Journal of Alloys and Compounds 747 (2018) 189–196

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

# Synthesis of ceria nanorods as adsorbent for the adsorption desulfurization of gasoline fuel

Yongxing Yang [a, *], Guangqiang Lv [b, **], Jing Li [a], Wei Guo [a], Ye Zhang [c]

[a] School of Chemistry and Chemical Engineering, Shanxi University, Wucheng Road 92, Taiyuan, 030006, PR China
[b] Shandong Povincial Key Laboratory of Fine Chemicals, School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250353, PR China
[c] Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China

ARTICLE INFO

*Article history:*
Received 24 November 2017
Received in revised form
6 February 2018
Accepted 3 March 2018
Available online 3 March 2018

*Keywords:*
Oxide materials
Nanofabrications
Adsorption
Desulfurization
SBA-15
Hard template

ABSTRACT

Ceria nanorods arrays (HT-$CeO_2$) were successfully synthesized by using mesostructured silica SBA-15 as hard template. The pore channel of the hard template SBA-15 could stabilize the $CeO_2$ particles, prevent sintering during the calcination process by the high temperature and shape their rodlike morphology. HT-$CeO_2$ was obtained by removing the silica matrix with diluted HF washing. Consequently, HT-$CeO_2$ nanorods have a significant improvement in the textural properties with a higher surface area and total pore volume than the reference sample synthesized in the absence of template. X-ray diffraction (XRD) revealed that the only crystalline phase present in this material was $CeO_2$ with fluorite structure. Transmission electron microscopy (TEM) shows that the HT-$CeO_2$ is mainly constituted by agglomerates of nanorods. EDX microanalysis confirms the efficient removal of silicon template. The Ni/HT-$CeO_2$ is more selective to the thiophene (aromatic sulfur compounds) as large amount of olefin coexisting as compared with Ni/SBA-15. The adsorption capacity of 5 wt% Ni/HT-$CeO_2$ is decreased only by 4% due to 10 vol.% olefin addition.



## 1. Introduction

Deep desulfurization for transportation fuels has become an increasingly important issue in the world. The organic sulfur compounds present in the transportation fuels could cause very serious environmental problems. On a global scale, more and more stringent laws restrict the sulfur level of transportation fuels. So the world's oil refining industry must meet these increasingly stringent requirements for sulfur content in transport fuels, especially sulfur content in gasoline fuel. Sulfur content in gasoline is required to be less than 10 ppm in Euro V emission limitation. However, it is difficult for conventional hydrodesulfurization (HDS) to reduce the sulfur to a very low level for gasoline fuel without loss of octane number. Therefore, new strategies for desulfurization have been exploring to meet the urgent needs to produce cleaner transportation fuel [1–4]. The adsorption desulfurization is considered to be one of the most promising methods for deep desulfurization [1,5–8]. At present, the main restriction of the process to industrial application is the low adsorption capacities and selectivity of adsorbents. In recent years, the adsorptive trap of the organic sulfur compounds by using molecularly imprinted chitosan materials have been reported [9]. It displays excellent affinity to organic sulfur compound. Novel titania-silica nanocomposite with microporous structure has been reported as catalyst-adsorbent for ultra-deep oxidative desulfurization [10,11]. It could remove more than 98% organic sulfur compounds and reduce the sulfur level below 10 ppm. Novel $Ni_2P$/SBA-15 adsorbent was prepared by the urea matrix combustion method and was studied for the adsorptive removal of sulfur compounds at room temperature and pressure without the presence of hydrogen. It displays a high sulfur capacity [12]. BN mesoporous nanowires are promising candidates of the adsorptive desulfurization adsorbent and display good adsorption capacity for organic sulfur compounds [13,14]. Magnetically responsive core–shell microspheres, Fe3O4@C have been prepared and used as the adsorbent for the removal of organic sulfur compounds [15].

Mobil oil researchers have found the ordered mesoporous silica M41S series in 1992. Since then many different mesoporous

* Corresponding author.
** Corresponding author.
*E-mail addresses:* yangyongxing@sxu.edu.cn (Y. Yang), lvguangqiang@qlu.edu.cn (G. Lv).

https://doi.org/10.1016/j.jallcom.2018.03.026
0925-8388/

inorganic materials have been synthesized using various types of organic template. Applications of mesoporous material now have extended to catalysis, control-release, sensors, capacitors, and so on [12,16–26]. There has been considerable interest in the synthesis of non-silica nano-materials using the ordered mesoporous silica as hard template, and the synthesis of numerous novel ordered nanostructure or nanoarray materials, such as carbon, metal, transition metal oxides, sulfides, and polymer has been achieved successfully. Commonly, the transition metal oxides with nanostructure synthesized by this method are highly crystallized and hierarchical ordered structure on meso-scale as well as on atom-scale. Ceria is an important rare earth oxide and has been widely investigated in the automotive exhaust purification, oxygen storage and release catalysis, and solid oxide fuel cell applications. The ordered mesoporous ceria, which is replicated using mesoporous silica as templates, shows high surface area and pore volume, and the framework of this materials is composed of crystal nanorod with a "negative" phase corresponding to the mother silica template. Since the crystalline $CeO_2$ inside the channels is formed at high calcination temperature, the architecture of the crystalline ceria is expected to be thermally stable. The removal of the silica template which probably possesses oxygen linkage with ceria may produce high population of structural defects in ceria. Such materials are envisaged to provide more sites for the anchoring of nanosize active metal. The high amount of defects for oxygen adsorption and activation is also known to be beneficial to VOCs oxidation. Those special properties make this material suitable to be used as support: firstly, the crystalline nanorod framework can increase the thermal stability and favor the formation of defects on the surface. Secondly, the high surface area and pore volume are beneficial to load active metal homogeneously and with a high amount.

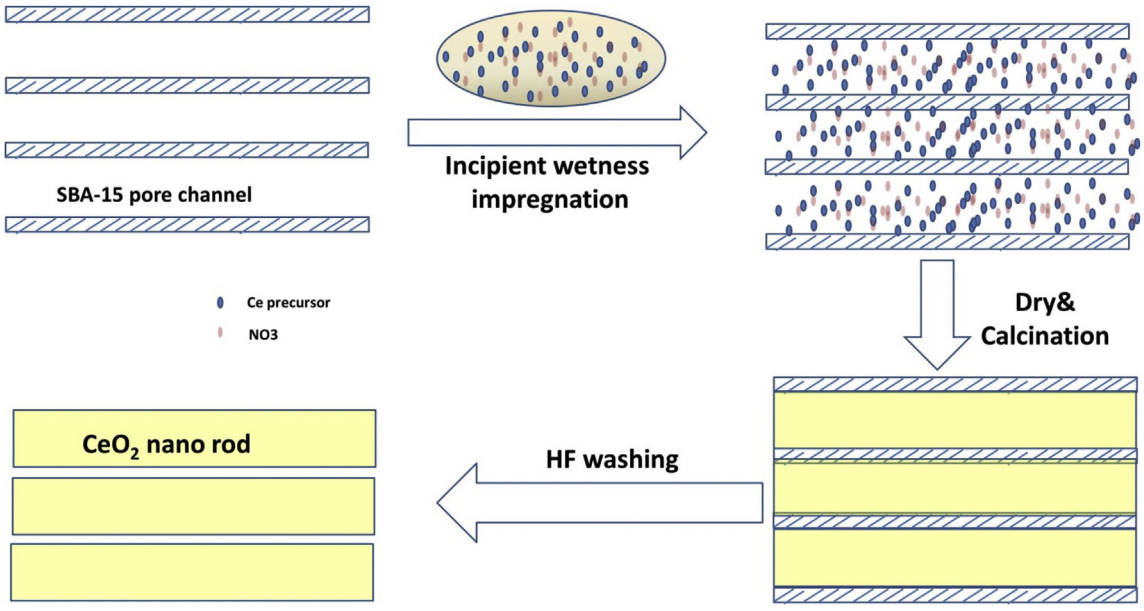
As shown in Scheme 1, in present work we have synthesized high surface area bulk $CeO_2$ materials by a nanocasting pathway using ordered mesoporous silica (SBA-15) as hard template. The resulting $CeO_2$ material possesses high surface area and total pore volume, and it is constituted mainly by nanorods, casted by the straight channels of SBA-15. Based on this material, a new type supported Ni adsorbent (Ni/HT-$CeO_2$) is prepared by an incipient wet impregnation of the supports and has been tested in the adsorption desulfurization of a model gasoline. Based on the evaluation results, new direct interaction between adsorbed organic sulfur compound molecules and HT-$CeO_2$ support surface by S atoms is presented.

## 2. Experimental

### 2.1. Preparation

Firstly, we synthesize the pure silica SBA-15 for the support via a hydrothermal method reported by Zhao et al. Pluronic 123 purchased from Aldrich Co. was dissolved in 350 mL of 1.9 M HCl in stiring and at room temperature. The solution was heated to 35 °C. The tetraethylorthosilicate purchased from Aldrich Co. was used as silica source, added drop by drop. The obtained solution was stirred continually for 24 h at 35 °C. Thereafter, the mixture was aged at 120 °C for 24 h under autogeneous pressure. The SBA-15 product was recovered by filtration, dried overnight and calcined at 500 °C for 5 h at a heating rate of 1.0 °C/min. The nanocasting process was performed using the as-prepared SBA-15 material as hard template. It started with an incipient wet impregnation of an aqueous solution of cerium nitrate with a total metal loading of 20%, limiting the solution amount to the pore volume. Then the sample was dried at 120 °C overnight and calcined at 500 °C for 5 h. The solid so obtained was named $CeO_2$/SBA-15. Finally, the silica template was removed using a 0.2 M HF aqueous solution at room temperature and this etching process was repeated three times, before washing and drying. The final solid so obtained was named HT-$CeO_2$. For comparison, a reference sample was also synthesized using the same synthesis procedure but in the absence of the hard template ($CeO_2$).

Supported Ni adsorbents (nominal 5 and 20 wt% Ni) are prepared by an incipient wet impregnation of the supports with an aqueous solution of Ni $(NO_3)_2 \cdot 6H_2O$ (Aldrich Co.), dried at 120 °C overnight, and calcined in air at 500 °C for 5 h.




**Scheme 1.** Schematic of $CeO_2$ synthesis by using hard template method