



Effects of ultrasonic impregnation combined with calcination in N₂ atmosphere on the property of Co₃O₄/CeO₂ composites for catalytic methane combustion

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ABSTRACT

Co₃O₄/CeO₂ composites with high surface areas and ultrafine crystalline sizes for catalytic combustion of methane were firstly prepared by a new sol-gel method which combined ultrasonic impregnation treatment and calcination in N₂ atmosphere. The samples were characterized by various means such as nitrogen adsorption/desorption, X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Results showed that the modified catalyst had the mesoporous structure, comparatively higher amount of surface oxygen and larger oxygen vacancies than others. As a result of the structure and surface composition merits, a high methane combustion conversion (50%) could be obtained at a low temperature of 262 °C for the modified Co₃O₄/CeO₂ composites catalysts. The experimental results demonstrated that ultrasonic impregnation treatment combined with the N₂ thermal treatment prior to calcination in air had a promising application for preparation of Co₃O₄/CeO₂ composites catalysts for low-temperature catalytic combustion of methane.

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1. Introduction

Recently, a very great deal of emphasis has been laid on developing alternatives for energy production since worldwide petroleum reserves are on the decline. Among numerous applications of renewable energy sources, natural gas (NG) as the fuel has drawn much attentions due to its large reduction availability of CO₂-emissions in natural gas vehicles (NGVs) compared to gasoline vehicles with similar performances [1]. However, CH₄ has been recognized to contribute more to global warming than CO₂ at equivalent emission rates, due to its quite long lifetime [2–4]. Therefore, besides NO_x and CO emissions from vehicle exhaust, there is still a great challenge in reduction of unconverted CH₄ exhausted from NGVs [5].

Catalytic combustion of CH₄ (defined as oxidation reaction over the catalyst surface) has been extensively studied in the past years, which has showed obvious advantages when compared with conventional thermal combustion. Previous studies have displayed

that the noble metal-based catalysts can exhibit excellent catalytic behavior at low temperatures [6–8]. However, noble metal-based catalysts are limited in industrial applications due to their higher volatility, higher cost than other catalyst as well as easy sintering at relatively high temperatures [9]. Single transition metal oxides, perovskites and hexaaluminates have been used for CH₄ oxidation, but they also suffer from some disadvantages, such as lower catalytic activity and higher light-off temperatures than noble metal-based catalysts [9–12]. From an economic standpoint, the doped transition metal oxides are more attractive.

Among the doped transition metal oxides for oxidation reactions, cobalt oxide catalysts have presented great potential and are usually used in low temperature CO oxidation, due to their unique high activity [13,14]. As an oxygen storage capacity (OSC) material and thermal stabilizer, cerium oxide has been widely applied and played a promising role for improving the metal dispersion in the automotive three-way catalytic (TWCs) converter [15,16]. In fact, cerium oxide also directly participates in chemical reaction processes like the decomposition of nitrogen oxides or the water-gas shift reaction [17], as well as processes involving the oxygen storage capacity (OSC) provided by the redox couple Ce⁴⁺/Ce³⁺, which produces more oxygen available for the oxidation processes [18,19]. Migration of oxygen on the catalysts surface is significant in

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oxidation reactions where catalysts are subjected to repeated oxidation-reduction cycles [20].

As well known, the catalytic performance of $\text{Co}_3\text{O}_4/\text{CeO}_2$ mixed oxides is significantly affected by the preparation methods and conditions. Previous studies have proved that the $\text{Co}_3\text{O}_4/\text{CeO}_2$ mixed oxides with ultrafine crystalline sizes and high specific surface area were achieved by an improved citrate precursor method, where a nitrogen treatment was employed prior to calcinations in air [21,22]. Furthermore, sonochemical processing has been proven as a useful technique for generating novel materials with unusual properties [23–29]. For instance, Zhang et al. found that the activity of the catalyst prepared by ultrasonic impregnation was significantly higher than that of the catalyst prepared by conventional impregnation for CO_2 reforming of CH_4 . The result showed that ultrasound can enhance the dispersity of the active metal over the carrier, thus improving the catalytic performance of the catalyst [28].

Based on the aforementioned favorable effects, the $\text{Co}_3\text{O}_4/\text{CeO}_2$ composites for CH_4 combustion were firstly prepared by a new sol-gel method which combined ultrasonic impregnation treatment and calcination in N_2 atmosphere prior to calcination in air. For comparison, other conventional methods were also applied. In addition, the effects of the cobalt loading on the catalytic performance for CH_4 oxidation were also studied in this work.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by a new sol-gel method. Typically, an aqueous solution containing various stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid ($\text{Co}/(\text{Co} + \text{Ce}) = 0, 0.25, 0.50, 0.75, 1.00$; citric acid/ $(\text{Co} + \text{Ce}) = 2.00$, molar ratio) were placed in an ultrasonic cleaning machine at a frequency of 120 kHz for 60 min, and then kept at 90°C with stirring until a viscous gel was formed. After being dried at 110°C overnight, the dried precursors were calcined initially at 600°C for 6 h in N_2 (40 mL/min) and then calcined at 400°C for 4 h in air [18] (denoted as $\text{CeCo}_x\text{-ul-N6A4}$, x is referred to $100 \times \text{Co}/(\text{Co} + \text{Ce})$).

To understand the role of ultrasound impregnation treatment combined with calcination in N_2 atmosphere, the catalysts with the molar ratio of 0.75 were prepared using the same process as above, but without ultrasonic impregnation before drying. The achieved products were named as CeCo75-N6A4 . Furthermore, the Co–Ce citrate precursors with ultrasonic impregnation before drying were directly calcined at 600°C for 6 h and the achieved products were represented as CeCo75-ul-A6 .

2.2. Characterization

The N_2 adsorption/desorption isotherms were measured at -196°C with an automated surface area and pore size analyzer (Quadrasorb SI apparatus). Before each measurement, the samples were degassed in vacuum at 120°C for 3 h. Specific surface areas (SSA) of samples were calculated by the Brunauer–Emmett–Teller (BET) method, and the Barrett–Joyner–Halenda (BJH) method was applied to desorption isotherms to analyze the pore size distribution and average pore diameter.

The power X-ray diffraction (XRD) patterns were performed on a DX-2700 diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 30 mA, $k = 0.15418$ nm, scanning step = 0.03). The average crystallite size was calculated by the Scherer equation based on the line broadening of CeO_2 (111) or Co_3O_4 (311) plane and the Scherer constant was taken as 0.89.

Table 1. Catalytic activities of Ce–Co–O samples.

Sample	T_{10} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)	T_{90} ($^\circ\text{C}$)
$\text{CeO}_2\text{-ul-N6A4}$	527	605	–
CeCo25-ul-N6A4	412	504	–
CeCo50-ul-N6A4	272	282	481
CeCo75-ul-N6A4	252	262	364
CeCo75-N6A4	291	303	445
CeCo75-ul-A6	332	348	527
$\text{Co}_3\text{O}_4\text{-ul-N6A4}$	271	281	357

The morphologies of the catalysts were determined using a JEOL JEM 2010 transmission electron microscope (TEM) operated at 120.0 kV.

The hydrogen temperature-programmed reduction (H_2 -TPR) was carried out at atmospheric pressure in a fixed-bed reactor. 50 mg sample was pretreated in 5% H_2/N_2 at a flow rate of 30 mL/min, while the temperature of the reactor was ramped from 100°C to 800°C at a rate of $10^\circ\text{C}/\text{min}$ by a temperature controller. The consumption of H_2 was detected using a SC-200 gas chromatograph with a thermal conductivity detector (TCD).

The X-ray photoelectron spectroscopy (XPS) were performed using the XSAM800 spectrometer with an $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) X-ray source. The charging effects were corrected by adjusting the binding energy of C 1s peak from carbon contamination to 284.6 eV.

2.3. Catalytic evaluation

Methane combustion test were performed in a fixed-bed quartz tube reactor (\varnothing 6 mm) with a continuous flow at atmospheric pressure and equipped with a temperature-programmed controller. 200 mg sample was diluted in a certain amount of silica sand to decrease the effect of exothermic reaction on bed-temperature. Subsequently, the reagent gas made up 33.3 vol% $\text{CH}_4 + 66.6$ vol% O_2 was continuously passed through the catalyst bed at a total flow rate of 60 mL/min, and the weight hourly space velocity (WHSV) was 18000 mL/(h·g_{cat}). The activities of catalysts were measured by increasing the temperature from 210°C to 610°C at a heating rate of $2^\circ\text{C}/\text{min}$ and the analysis of the effluent from the reactor was performed by the gas chromatograph (GC) with a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Catalytic evaluation

First of all, the catalytic activities were evaluated, and the light-off curves are shown in Fig. 1. Generally, the activity of methane catalytic combustion is characterized by T_{10} , T_{50} and T_{90} , representing the reaction temperature at which methane conversion is 10%, 50% and 90%, respectively and the results were summarized in Table 1. For pure $\text{Co}_3\text{O}_4\text{-ul-N6A4}$, though it possessed quite high activity and its T_{90} was only 357°C , the methane conversion increased slowly or declined with the temperature further increasing, indicating poor thermal stability at high temperatures (Fig. 1a). The mole ratio of Co/Ce at 0.75 displayed optimal catalytic performance. As shown in Fig. 1(b), the light-off temperature and catalytic activity were in the following order: $\text{CeCo75-ul-N6A4} > \text{CeCo75-N6A4} > \text{CeCo75-ul-A6}$. Taking the 10% CH_4 conversion (T_{10}) for example, the temperature decreased from 332°C for CeCo75-ul-A6 , to 291°C for CeCo75-N6A4 , and 252°C for CeCo75-ul-N6A4 , respectively. These results demonstrated ultrasound impregnation combined with the calcination in N_2 atmosphere played a crucial role in improving the catalytic activity.

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