



Size regulation and dispersion of ceria using confined spaces for adsorptive desulfurization



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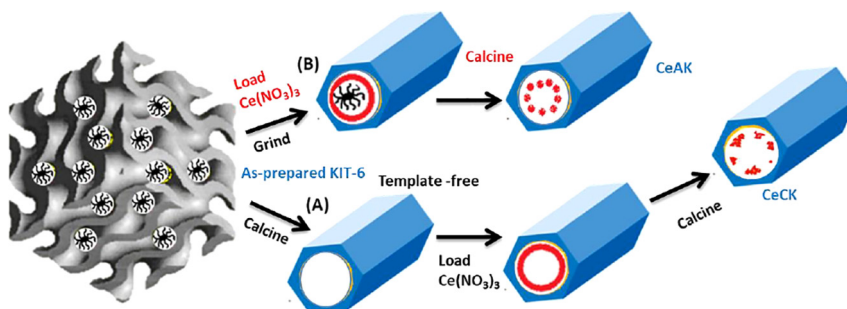
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HIGHLIGHTS

- Single step solid phase grinding improve $\text{Ce}(\text{NO}_3)_2$ dispersion over KIT-6 and ADS capacity.
- As-synthesized KIT-6 highly disperse CeO_2 NPs than calcined KIT-6.
- Confined spaces exist between template and silica wall of KIT-6 avoid aggregation of CeO_2 .
- Silanols increase the interaction of CeO_2 NPs with silica walls of KIT-6.
- The present strategy is time and energy efficient for functionalization of KIT-6 with ceria.

GRAPHICAL ABSTRACT

Synthesis of $\text{CeO}_2/\text{KIT-6}$ with aggregated large-size ceria NPs via (A) the conventional approach and highly dispersed small-sized ceria NPs (B) using the confined space in KIT-6.



ARTICLE INFO

Keywords:

Adsorption
Cerium oxide
As-synthesized KIT-6
Deep desulfurization
Thiophene

ABSTRACT

Transition-metal nanoparticles attracted tremendous attention in desulfurization technology because of their excellent sulfur adsorption activity. However, such activity is heavily relying on the size and dispersion degree of metal nanoparticles (NPs). Therefore, dispersion and regulation of NPs size is of significance importance. Herein, an efficient strategy is developed for the first time to regulate the size and highly disperse ceria NPs in a typical 3-D mesoporous silica KIT-6 by using silanols and confined spaces. The Ce-containing precursor is directly inserted into the confined spaces exist between template P123 and silica walls of as-prepared KIT-6 by solid-phase grinding. The subsequent calcination not only remove template from KIT-6 structure but also convert cerium precursor to CeO_2 active sites in a single step, and hence avoided multiple calcination steps as reported in other strategies, and efficient in terms of time and energy. In contrast to reported strategies, the present approach is more convenient for synthesis of CeO_2 -based KIT-6 adsorbents. The synthesized materials (CeAK) were characterized via N_2 adsorption, XRD, TEM, SEM, elemental distribution mapping, FT-IR, TG, and UV-Vis DRS and compared with materials obtained from calcined KIT-6 (CeCK). Compared with CeCK sorbent, CeAK demonstrated smaller Ce particles and stronger interaction with silica support. As a result, it exhibited high thiophene adsorption capacity and can reach 0.14 mmol.g^{-1} over CeAK-20, which is higher than that 0.07 mmol.g^{-1} of CeCK-20. Furthermore, the desulfurization activity can be recovered well even after regeneration. Facile synthesis, high desulfurization activity, excellent stability and regeneration ability make the synthesized material highly attractive in deep desulfurization technology.

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1. Introduction

Nowadays, deep desulfurization for cleaner fuels production is quite imperative due to rigorous environmental regulations worldwide and for other applications [1–3]. To date, petroleum refineries are using hydrodesulfurization (HDS). However, the HDS process is effective for thiols and sulfides removal, but less efficient for thiophene and its derivatives [4,5]. Therefore, it is hard to apply HDS to obtain zero-level sulfur fuels to meet the recent strict environmental regulations and, hence, there is a great desire to further reduce the sulfur level.

Until now, different technologies were adopted, however, among different available alternatives, adsorptive desulfurization is attractive because of ease in operation and selectivity for capturing aromatics sulfur without using hydrogen [6–8]. Irrespective of different bonding mechanisms (π -complexation and sulfur-sorbent (S-M) interactions), the chemical interactions of sulfur compounds with metal nanoparticles in adsorbents are crucial for deep desulfurization [2,9,10]. Because, thiophene molecules can interact only with “touchable” metal nanoparticles located on the surface of adsorbent. Therefore, the dispersion degree of metal nanoparticles is important for the increased adsorption capacity of adsorbents [6].

Transition metals such as Cu(I) and Ag(I) received great interest as active metal sites and extensively used in adsorption desulfurization due to their superior activity. Unfortunately, Cu(I) is very unstable and easily oxidized, whereas Ag(I) is light-sensitive [11,12]. Hence, the synthesis of stable metal nanoparticles is eagerly anticipated not only for academic but also in practical applications.

Among many active metals sites, herein, Ce(IV) is selected due to its stability to capture sulfur species from fuels. Compared with bare metal nanoparticles including Ce(IV), metal-based supports could be more effective for adsorptive desulfurization [13]. As a kind of support, mesoporous silicas exhibits high BET surface area with big pore volume, and can play active role to regulate size and dispersion of Ce(IV) NPs. To functionalize mesoporous silicas with Ce(IV) species for adsorption applications, various strategies including impregnation and hydrothermal synthesis have been adopted [14,15]. Despite great efforts, the fabrication of mesoporous silica with smaller ceria NPs remained a challenge. Take Ce/KIT-6 as an example: the synthesis consisted of 3 steps as illustrated in Scheme 1A [15]. KIT-6 occluded with template is first calcined to produce template free support. Then, Ce(NO_3)₃·6H₂O was introduced via impregnation in the presence of solvent. Finally, the material was subjected to a second calcination at high temperature to decompose Ce-precursor and the adsorbent with target CeO₂ is produced. Apparently, the conventional approach for Ce/KIT-6 is rather complicated by ignoring nature of KIT-6 silica and consuming more energy and time. Hence, the development of a new approach for synthesis of Ce based KIT-6 is eagerly anticipated.

It is worth mentioning that mesoporous silica was used as a support after template removal, and less attention were given to template

containing KIT-6. Actually, there exists special microenvironment in between template and silica wall of as-synthesized KIT-6, which provide confined spaces and large number of silanols; highly beneficial for size regulation and dispersion of active sites. Unfortunately, such microenvironment is not explored yet to the best of our knowledge for size regulation and dispersion of ceria NPs over KIT-6.

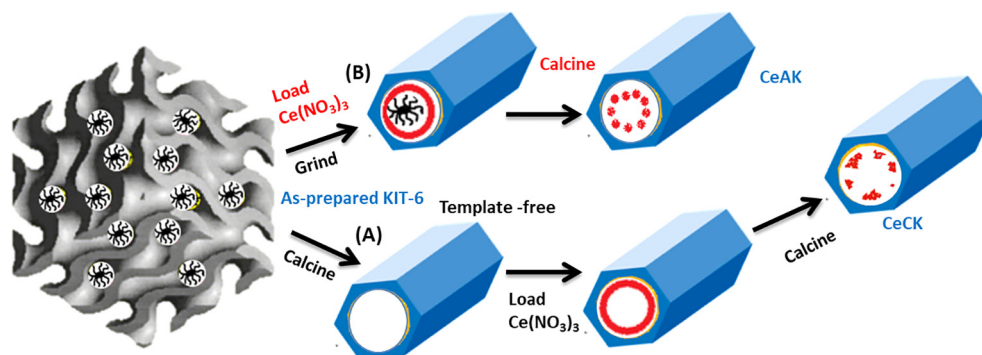
In this study, for the first time, a strategy was developed to regulate size and highly disperse CeO₂ NPs by utilizing the confined spaces. The Ce-containing precursor is directly introduced into the confined spaces of as-prepared KIT-6 as host by solvent free solid-state grinding. The decomposition of precursor occurred inside the confined spaces present between template and silica wall (Scheme 1B). Aggregation that normally occurred in conventional approach during calcination (Scheme 1A) can be avoided and the size of CeO₂ NPs was controlled due to the confined effect (Scheme 1B). Our strategy is facile and easy, which accomplish removal of template removal and precursor decomposition in single step instead of multiple one in conventional modification process. This strategy not only efficient in saving time but also reduces energy consumption. Moreover, 20 wt% CeO₂ was highly dispersed with extremely small particle size. To our knowledge, this is the first report about fabrication of 3-D KIT-6 mesoporous silica with such a high dispersion of CeO₂. The synthesized CeAK material was well characterized and compared with CeCK. We also demonstrated that the synthesized CeAK materials showed higher sulfur capture activity than CeCK, and desulfurization capacity can be well-recovered after regeneration.

2. Experimental

2.1. Synthesis and fabrication of KIT-6

KIT-6 was prepared as reported in Ref. [16]. First, 4 g of pluronic 123 was completely dissolved in 144 mL solution of HCl (35%) with constant stirring for 4 h at 35 °C. Then, n-butanol (4.95 mL) was added and the whole solution was kept on stirring for 1 h. 9 mL tetraethyl orthosilicate (TEOS) was dropwise added and the whole solution was kept on continuous stirring at 35 °C for a period of 24 h. Finally, the obtained mixture was transferred into autoclave and treated at 100 °C for 24 h hydrothermally. After hydrothermal synthesis; the as-prepared mesoporous silica (AK) was collected by filtration and subsequently dried overnight at 100 °C. Thermogravimetric (TG) results revealed that there is a weight loss of 35% at temperature lower than 600 °C, possibly due to template P123 decomposition. This value is consistent with the reported one (35%) [17], implying the preservice of template in KIT-6 pores. Template P123 from AK was removed by calcination at 550 °C in the presence of air for 6 h and denoted as CK.

Fabrication of KIT-6 with ceria: Cerium-containing precursor (Ce(NO_3)₃·6H₂O) was directly introduced into as-prepared KIT-6 by manually solid-phase grinding at room temperature and pressure for



Scheme 1. Synthesis of Ce/KIT-6 with aggregated large-size ceria NPs via (A) the conventional approach and highly dispersed small-size ceria NPs (B) using the confined space in KIT-6 mesoporous silica.

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