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The microstructure and methane catalytic combustion of ceria composite materials modified with tourmaline particles

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ABSTRACT

The ceria (CeO_2) composite catalysts were prepared by sol-gel method via adding the different amounts and particle sizes of tourmaline particles. The effects of additive tourmaline on the microstructure and methane catalytic combustion of the composite materials were investigated. It was revealed that the CeO_2 nanoparticles modified with tourmaline got smaller crystallite size and the composite materials had the higher catalytic activity. As adding 2 wt% of tourmaline particles (mean particle size = 180 nm), the crystallite size of CeO_2 nanoparticles reduced to 40.2 ± 0.1% compared with the control; the ignition and complete conversion temperature of methane combustion were successfully lowered to 411 °C and 470 °C, respectively.

1. Introduction

As a kind of clean energy, natural-gas (mainly methane) has the advantage of large storage, high calorific value, low price and small pollution. In the past decades, the novel methane-based technologies, such as natural-gas vehicles, has been widely developed and desirable alternative to currently used gasoline or diesel [1]. But the unburned methane in combustion is the main reason of greenhouse effect, which possesses a 25 times higher global warming potential than carbon dioxide (CO_2) [2]. Additionally, NO_x also appears in the combustion procedure over 1300 °C. Consequently, it is an effective approach to abate the non-conversion methane and NO_x emissions through the highly-efficient catalytic oxidation of methane at a lower temperature [3–5]. Recently, the common catalysts is composed of noble metals or perovskite-type composite oxides, which need the more modification or carrier to improve their specific surface area and thermal stability for promoting their catalytic activity [6–8].

As a well-known and extensively studied rare earth oxide, CeO_2 has attracted considerable attention for its promising application in catalysts. Because of the efficient oxidation-reduction cycle between Ce^{4+} and Ce^{3+} [9–14], CeO_2 has the excellent ability to store and release oxygen, which is widely used in catalytic oxidation reaction such as methane catalytic combustion [15–24]. The microstructure of CeO_2 nanoparticles, including the crystallite size and their accumulation, could affect its specific surface area and the molar fraction of exposed oxygen on the active facets, which is important to strengthen its catalytic activity [25–28]. As a common addition of catalysts, the complex borosilicate mineral tourmaline possesses exceptional properties because of the heteropolar structure. It was found that the properties of tourmaline, including the spontaneous polarization and far-infrared radiation, could promote the nucleation of crystal and accelerate their growth in the preparation procedure, which resulted in the more and smaller nanoparticles [29–31]. Therefore, this study prepared CeO_2 nanoparticles by sol-gel method via adding different tourmaline particles to research their microstructure and the catalytic combustion

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Table 1
The crystallite size, S_{BET} and methane combustion temperature of different catalyst samples.

Samples[a]	Proportion of tourmaline (wt%)	Ratio of crystallite size (%)[b]	S_{BET} (m^2/g)	T_{50} of CH_4 (°C)	T_{90} of CH_4 (°C)
Control	–	100.0[c]	28.39 ± 0.92	520	>600
2.0%T_{800}/CeO_2	2.0	70.1 ± 0.1	43.57 ± 1.13	476	551
2.0%T_{500}/CeO_2	2.0	62.3 ± 0.4	44.03 ± 0.80	462	549
2.0%T_{280}/CeO_2	2.0	48.5 ± 0.2	52.94 ± 0.67	455	512
0.5%T_{180}/CeO_2	0.5	63.7 ± 0.5	37.64 ± 0.56	505	580
1.0%T_{180}/CeO_2	1.0	56.9 ± 0.3	45.67 ± 1.29	449	546
2.0%T_{180}/CeO_2	2.0	40.2 ± 0.1	63.74 ± 0.66	411	470
3.0%T_{180}/CeO_2	3.0	49.5 ± 0.2	48.85 ± 0.78	445	517

[a] The subscript of sample mark showed the tourmaline particle size in different samples.
[b] The mean crystallite size of CeO_2 nanoparticles (D value) was calculated using XRD results through the Scherrer equation, and the ratio of crystallite size was obtained by D_{sample} to $D_{control}$.
[c] The $D_{control}$ was 20.4 ± 0.3 nm (as 100%).

of methane, which provided a facile technology to prepare catalyst nanoparticles with the high specific surface area and catalytic activity.

2. Experimental

For the tourmaline/CeO_2 composite catalyst samples, $Ce(NO_3)_3 \cdot 6H_2O$, citric acid and tourmaline particles (chemical formula is $NaFe_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$) with different particle sizes and amounts were added into deionized water and fully mixed. The molar ratio of the cerium ion and citric acid was 1:3. Firstly, the different samples were stirred for 3 h at 65 °C, the sol were formed and gradually turned to the gel with the evaporation of water. The gel samples were quietly maturated for 1 h at 65 °C and overnight at room temperature. Thus the samples were dried at 120 °C for the decomposition of citric acid. Finally the grinded tourmaline/CeO_2 composite catalysts and pure CeO_2 were prepared by heat treatment at 600 °C for 2 h. For the control sample, the synthesis procedure of pure CeO_2 was the same as the above preparation except adding tourmaline. The catalyst samples with different ultimate proportion of tourmaline were shown as Table 1. In the preparation, $Ce(NO_3)_3 \cdot 6H_2O$, citric acid and other chemicals used were analytical reagents and purchased from Kermel Ltd., China.

The particle sizes of additive tourmaline were detected by laser diffraction particle size analyzer (Malvern Mastersizer 2000, UK). The far-infrared radiation performance of different tourmaline particles were tested by Fourier transform infrared spectroscopy (FTIR, BRUKER-80V, Germany). The far-infrared emission intensity (I) of the blackbody (B, as the control) and different tourmaline particles samples (T) were detected in the wavenumber of 500–2000 cm^{-1} (corresponding to wavelength range of 5–20 μm) at 80 °C and 120 °C, respectively. The far-infrared emissivity of tourmaline particles were calculated according to the formula: $\eta_E = (IT_{120°C} - IT_{80°C})/(IB_{120°C} - IB_{80°C})$, and the control blackbody as 100%. For the spontaneous polarization of tourmaline, the electrical conductivity of the deionized water (0.875 g tourmaline particles in 200 mL water, the amount of tourmaline was the same as the addition of 2 wt% in samples) was observed by a digital conductivity meter (DDS-11AT, China).

The catalyst samples were characterized via X-ray diffraction (XRD, BRUKER D8 Focus, Germany) with Cu Ka radiation ($\lambda = 0.15406$ nm, 2θ range with 20–85°). The average crystallite size of catalyst samples could be calculated using XRD results through the Scherrer equation and Jade 6.0. The morphologies and microstructure of the catalysts were observed by scanning electron microscopy (SEM, FEI Nova Nano SEM450, US, under the accelerating voltage of 1.00 kV) and transmission electron microscopy (TEM, PHILIPS Tecnai G2 F20, US, under the accelerating voltage of 200 kV) with energy dispersive spectroscopy (EDS, EDAX Genesis Apollo XL, US). The multiple point Brunauer–Emmett–Teller (BET) surface area of different samples were determined by nitrogen adsorption measurements (Quantachrome, Autosorb-iQ, USA) at 77 K after degassed at 150 °C for 3 h. The catalytic performance of the catalysts samples were test through the ignition temperature (T_{50}) and complete conversion temperature (T_{90}) of methane (CH_4)

Table 2
The far-infrared emissivity of tourmaline and the electrical conductivity of deionized water with tourmaline.

D_{50} of tourmaline particles (nm)	Far-infrared emissivity of tourmaline[a] (%)	Electrical conductivity of deionized water[b] (μs/cm)
800	89.8	1.94 ± 0.02
500	91.2	2.03 ± 0.01
280	92.4	2.12 ± 0.02
180	93.3	2.23 ± 0.01

[a] The far-infrared emissivity of black body (as the control) was 100%.
[b] The electrical conductivity of deionized water without tourmaline was 1.57 ± 0.01 μs/cm.

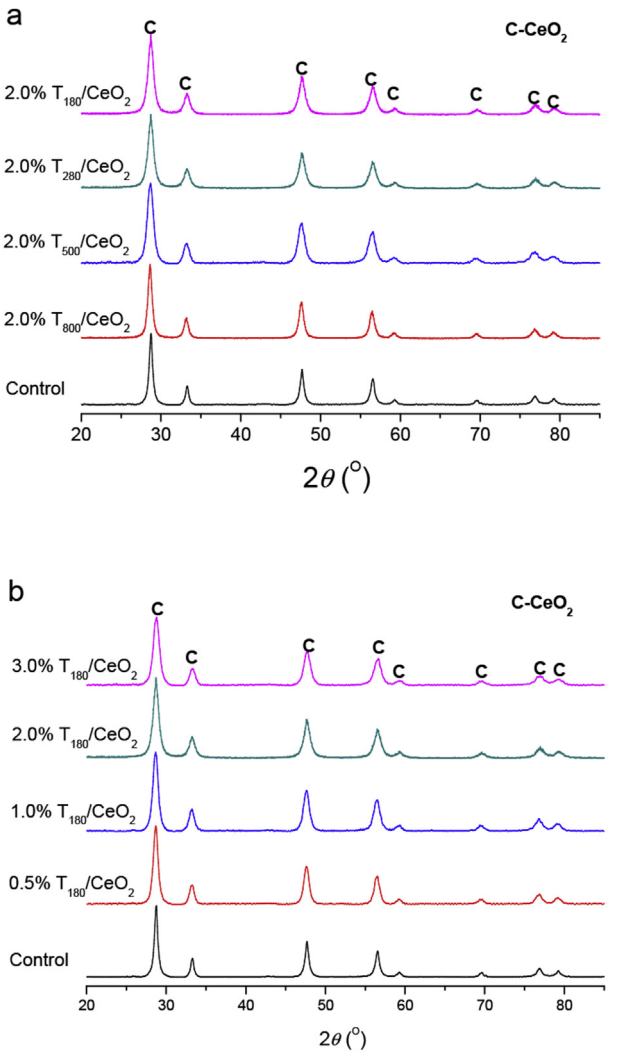

Fig. 1. XRD patterns of catalyst samples with different sizes (a) and amounts (b) of tourmaline particles.