15 wt%, in agreement with Delimaris’s work [5]. This phenomenon was also detected for a series of CuCeFe samples. However, the characteristic peak of Fe$_2$O$_3$ at 35° could not be obviously observed, it may due to the peak of α-Fe$_2$O$_3$ was near the CuO peak at 35.5° or Fe might be highly dispersed in the samples/only small amount of Fe$_2$O$_3$ was formed. It should be noted that 5CuCeFe exhibited the peak near 35.5° and the spike peak at 54° without the peak at 38.7°, confirming that it was not CuO particles but Fe$_2$O$_3$ was formed in a series of CuCeFe catalysts. Interestingly, the peaks of CeO$_2$ in the Fe-containing samples slightly shifted to higher diffraction angles and peak broadening was also observed, demonstrating that the Fe ions incorporated into CeO$_2$ lattice to form a Ce–Fe–O solid solution [7]. The calculated crystallite sizes of CeO$_2$ by Scherer equation are shown in Table 1. For a series of xCuCe samples were 11.8, 8.9 and 16.8 nm for 5, 10 and 15 wt% Cu, respectively. While the crystallite sizes of xCuCeFe samples remained in the range 7.8 to 9.4 nm. This demonstrated that addition of Fe retarded the agglomeration of CeO$_2$ crystallinity which can be attributed to the formation of Ce–Fe–O solid solution.

Figure 1. XRD patterns of all catalysts.

Table 1 also presented the summary results of N$_2$ physisorption and EDS. The BET surface area of 5, 10 and 15CuCe were 15.5, 19.7 and 7.6 m$^2$/g, respectively. The enormous drop for 15CuCe sample may due to the higher combustion temperature when increased the portion of Cu precursor. The BET surface area were 15.5, 15.2 and 21.8 m$^2$/g for 5, 10 and 15CuCeFe, respectively. Obviously, the BET surface area of 15 wt% Cu did not decline when Fe was added in the sample. Moreover, the addition of Fe into CuCe samples also increased pore volume and mean pore diameter at least about 2 times, corresponding to the [9]. The physical properties demonstrated that the addition of Fe inhibited the
sintering of CuCe oxides and improved the textural properties during the solution combustion synthesis.

| Catalyst   | Crystallite size of CeO2 (nm) | S_BET (m²/g) | Pore volume (cm³/g) | Mean pore diameter (nm) | T₂5 (°C) | X₅₀₀ (%) |
|------------|-------------------------------|--------------|----------------------|-------------------------|-----------|----------|
| 5CuCe      | 11.8                          | 15.5         | 0.02                 | 6.0                     | 425       | 43       |
| 10CuCe     | 8.9                           | 19.7         | 0.02                 | 4.2                     | 413       | 46       |
| 15CuCe     | 16.8                          | 7.6          | 0.01                 | 4.8                     | >500      | 20       |
| 5CuCeFe    | 8.1                           | 15.5         | 0.04                 | 11.5                    | 479       | 47       |
| 10CuCeFe   | 9.4                           | 15.2         | 0.05                 | 12.6                    | 479       | 46       |
| 15CuCeFe   | 7.8                           | 21.8         | 0.07                 | 12.9                    | 440       | 57       |

3.2. Temperature-programmed reduction of H₂ (H₂-TPR).

H₂-TPR profiles are shown in figure 2. The main reduction region of CuO was in the range of 125-280 °C, which can be attributed to the reduction of Cu²⁺ to Cu⁺ (2CuO + H₂ → Cu₂O + H₂O) and Cu⁺ to Cu (Cu₂O + H₂ → 2Cu + H₂O), respectively [5]. For 5 and 10 wt% of Cu for both series revealed the main peak at approximately 180 °C and this peak was shifted to a higher temperature when increased Cu content to 15 wt%. The low-temperature peak is generally assigned to the very small CuO particles while the high-temperature peaks are larger CuO particles [10]. This is consistent with the XRD results as CuO crystallite can be found for the 15 wt% Cu sample. For a series of CuCeFe catalysts, the additional broad peaks between 375 to 720 °C appeared and the center shifted to lower temperature from 610 to 570 and 560 °C when increase Cu to 10 and 15 wt%, respectively. This region could be assigned to the α and β peaks, corresponding to the reduction of surface oxygen and bulk oxygen of surface layer Fe³⁺ and Ce⁴⁺ (430 °C), and Fe³⁺ in the Ce-Fe-O solid solution (560 – 610 °C), respectively [7]. This may due to the CuO facilitate the reduction of Fe³⁺ in the Ce-Fe-O solid solution [9].

3.3. Catalytic methane combustion.
Figure 3 presents the catalytic activity of catalysts for methane combustion as a relationship between methane conversion and reaction temperature. The CO gas could not be observed for all samples, indicating that the catalytic methane combustion produced only CO2. In order to compare the catalytic activity, it is expressed in two functions including temperature at 25% methane conversion (T25) and methane conversion at 500 °C (X500), which are shown in Table 1. The results showed that 5 and 10CuCe gave a nearly similar catalytic performance as T25 were 425 and 413 °C and X500 were 43 and 46% for 5 and 10CuCe samples. However, the catalytic performance significantly dropped for 15CuCe (T25 > 500 °C and X500 = 20%), which can be attributed to the collapse textural properties as seen from the larger crystallite size and the drop of BET surface area. Moreover, the separate phase of CuO at higher Cu loading influenced the drop of methane combustion activity was also reported [11], in agreement with the H2-TPR profile.

Figure 3. Methane conversion as a function of reaction temperature.

In addition, both of 5 and 10CuCeFe also gave a nearly similar catalytic performance (T25 = 479 °C and X500 = 47%). The best catalyst in this series was 15CuCeFe (T25 = 440 °C and X500 = 57%). It should be noted that 5 and 10CuCeFe had lower catalytic performance than 5 and 10CuCe at 475 °C and less, however, the methane conversion was sharply increased to even slightly higher when the temperature was raised to 500 °C. This behavior can be observed for 15CuCeFe as well. Li et al. [6] reported that dispersed Fe2O3 on the surface of catalyst can improve the methane combustion. Thus, the superior catalytic activity at high-temperature of CuCeFe catalysts might be explained by the creation of Ce-Fe-O solid solution and relatively higher reducibility, improving physical properties and reactant activation. The reduction of Fe2O3 by methane at temperature above 300 °C may cause the less-active in low-temperature range of the CuCeFe catalysts [7].

Conclusion
Increasing Cu content to higher than 10 wt% for a series of CuCe catalyst by solution combustion method leads to a collapse textural structure and formation of larger CuO phase, resulting in the substantial drop of the catalytic activity for methane combustion. Incorporation of Fe into Cu-Fe mixed oxides causes the formation of Fe2O3 and Ce-Fe-O solid solution, improving the physical properties, oxygen vacancies, and oxygen mobility. The superior catalyst was 15CuCeFe because it gave the highest methane conversion at 500 °C and relatively high conversion at lower temperature. Solution combustion is a promising method to prepare the mixed-oxide catalysts and incorporating the
promoters in one-pot. The Cu, Ce and Fe metals play a significant role in catalytic methane combustion not only providing active sites for reactants (methane and oxygen) activation but also improving the physical properties.

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