

Catalytic combustion properties of nanocomplex oxide for natural gas *

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Abstract The catalysts of copper oxide supported on cerium dioxide were prepared by different methods for methane catalytic combustion. The effects of copper content in the catalysts and calcination temperatures of the catalysts on the catalytic activity are investigated. Results show that the complex oxide catalyst exhibits high catalytic activity for methane combustion due to the synergistic effect of CuO and CeO₂. The catalyst prepared by impregnation is more active than that prepared by controlled coprecipitation even if CuO content is the same. When $W(\text{CuO}) < 13\%$, the light-off temperature and full conversion temperature for the CH₄ reaction decrease with the increasing of CuO content in the catalysts. However, when the copper content is above 13%, the excess CuO has a negative effect on the catalytic activity owing to the formation of bulk CuO particles. A proper calcinations temperature of 650 °C can lead to a high dispersion of CuO and accordingly can enhance the catalytic activity of the composites.

Keywords: natural gas, cerium dioxide, copper oxide, catalytic combustion, catalytic activity.

Combustion of methane is a superior alternative to combustion of coal or long-chain hydrocarbons in power generation and other processes, because it has the potential to reduce the emission of greenhouse gases. Due to the high hydrogen to carbon ratio, the energy generated in methane combustion is two times higher than that generated in coal combustion for emitting the same amount of CO₂. However, methane requires a higher flame temperature for stable combustion than other hydrocarbon, due in part to the absence of carbon-carbon bonds in the molecule, which makes it relatively unreactive.

Catalytic combustion of methane and natural gas has been studied as an alternative to gas-phase homogeneous combustion. The use of a suitable catalyst can lead to oxidation of the fuel without a flame and decrease the combustion temperature at which a stable flame is produced and maintained^[1], thus can minimize the production of NO_x. The use of a catalyst also allows combustion to occur at high levels of excess air, leading to a more complete combustion and reduced hydrocarbon emission. Traditionally, noble metals such as platinum and palladium have been used as catalysts of methane combustion and showed excellent catalytic activity at low temperature. However, they suffer from sintering and vaporization at 800 °C, which can lead to a significant loss of catalytic activi-

ty^[2]. Recent efforts have been made to examine complex metal oxides substitutes for noble metal as catalysts for methane combustion. The results in this paper show that CuO/CeO₂ as a catalyst is highly active and certainly heat-resistant for methane combustion. The above studies indicate that the high activity of the composites should be attributed to synergistic chemical effects between CuO and CeO₂ in methane combustion, owing to an intense interaction between them, which makes the main active component CuO disperse high activity on the catalyst surface. Meanwhile, CeO₂ as an oxygen storage medium may have improved oxygen storage properties of the catalytic materials, which is helpful to the formation of lattice oxygen^[3]. Considering the rich resource of rare-earth metals in our country, it is necessary to investigate the performance of them in methane combustion.

1 Experiment

1.1 Preparation of catalysts

CeO₂ was prepared by thermal decomposition of cerous nitrate for 4 h at 650 °C in air. The Brunauer-Emmett-Teller (BET) surface area of the obtained material powder was about 50 m²/g. The supported CuO/CeO₂ catalysts were prepared by the conventional wet impregnation method^[4] and the CeO₂ powder

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was impregnated throughout by aqueous solution of $\text{Cu}(\text{NO}_3)_2$ with different concentrations. The prepared samples were dried for 18 h in an oven at $120\text{ }^\circ\text{C}$ and then calcined at $650\text{ }^\circ\text{C}$ in air for 4 h. The samples with 6.3% CuO (w/w) were also calcined at $800\text{ }^\circ\text{C}$ and $1050\text{ }^\circ\text{C}$ respectively to examine the influence of calcination temperature. The catalysts prepared by the impregnation method are denoted as CuO/CeO_2 .

For comparison, CuO/CeO_2 powders were also prepared by controlled coprecipitating an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$. The reaction was induced by dropwise addition ammonium hydroxide, and the solution pH was between 2 and 10. After precipitation, the slurry was aged for 24 h, and then centrifuged, washed three times with deionized water, dried at $120\text{ }^\circ\text{C}$ for 18 h and ground to break up any weak agglomerates^[5]. The dried powder was calcined in air for 4 h at $650\text{ }^\circ\text{C}$. These samples are denoted as Cu-Ce-O_2 .

1.2 Characterization and activity evaluation of catalysts

X-ray diffraction (XRD) analyses of the catalyst samples were performed on an X'pert X-ray Diffractometer from Holland with $\text{Cu K}\alpha$ ($\lambda = 0.15406\text{ nm}$) radiation. BET surface areas of the catalyst samples were determined on the ST08 Auto-Physical Adsorption meter from Beijing Auto-Analyzing Factory by nitrogen adsorption method. Measurements of the CuO Content were performed on Canon 3013 X-ray Fluoroscope made in Japan. All catalytic activity testings were performed on a fixed-bed flow reactor under atmospheric pressure. The reaction temperature was monitored by a thermocouple placed at the top of the packed catalyst bed. Typically 300 mg catalyst was used for evaluation. The typical feed gas consists of 1% CH_4 and 20% O_2 balanced by N_2 for methane oxidation activity tests. The total space velocity was $5.0 \times 10^4\text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. The product gas stream was analyzed by a gas chromatograph with a thermal conductivity detector. The schematic diagram of the catalytic evaluation system is shown in Fig. 1.

2 Results and discussion

2.1 Catalytic activity of the catalyst samples for methane combustion

Figure 2 shows that pure CuO has certain catalytic activity for methane combustion. However,

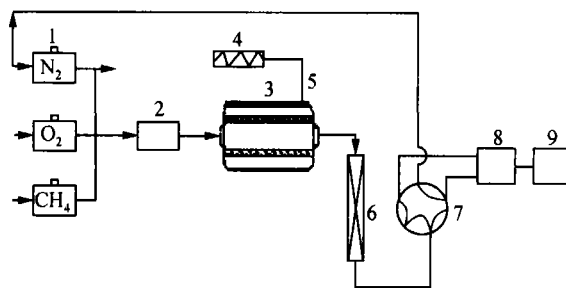


Fig. 1. Schematic diagram of the catalytic evaluation system. 1, Flow meter; 2, gas mixer; 3, fixed-bed reactor; 4, temperature controller; 5, thermocouple; 6, gas purifier; 7, six-through valve; 8, gas chromatograph; 9, processing system.

compared to other complex catalysis, its activity is very poor and remarkably declines when the temperature rises up to $680\text{ }^\circ\text{C}$ ^[6]. The result implies that chemical synergism effects exist between CuO and CeO_2 in nanocomposites. Such synergism effects make the activities of the sample catalysts significantly higher than that of pure CuO or pure CeO_2 . Therefore, we suppose that there are two synergism aspects^[7]: (1) The reducibility and the excellent oxygen storage of CeO_2 are helpful for the formation of lattice oxygen, which is the main active oxygen species at high temperature stage for methane combustion. (2) Because the valences and atomic diameter of Cu^{2+} are different from that of Ce^{4+} , the crystal surface defects, such as oxygen vacancies, are easily formed, which can enhance the oxygen adsorption behavior.

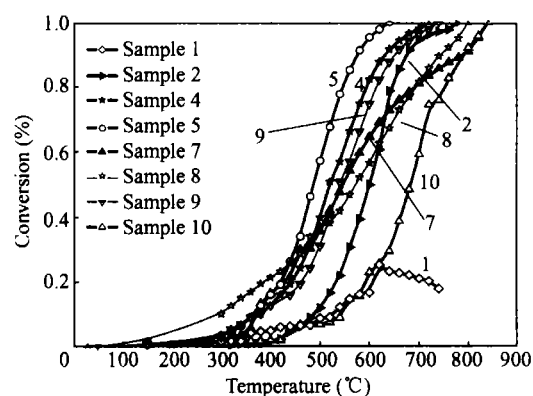


Fig. 2. Catalytic activities of different catalysts calcined at $650\text{ }^\circ\text{C}$ for methane combustion.

It can be seen from Table 1 that the light-off temperatures of all samples are almost below $400\text{ }^\circ\text{C}$ except samples 1, 2 and 10. Fig. 2 also shows that except samples 1, 7 and sample 10, the full combustion temperatures (temperature at which methane

conversion is 90%) of all samples are lower than 700 °C, and specifically, sample 5 has the highest activity and the temperature of full combustion is 570 °C.

Table 1. Catalytic characteristic of samples^{a)}

Samples	W(CuO) (%)	A(m ² ·g ⁻¹)	T _{10%} (°C)
1 CuO	100.00	6.65	500
2 CuO/CeO ₂ (0.1 M)	0.68	13.29	490
3 CuO/CeO ₂ (0.3 M)	1.20	33.05	420
4 CuO/CeO ₂ (0.5 M)	6.30	31.36	370
5 CuO/CeO ₂ (0.7 M)	7.80	30.80	370
6 CuO/CeO ₂ (1.0 M)	8.50	28.82	380
7 CuO/CeO ₂ (1.5 M)	13.00	11.79	370
8 Cu-Ce-O	0.68	20.83	300
9 Cu-Ce-O	4.00	31.62	370
10 Cu-Ce-O	6.00	27.74	450

a) T_{10%} is the light-off temperature, at which CH₄ conversion is 10%; W(CuO) is the percentage of CuO in the catalysts calcined at 650 °C; A is the specific surface.

2.2 Effect of the preparation methods on catalytic activities

The experimental results also show that the preparation methods have a dramatic effect on the catalytic activities of the catalytic materials. In Table 1, samples 2 and 8, samples 4 and 10 have respectively the same CuO content, sample 8 has higher surface area and lower light-off temperature than sample 2, but the catalytic activity of sample 2 at high temperature is much greater than that of sample 8 (Fig. 2). Similarly, Fig. 2 shows that sample 4 has higher catalytic performance and activity than sample 10. In Table 1, the light-off temperatures of samples 5 and 9 are both 370 °C, their BET surface areas are almost identical. However, these samples were prepared using different methods. They had different CuO contents and their catalytic activities were also much different (Fig. 2). In Fig. 3, a faint CuO diffraction peak indicating the formation of some bulk CuO appears in the XRD pattern of sample 7, which shows that the CuO content leading to the formation of bulk CuO is 13% CuO (w/w) for the samples prepared with impregnation method, while for those prepared by coprecipitation method, the corresponding CuO content is reduced to 6% (w/w) (sample 10), at which the formation of CuO crystal phase begins. The study of the catalytic activity of these materials reveals that: (1) Different preparation methods can lead to different particle size and specific surface of the sample catalysts. CuO prepared by impregnation method can be dispersed better on the surface of the

catalysts than that prepared by coprecipitation method. (2) The sample catalysts prepared by impregnation method can lead to higher BET surface areas when CuO contents are the same.

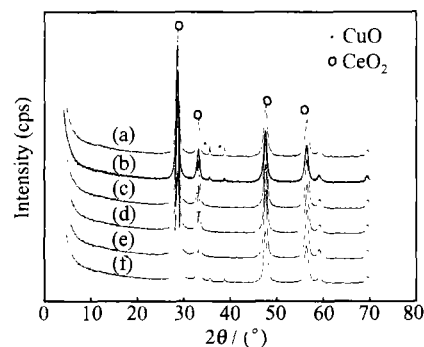


Fig. 3. XRD patterns of the catalysts. (a) Sample 7; (b) sample 5 (calcined at 800 °C); (c) sample 5; (d) sample 4; (e) sample 8; (f) sample 10.

2.3 Effect of the CuO content on catalytic activities

The CuO contents in samples are examined to determine the optimum composition of the catalyst. Table 1 shows that the BET surface areas of the sample catalysts reach the maximum when CuO contents are between 1.2% and 7.8%. At the same time, T₁₀ declines gradually with the increasing CuO content. T₉₀ also has the same tendency, which can be seen from Figs. 2 and 4. These results show that the activities of catalysts increase with CuO contents within the range of 1.2%—7.8%. Figures 2 and 4 also show that the catalytic activity declines obviously when the CuO content reaches 13% (the impregnation concentration is more than 1.5 mol·L⁻¹). As the T₉₀ rises up to 800 °C, the temperature difference of 430 °C can be achieved between the T₉₀ and the T₁₀. Fig. 3 displays only the CeO₂ peaks in the XRD pattern and there are no CuO peaks when the CuO content is below 13%. However, when the CuO content reaches this amount, there are both CeO₂ and CuO peaks in the pattern, which means that bulked CuO is formed on the surface of the catalyst. Based on the characteristics and activities of the sample catalysts discussed above, it can be concluded that it is the bulked CuO on the surfaces that reduces the BET surface areas, and accordingly leads to the worse activities. Dong et al.^[8] pointed out that CuO can spontaneously disperse on the surface of CeO₂ with the content of 12 μmol/m². When the CuO content is below this value, CuO will disperse very well on the surface. However, when the content is above this

value, crystal CuO is formed. These results agree well with the results obtained in this work.

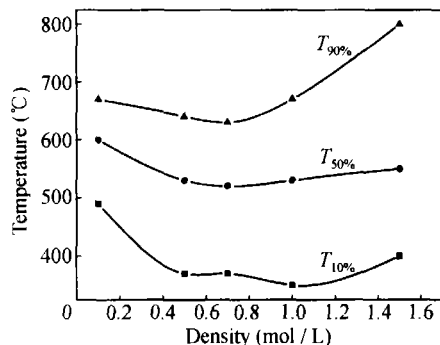


Fig. 4 Comparisons of $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ of the catalysts with different CuO contents. $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ represent temperature, at which CH₄ conversion is 10%, 50% and 90%.

2.4 Effect of calcination temperature on catalytic activities

Selecting sample 4 as an example, the effect of calcination temperature on catalytic activity of materials was studied (Fig. 5). When sample 4 was calcined at 800 °C, its BET specific surface area reduced to 12.57 m²/g, whereas its $T_{10\%}$ rose up to 560 °C. Interestingly, no evident change happened to its $T_{90\%}$. Such result implies that this catalyst is heat-resistant to a certain degree. Fig. 3 shows that both the CeO₂ and CuO peaks can be found in the XRD pattern when the sample is calcined to 800 °C, which means the formation of bulk CuO. In addition, when calcined to 1050 °C, the BET surface area declines to 7.3 m²/g, which corresponds to the faint catalytic activity. All these discussions can reveal that the catalyst calcined at 650 °C has the highest catalytic activity.

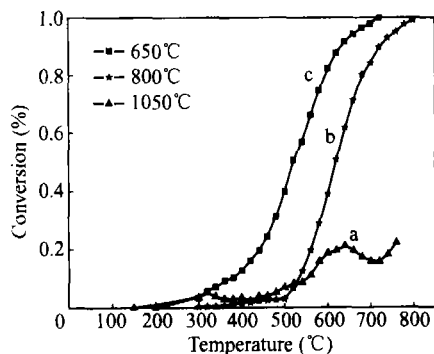


Fig. 5. Comparison of the catalytic activities of catalyst containing 6.3% CuO calcined at (a) 1050 °C, (b) 800 °C, and (c) 650 °C.

3 Conclusion

The catalysts of copper oxide supported on cerium dioxide have been prepared by the wet impregnation method and controlled coprecipitating, and their catalytic activities for methane combustion have been investigated. Our conclusions are as follows:

(1) CuO/CeO₂ catalyst is catalytically active for methane combustion. When the CuO content is appropriate, its light-off temperature may reach 350 °C and the temperature of full combustion may be 570 °C.

(2) The CuO content can significantly affect the catalytic activity, which declines when CuO% is more than 13% due to the formation of bulked CuO on the material surface. The catalytic material containing 6.8% CuO (w/w) by impregnation preparation has the highest activities.

(3) CuO/CeO₂ catalyst is heat-resistant. When calcined at 800 °C, the catalyst will still keep its catalytic activity. But the appropriate calcination temperature is 650 °C and the enhancement of catalytic activity can be attributed to the high dispersion performance of CuO on the surface of CeO₂ and the synergistic effects between CuO and CeO₂.

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