

Rapid synthesis of nano-scale CeO₂ by microwave-assisted sol–gel method and its application for CH₃SH catalytic decomposition



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ABSTRACT

A time-saving and efficient method, which is microwave-assisted sol–gel method, by using citric acid as a chelating agent, has been employed to synthesize CeO₂ nanoparticles as a high-performance catalyst for CH₃SH catalytic decomposition. Microwave-assisted sol–gel process is superior in terms of shortening reaction time, and a viscous gel can be obtained with the aid of uniform and rapid heating process within several minutes. Combined with N₂ adsorption–desorption, TEM, XRD, H₂-TPR and XPS results, CeO₂ nanoparticles obtained by microwave-assisted sol–gel method exhibited larger surface area and smaller crystallite size than that prepared by conventional sol–gel method. The method should be beneficial to form more lattice oxygen species and more structural defects, which are in favor of CH₃SH catalytic decomposition. TPS results illustrated that CeO₂-based catalysts were typical sulfur absorbents at high temperature. According to the characterization results of XPS and XRD, various Ce–O–S compounds including cerium sulfide (Ce₂S₃) and cerium sulfate (Ce(SO₄)₂) were formed after the relevant reactions between CeO₂ and gaseous sulfur species, and the formation of Ce₂S₃ in the later period of reaction might cause severe decline of the catalytic activity.

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1. Introduction

Methyl mercaptan (CH₃SH) is widely known as a highly odorous and volatile compound, which exhibits high toxicity to human health. It was confirmed that high concentration of CH₃SH is extremely toxic, and even the presence of trace CH₃SH in air (about 5 ppm) would make people uncomfortable [1,2]. Meanwhile, CH₃SH is generally associated with many industrial processes, including natural gas industry, petroleum refining, wood-pulping, sewage treatment as well as energy-related activities [3,4]. Therefore, in view of increasingly stringent environmental regulations, deeper removal of CH₃SH is urgently needed. The normal processes used for the removal of CH₃SH mainly include alkaline treatment [5], biological degradation [6], adsorption [7,8] and catalytic conversion. As we know, the process for more complete elimination of CH₃SH is generally based on catalytic conversion, including catalytic oxidation [9,10] and catalytic

decomposition [11–13]. Thereinto, catalytic decomposition process has the advantages of requiring no addition of any reagents (e.g., O₂) and producing low waste, which has attracted much attention for the past few years.

Recently, cerium oxide (CeO₂) with abundant mobile oxygen vacancies has been extensively employed as catalyst and/or support for various catalytic conversion processes [14–17]. Moreover, the regenerative adsorption of sulfur species with CeO₂ at high temperature has also been addressed [18–20]. It is also noteworthy that nano-sized CeO₂ crystallite has been proved to exhibit better catalytic performance due to its down-sizing effect [21,22]. Therefore, it is of interest to investigate the behavior of nano-sized CeO₂ material towards the adsorption and catalytic conversion of CH₃SH. Note that an open literature [11] offered a discussion concerning the catalytic decomposition of CH₃SH at high temperature (above 900 °C) over CeO₂ catalyst synthesized by cationic surfactant assisted method. According to the experiment results, poisonous CH₃SH can be catalytic converted into inorganic carbon-containing compounds such as CO, CO₂ and CH₄, and the final sulfur product, H₂S, as we know, can be either adsorbed efficiently by amine extraction process, or converted commercially

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to elemental sulfur from Claus process [23,24]. However, reaction temperature required in the aforementioned study is too high, and it is thus not energetically favorable. In addition, catalyst synthetic method in this research as well as many other routes such as coprecipitation [25,26], template-assisted [27], hydrothermal [28], combustion [29] and sol–gel [30] for preparing nano-CeO₂ are faced with the drawback of long synthesis time. A perfect example can be found that the corresponding aging time of template-assisted method usually need be ranged from 24 to 72 h [11,31]. As for conventional sol–gel method, a few hours are spent only to obtain viscous gel [32–36]. Therefore, further studies in this area especially in relation to shortening the synthesis time are desirable.

As far as we know, sol–gel process is regarded as one of the most effective methods to obtain catalysts with high activity, since the intimate mixing of components promotes the homogeneity of the final product [37]. Citric acid has been widely used as a chelating agent to obtain the complete complexation of the metal ions via sol–gel method, which has been employed to synthesize nano-CeO₂ [32–36]. Meanwhile, microwave-assisted synthesis has drawn widespread concern in recent years because it has advantages of fast, simple and low energy requirements. Consequently, microwave-assisted hydrothermal and microwave-assisted solvothermal methods have been successfully developed to prepare CeO₂ nanoparticles [38–40]. With these considerations, an improved sol–gel method, which is microwave assisted sol–gel method, by using citric acid as chelating agent, has been applied to synthesize nano-sized CeO₂ in this work. Herein, the precursor solution (the mixture of Ce(NO₃)₃·6H₂O and citric acid) is irradiated by a microwave source and the viscous gel can be obtained with the aid of uniform and rapid heating process within several minutes. Therefore, the synthesis time can be substantially shortened. And to the best of our knowledge, no report on the synthesis of CeO₂ nanoparticles in this method can be found in the previous researches.

In this study, a simple, convenient, and rapid method for the synthesis of nano-scale CeO₂ particles has been developed. The aforementioned materials were characterized by N₂ adsorption–desorption, TEM, XRD, H₂-TPR and XPS. Furthermore, their catalytic properties for CH₃SH decomposition were investigated under a moderate condition, with reaction temperature decreased below 500 °C.

2. Experiment

2.1. Materials

Ceria nitrate (Ce(NO₃)₃·6H₂O), citric acid (C₆H₈O₇·H₂O) were purchased from Shanghai Chemical Reagent Company of 6CeO₂

samples were prepared by a microwave-assisted sol–gel method. In typical preparation batch, 0.025 mol of cerium nitrate (Ce(NO₃)₃·6H₂O) mixed with 0.025 mol of citric acid (C₆H₈O₇·H₂O) were completely dissolved in 5 mL hot deionized water (about 50 °C). The mixture was then placed in a domestic microwave oven (SANYO, Model: EM-208MS1, Power: 110 W) to form viscous gel for 5, 10, 15, 20 min, respectively. Subsequently, the obtained dried viscous gel were calcined at 500 °C for 2 h. The prepared samples were defined as M-CeO₂-x, where x represents microwave time. A schematic pathway for preparing nano-CeO₂ samples by microwave-assisted sol–gel method is suggested in Scheme 1.

For comparison purpose, CeO₂ was also synthesized by conventional sol–gel method [34]. An aqueous solution (10 mL) of 0.025 mol Ce(NO₃)₃·6H₂O and 0.025 mol C₆H₈O₇·H₂O was heated at 90 °C in continuous stirring until it became a viscous gel, the gel was then dried at 110 °C overnight and finally calcined at 500 °C for 2 h. The obtained sample was defined as C-CeO₂.

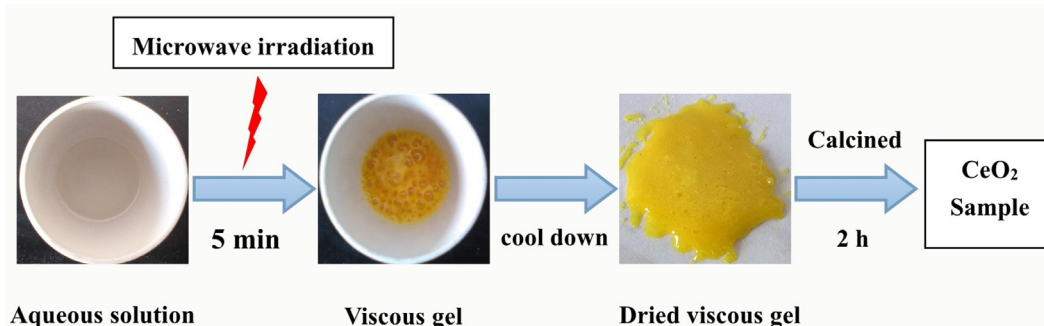
2.3. Characterization

XRD patterns were performed on a Rigaku D/max-1200 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 30 mA. TEM images were obtained on a JEM-2010HR transmission electron microscope, operating with an accelerate voltage of 200 kV. N₂ adsorption–desorption was carried out on a Micromeritics-ASAP-2000 apparatus at –196 °C. X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD spectrometer using Al K α radiation (1486.6 eV) as the excitation source. The analysis was performed at room temperature. Binding energies were calibrated using the containment carbon (C1s = 284.6 eV). H₂-TPR experiments were performed under the mixture of 10 vol% H₂ in Ar over 100 mg catalyst with the heating rate of 10 °C/min. Prior to analysis, catalyst was pretreated at 400 °C for 60 min with the mixture of 5 vol% O₂ in Ar. The consumption of hydrogen was measured by TCD detector.

Sulfur adsorption experiments were done with a similar temperature-programmed sulfiding (TPS) method described in previous research [41]. Prior to TPS measurement, each catalyst (0.20 g) was pre-treated with dried air (30 mL/min) at 400 °C for 2 h. After that, the reactor was cooled to room temperature with N₂ (30 mL/min). The catalyst was then heated up to 1000 °C with a rate of 10 °C/min under sulfiding gas (10 vol% H₂S in N₂, 30 mL/min) and the outlet gas was monitored by FPD detector.

2.4. Catalytic activity test

The catalytic activity measurement for CH₃SH decomposition was carried out in a fixed bed reactor, and 0.2 g catalyst diluted with quartz sand was loaded into the quartz tube. The total flow



Scheme 1. Pathway for synthesizing CeO₂ samples by microwave-assisted sol–gel method.

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