Conversion of poisonous methanethiol to hydrogen-rich gas by chemisorption/reforming over nano-scale CeO$_2$: The use of CeO$_2$ as catalyst coating material

N. Laosiripojana [a,*], S. Assabumrungrat [b]

[a] The Joint Graduate School of Energy and Environment, CHE Center for Energy Technology and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand
[b] Department of Chemical Engineering, Faculty of engineering, Chulalongkorn University, Bangkok, Thailand

ARTICLE INFO

ABSTRACT

Synthesized nano-scale CeO$_2$ enables to convert poisonous methanethiol (CH$_3$SH) to hydrogen-rich gas via the solid–gas reaction between CeO$_2$ and CH$_3$SH under sufficient condition. In the presence of H$_2$O, the phase of Ce(SO$_4$)$_2$ occurs from the reaction and offers high CH$_3$SH reforming activity. In contrast, without H$_2$O adding, Ce$_2$O$_2$S is formed instead and results in low catalyst activity. Further catalyst improvement was performed by coating this synthesized nano-scale CeO$_2$ over cylindrical-shape Rh/Al$_2$O$_3$ pellet (as called CeO$_2$-coated Rh/Al$_2$O$_3$). This developed catalyst was found to enhance good activity, stability, and reusability (over 5 reaction cycles; 72 h) for converting CH$_3$SH to hydrogen-rich gas with high hydrogen yield achievement. For more practical application, this catalyst was also tested over olefin offgas containing CH$_3$SH and ethanethiol (CH$_3$SCH$_3$) from an olefin manufacturing; and was found to efficiently convert this offgas to hydrogen-rich gas without sulfur present in the product gas under a proper regeneration time. This result highlights a great benefit of CeO$_2$-coated Rh/Al$_2$O$_3$ for integrating the clean energy generation with toxic-waste treatment, which offers significant energy and environmental benefits.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Industrial offgas is a gaseous by-product, which usually generated from the petrochemical and olefin manufacturing processes. Sulfur-containing compounds (e.g., hydrogen sulfide, sulfur oxides, thiophenes, mercaptans, and others) are typically present in this vent gas; and are commonly known to cause serious environmental and human health problems when emitted to the atmosphere [1]. Among these emissions, it has been reported that mercaptan compounds (e.g. methanethiol or CH$_3$SH) exhibit high toxicity to human health by affecting nervous system and causing convulsion and narcosis. It is known that CH$_3$SH causes paralysis of the respiratory system at high concentrations, while it produces pulmonary edema at lower levels [2]. Apart from the environmental and health problems, CH$_3$SH is also regularly known as poisonous gas for several catalytic conversion processes, particularly the reaction over metallic-based catalysts. In addition, regarding its high acidity, CH$_3$SH is corrosive to metals, which is harmful for storage and usage of oil products. Therefore, it is necessary to remove CH$_3$SH from the feedstock either by extracting or by transforming to innocuous disulfides prior the catalytic conversion processes. Importantly, this separated CH$_3$SH gas needs to be treated before venting out to the environment; and normally the adsorption and/or combustion processes are applied for this purpose [3–11].

Recently, the regenerative sulfur adsorption capability of cerium oxide (CeO$_2$) at high temperature was reported [12]. In addition, the capability of this material as catalyst and support in various reactions involving oxidation of hydrocarbons has also been addressed [13–18]. Hence, it is interested to study the behavior of CeO$_2$ towards the adsorption and conversion of CH$_3$SH. Theoretically, CeO$_2$ contains high concentration of highly mobile oxygen vacancies, which act as local sources or sinks for oxygen involved in reactions taking place on its surface; this behavior renders CeO$_2$-based materials of interest for a wide range of catalytic hydrocarbon conversion applications [19–28]. Previously, we have successfully synthesized nano-scale CeO$_2$ with high specific surface area and thermal stability by cationic surfactant-assisted method and found that this material efficiently converts several hydrocarbons (i.e. CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_4$H$_{10}$, CH$_3$OH and C$_2$H$_5$OH) via the steam and dry reforming reactions to hydrogen-rich gas with high resistance toward carbon formation [29,30]. It is known that these reforming reactions occur via the solid–gas reaction between the lattice oxygen (O$_0^x$) in CeO$_2$ and hydrocarbon (C$_n$H$_m$ + nO$_0^x$ = 0.5mH$_2$ + nCO + nV$_O^{\bullet\bullet}$ + 2ne′), from which V$_O^{\bullet\bullet}$

* Corresponding author. Tel.: +66 2 872 9014; fax: +66 2 872 6736.
E-mail address: navadol_l@jgsee.kmutt.ac.th (N. Laosiripojana).

denotes an oxygen vacancy with an effective charge 2$^+$, e′ is an electron which can either be more or less localized on a cerium ion or delocalized in a conduction band. In addition, the reactions of the reduced CeO_2 with CO_2 and H_2O could produce CO and H_2 along with regenerate O_0^x ($V_O^{\bullet\bullet} + 2e' + CO_2 = O_0^x + CO$; and $V_O^{\bullet\bullet} + 2e' + H_2O = O_0^x + H_2$).

In the present work, the potential use of nano-scale CeO_2 for the reaction (adsorption and conversion) with CH_3SH was studied under several operating conditions (i.e. without inlet steam, with various inlet steam/CH_3SH molar ratios, and under different operating temperatures). Several characterizations including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and $^{18}O/^{16}O$ isotope exchange methods were also performed over both fresh and spent catalysts from the reaction under various conditions in order to determine the changing of catalyst phase formation and the redox properties associated with the oxygen storage capacity (OSC) and the mobility of lattice oxygen. Based on the relation between the experimental results and the above characterizations, the mechanistic of CH_3SH reaction over nano-scale CeO_2 was explained. In addition, further catalyst improvement with respect to the study, i.e. by using this ultrafine CeO_2 as catalyst support and as coating material over metallic-based catalyst were investigated with an aim to develop the efficient catalyst for converting CH_3SH and olefin offgas (containing CH_3SH and CH_3SCH_3) to hydrogen-rich gas with high resistance toward sulfur poisoning.

2. Experimental

2.1. Preparation and characterizations of CeO_2

Nano-scale CeO_2 was synthesized by cationic surfactant-assisted method. This preparation technique was reported to offer ultrafine material with high surface area and good thermal stability due to the interaction of hydrous oxide with cationic surfactants under basic condition and the incorporation of surfactants during preparation, which reduces the interfacial energy and eventually decreases the surface tension of water contained in the pores [31]. In preparation, 0.1 M of cerium nitrate ($Ce(NO_3)_3 \cdot H_2O$ from Aldrich) was mixed with 0.1 M cetyltrimethylammonium bromide by keeping the ([Ce])/[cetyltrimethylammonium bromide] molar ratio constant at 0.8. This solution was continually stirred and added aqueous ammonia until the pH reaches 11.5. It was then sealed and placed in the thermostatic bath before filtering and washing the precipitate with deionized water to remove the free surfactant. The precipitate was dried overnight at 110 °C and calcined at 900 °C for 6 h to prevent the catalyst thermal sintering during the reaction. After calcination, the nano-scale fluorite-structured CeO_2 with good homogeneity was achieved.

The redox properties associated with the OSC and the mobility of lattice oxygen for this synthesized CeO_2 were examined by applying TPR and $^{18}O/^{16}O$ isotope exchange methods. The TPR experiment was carried out in a quartz reactor, which was mounted vertically inside tubular furnace. A Type-K thermocouple was placed into the annular space between the reactor and furnace, while another thermocouple, covering by closed-end quartz tube, was inserted in the middle of the quartz reactor to re-check the possible temperature gradient. The sample (100 mg) was heated from 25 °C to 1000 °C under 5%H_2 in N_2 with the flow rate of 50 cm^3 min^{-1} and the amount of H_2 consumed during the TPR process at different temperatures was monitored online by the thermal conductivity detector (TCD) and quantified by calibrating the peak areas against the TPR of known amount CuO. The $^{18}O/^{16}O$ isotope exchange experiment was carried out to investigate the lattice oxygen mobility of CeO_2 by placing the sample in the quartz reactor and

thermally treated under the flow of high-purity helium (99.995%) at the desired temperatures for 1 h. Then, $^{18}O_2$ (98% purity) were multiply pulsed to the system by six-port valve with sample loop (using helium as carrier gas) the outlet gases were monitored by the mass spectrometer (MS; Omistar GSD 301O3).

2.2. Preparations of Rh/CeO_2 and CeO_2-coated Rh/Al_2O_3

Apart from the synthesis of nano-scale CeO_2, Rh/CeO_2 and CeO_2-coated Rh/Al_2O_3 were also prepared and tested. Rh was selected as metallic material since this precious metal is known as one of the most active catalysts for reforming and relevant reactions. Rh/CeO_2 (5 wt% Rh) was prepared by the wet impregnation of synthesized CeO_2 with an aqueous solution of $Rh(NO_3)_2$ (from Aldrich); furthermore, Rh/Al_2O_3 was also prepared by impregnation of Al_2O_3 with $Rh(NO_3)_2$ for comparison. Prior the reaction testing, these catalysts were calcined in air at 900 °C and reduced with H_2 at 500 °C for 6 h. It is noted that the catalysts (after calcination and reduction) were characterizations by XRF analysis and TPR (with 5% H_2 in helium) to determine the Rh weight contents and reducibility, while the dispersion percentage of Rh was identified from the volumetric H_2 chemisorption measurement using a chemisorption analyzer. From these characterizations, the Rh weight contents for Rh/CeO_2 and Rh/Al_2O_3 were 4.9 and 5.1%; the metal reducibility of Rh/CeO_2 was 91.6%, while that of Rh/Al_2O_3 was 94.8%; and the metal dispersion percentages for Rh/CeO_2 and Rh/Al_2O_3 were 4.78 and 5.04%, respectively.

As another approach, nano-scale CeO_2 was used as a coating barrier over cylindrical-shape Rh/Al_2O_3 pellet. The preparation is divided into 3 main steps: (i) CeO_2 was prepared as a suspension by adding polyvinyl alcohol (PVA; Aldrich) as the suspension solvent to suspend CeO_2 powder into the solution, (ii) Rh/Al_2O_3 pellets were introduced into this suspension solution, and (iii) these pellets were dried and pre-treated. In detail, 10 wt% of CeO_2 powder was suspended into a 0.3 M of PVA solution; this solution was then stirred by magnetic stirring (500 rpm) at room temperature for 1 h. Then, CeO_2 powder was completely suspended in this solution by ultrasonic probe. As the next step, 5 pellets of Rh/Al_2O_3 (∼100 mg for each pellet) were dropped into the stirring CeO_2 suspension for 6 h. These pellets were then removed, dried overnight in oven at 110 °C and calcined in air at 900 °C for 6 h before reducing with 10% H_2 for 6 h. It is noted that, after calcination, the catalyst was coated more than 1 time to improve the thickness of coating. After 5 times coating, SEM micrograph confirms a porous and homogeneous structure of coating pellets.

2.3. Reaction testing and analyses

To perform the reaction testing, an experimental reactor system was constructed as presented elsewhere [29]. The feed gases including CH_3SH (20 vol% in helium) and helium were controlled and introduced to the system by the mass flow controllers, while deionized H_2O was fed by a syringe pump passing through an evaporator. For the steam reforming testing, various steam concentrations were added to achieve the steam/CH_3SH ratio between 0.5 and 3.0. The inlet gas mixtures were introduced to the reaction section, in which a quartz reactor was mounted vertically inside tubular furnace. The catalyst (1.0 g) was diluted with SiC in order to avoid temperature gradients and loaded in the quartz reactor, which was packed with quartz wool to prevent the catalyst moving. A Type-K thermocouple was placed into the annular space between the reactor and furnace to measure the reaction temperature; furthermore, another Type-K thermocouple covering by closed-end quartz tube was inserted in the middle of the quartz reactor to re-check the temperature deviation.