



Insight into the improvement effect of the Ce doping into the SnO₂ catalyst for the catalytic combustion of methane



Cheng Liu^a, Hui Xian^b, Zheng Jiang^c, Lihua Wang^c, Jing Zhang^d, Lirong Zheng^d, Yisheng Tan^e, Xingang Li^{a,*}

^a Collaborative Innovation Center of Chemical Science & Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science & Technology, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, PR China

^b School of Computer Science & Software Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

^c Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, PR China

^d Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, PR China

^e State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Science, Taiyuan 030001, PR China

ARTICLE INFO

Article history:

Received 12 February 2015

Received in revised form 2 April 2015

Accepted 20 April 2015

Available online 21 April 2015

Keywords:

Ce dopant

SnO₂ catalyst

Catalytic combustion of methane

Surface Sn⁴⁺ cations

Mars–van Krevelen model

ABSTRACT

Herein, we report the performance of the catalytic combustion of methane over the Ce-doped SnO₂ catalysts. Doping with Ce increases the surface areas, decreases the crystallite sizes, and activates both the surface metal cations and surface oxygen species. Upon methane combustion, the surface Sn⁴⁺ cations are active sites, and the surface lattice oxygen plays an important role, as well. Kinetics results suggest that the activation energy (E_a) and pre-exponential factor (A) are determined by the reducibility and the area-specific quantity of the surface Sn⁴⁺ cations, respectively. The Sn_{0.7}Ce_{0.3}O₂ catalyst exhibits the highest area-specific rate because of its lowest E_a and relatively bigger A values. Its turnover frequency is five times higher, as compared with the SnO₂. The reaction pathways upon the Sn-rich catalysts (SnO₂ phase) follow the Mars–van Krevelen model, while they become more complex upon the Ce-rich ones (CeO₂ phase). Additionally, these SnO₂-based catalysts display the high water resistance.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Methane, an economical and clean alternative to fuels, is widely used in power plants and new energy vehicles. However, the emission of the unburned methane will cause the serious greenhouse effect, which is approximately 25 times higher than carbon dioxide [1].

The catalytic combustion technology is a promising strategy to solve this problem by directly oxidizing methane into carbon dioxide and water. Noble metal based catalysts, such as platinum and palladium oxide, are effective in the catalytic combustion of methane [2–7]. Unfortunately, these catalysts are expensive and easily sintered at high operating temperatures. Therefore, upon this reaction there is a strong desire to design and synthesize non-noble metal catalysts, such as the reported Co_{1-x}Zr_xCr₂O₄ [8], Ni_{1-x}Ce_xO₂ [9], Mn_{1-x}Ce_xO₂ [10], Mn_{1-x}Ni_xO₂ [11], and perovskite-type catalysts [12–14].

SnO₂-based materials have a lot of active surface oxygen species, as well as oxygen vacancies [15,16]. Consequently, they are regarded as one of potential alternatives for noble metal based catalysts in specific catalytic reactions, such as removal of nitrogen oxides [15,17] and CO oxidation [18,19]. It was reported that doping Cr [20] and Fe [21] into the SnO₂ catalyst could enhance the catalytic performance for methane combustion, probably due to the increased amount of the active oxygen species [20,21].

The CeO₂-based materials are well known because of their high oxygen storage capacity (OSC) [22–26], which are strongly related to the reversible Ce⁴⁺ ↔ Ce³⁺ redox reaction [22]. Attempts have been made to increase the amount of the Ce⁴⁺/Ce³⁺ redox couples, and thus, to increase the OSC by substituting a part of Ce with other elements, such as Zr [22], Ti [23], Hf [24], and Sn [25,26]. Because the reversible Sn⁴⁺ ↔ Sn²⁺ redox process involves two-electron transfer, the OSC of the Ce_{1-x}Sn_xO₂ materials are higher than other CeO₂-based materials, such as Ce_{1-x}Zr_xO₂ [25,26] and Ce_{1-x}Ti_xO₂ [26]. Accordingly, the SnO₂-CeO₂ composite oxides may highly active as a potential oxidation catalyst [26].

Up to now, few reports deeply discussed the reaction mechanism upon the catalytic combustion of methane over the SnO₂-based catalysts. Additionally, the roles of surface oxygen

* Corresponding author at: School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, PR China. Tel.: +86 22 27892275; fax: +86 22 27892275. E-mail address: xingang.li@tju.edu.cn (X. Li).

species, such as surface adsorbed oxygen and surface lattice oxygen, are still debated for the specific catalysts [27,28]. Despite of the expected high performance for the catalytic combustion of methane over the SnO₂–CeO₂ composite oxides, little attention has concerned this catalyst system. Herein, we report the catalytic performances of the Sn_{1-x}Ce_xO₂ composite oxides upon the methane combustion reaction. The Sn_{1-x}Ce_xO₂ catalysts were characterized by the X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, H₂ temperature-programmed reduction (H₂-TPR), O₂ temperature-programmed desorption (O₂-TPD), X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structures (XAFS), and CH₄ temperature-programmed surface reactions (CH₄-TPSR). We intrinsically clarified the effect of the Ce dopant on the structures and physiochemical properties of the SnO₂-based catalysts. Thereafter, we determined the active species including the metal cations and oxygen species by combination of the above mentioned characterizations and kinetics measurements. On this basis, we calculated and analyzed the turnover frequency (TOF) data via the surface active metal cations. We discussed the factors determining the activation energy (*E_a*) and pre-exponential factor (*A*). The possible reaction mechanism, as well as the rate determining step, was proposed accordingly.

2. Experimental

2.1. Catalyst preparation

The SnO₂, CeO₂, and Sn_{1-x}Ce_xO₂ (*x* = 0.1, 0.3, 0.5, and 0.7) catalysts were prepared by the co-precipitation method. A stoichiometric amount of SnCl₄·4H₂O and/or Ce(NO₃)₃·6H₂O (Tianjin Guangfu Technology Development Co., Ltd.) was dissolved together in distilled water. Thereafter, an aqueous ammonia solution was added to the mixed solution by keeping pH 9. The obtained precipitates were filtered and washed with distilled water till no Cl⁻ was detected by the 0.1 mol L⁻¹ AgNO₃ solution. The achieved powder was dried at 120 °C overnight, and then calcined at 650 °C in flowing air (300 mL min⁻¹) for 6 h. The resulting catalysts were named as Sn_{1-x}Ce_xO₂ (*x* = 0.1, 0.3, 0.5, and 0.7). The notation “*x*” represents the theoretical molar proportion of Ce to substitute Sn.

For comparison, the 0.1CeO₂/SnO₂ catalyst with a molar ratio of Sn:Ce = 9:1 was prepared by the impregnation method. Briefly, the SnO₂ support prepared as described above was added to the Ce(NO₃)₃ aqueous solution under continuous stirring. The solution was heated at 80 °C to remove water. The formed powder was dried at 120 °C overnight, and then calcined at 650 °C in flowing air (300 mL min⁻¹) for 2 h.

2.2. Catalyst characterizations

The XRD tests were conducted with a Bruker D8-focus diffractometer, using Cu Kα (*λ* = 0.15418 nm) as the radiation source. The X-ray tube was operated at 40 kV and 40 mA. The lattice parameter was determined by the Rietveld refinement method using the JADE 6.0 software. The crystallite size (*D*) was calculated by Scherrer equation:

$$D = \frac{0.89\lambda}{(B\cos\theta)} \quad (1)$$

here, *λ* is the wavelength of the radiation source (0.15418 nm); *B* is the half width of the strongest diffraction peak in the radian unit; and *θ* is its diffraction angle.

The specific surface area (SSA) was determined by a N₂ physisorption experiment using an automatic gas adsorption system (NOVA 2000, Quantachrome Co.) at -196 °C.

The Raman spectra were recorded with a Raman spectrometer (in via Reflex, Andor) equipped with the NIR laser source (785 nm,

objective × 100) and TE-cooled CCD detector (Andor) with a resolution of 1.7–2 cm⁻¹.

TEM images were taken on a JEM-2100F (JEOL Co.) microscope operating at an acceleration voltage of 200 kV.

The temperature-programmed measurements were performed on a TPDRO (TP-5080, Xianquan Co.) instrument with a thermal conductivity detector (TCD). Before detection, the introducing gas was purified by a trap containing CaO and NaOH materials in order to remove H₂O and CO₂.

During the H₂-TPR operation, the sample (30 mg) was heated from room temperature (RT) to 900 °C with a rate of 10 °C min⁻¹ in the 8% H₂/N₂ flow (30 mL min⁻¹). The amount of H₂ consumption was calibrated by the quantitative reduction of the standard CuO sample to the metallic copper.

For the O₂-TPD experiments, the sample (100 mg) was pretreated in pure O₂ (50 mL min⁻¹) from RT to 450 °C, and held for 0.5 h. After cooling to RT in pure O₂ (50 mL min⁻¹), the sample was purged by the He flow (30 mL min⁻¹) to get a stable TCD signal baseline, and then heated to 900 °C with a rate of 10 °C min⁻¹.

The CH₄-TPSR experiments were carried out with a fixed-bed reactor (i.d. = 4.5 mm). Prior to the CH₄-TPSR test, 200 mg of the sample was pretreated in the flow (50 mL min⁻¹) of pure N₂ or 20% O₂/N₂ from RT to 450 °C or 700 °C, and held for 0.5 h. After cooling to RT, the sample was heated to 900 °C in 5% CH₄/N₂ (50 mL min⁻¹) with a rate of 8 °C min⁻¹. The outlet gas was analyzed by an infrared gas analyzer (GXH-104C, Beifenpuqi Co.).

The XPS measurements were carried out on a Scienta ESCA-200 spectrometer with an accuracy of 0.3 eV. Al-Kα (1486.6 eV) was used as radiation source. The recorded spectra were calibrated by the characteristic binding energy (BE) peak at 284.6 eV belonging to the contaminant carbon in the 1s region.

The XAFS data of the Sn K-edge were collected with the fluorescence mode at 14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) with the storage ring energy of 3.5 GeV and the current of 250 mA. The XAFS measurements of the Ce L₃-edge were collected on the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) (120 mA and 2.5 GeV) with the fluorescence mode.

2.3. Catalytic tests

The methane combustion activities of all the catalysts were evaluated in a fixed-bed reactor (i.d. = 4.5 mm) by using 200 mg catalyst. Reaction conditions: feeding gas = 0.6 kPa CH₄, 19 kPa O₂, N₂ balance; and flow rate = 235 mL min⁻¹. The space velocity was about 80,000 h⁻¹. Prior to each measurement, the catalyst was activated at 500 °C for 2 h in 20% O₂/N₂ (150 mL min⁻¹). A thermocouple was inserted into the catalyst bed to monitor reaction temperatures. The data were collected at each temperature after the catalyst was stabilized for 0.5 h. The outlet gas was analyzed by the infrared analyzer as mentioned in the CH₄-TPSR experiments. The conversion of CH₄ (*X*_[CH₄]) was calculated as follows:

$$X_{[\text{CH}_4]} = \frac{(C_{[\text{CO}]} + C_{[\text{CO}_2]})}{C_{[\text{CH}_4]}} \times 100\% \quad (2)$$

the *C*_[CO] and *C*_[CO₂] are the CO and CO₂ molar flows in the outlet gas, respectively, and the *C*_[CH₄] is the CH₄ molar flow in the feeding gas.

2.4. Kinetics tests

The kinetics studies were conducted in the same fixed-bed reactor as mentioned in Section 2.3. Before the experiments, the internal and external diffusion limitations were eliminated (see Fig. S1). The tests were conducted at the certain temperatures, at which

Download English Version:

<https://daneshyari.com/en/article/6499956>

Download Persian Version:

<https://daneshyari.com/article/6499956>

[Daneshyari.com](https://daneshyari.com)