Chemical Engineering Journal 302 (2016) 239–248

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Facile fabrication of Ni-based KIT-6 for adsorptive desulfurization

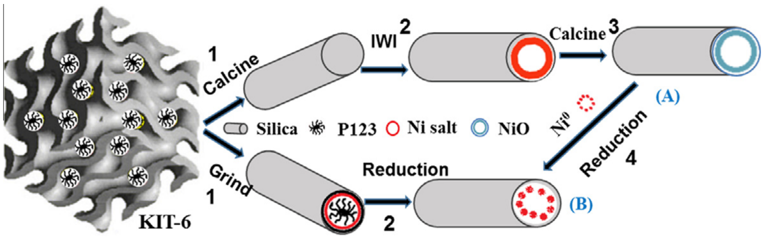
Sobia Aslam [a,b], Fazle Subhan [a,b,*], Zifeng Yan [a,*], Peng Peng [a], Ke Qiao [a], Wei Xing [a], Peng Bai [a], Rooh Ullah [a], U.J. Etim [a], Jingbin Zeng [a], Muhammad Ikram [b]

[a] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China*
[b] *Department of Chemistry, Abdul Wali Khan University Mardan, Pakistan*

HIGHLIGHTS

- Nickel was fabricated on as-synthesized-KIT-6 for the first time by one-step reduction strategy.
- Silanols and confined space between template and silica walls promoted Ni-dispersion.
- Shielding effect of capping anions of nickel precursors affect nickel dispersion and sulfur removal.
- One-step-reduction strategy save time and energy for fabricating Ni-based mesoporous silica.
- The present work may open an avenue of research by use of such confined spaces.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 March 2016
Received in revised form 7 May 2016
Accepted 9 May 2016
Available online 10 May 2016

Keywords:
One-step H_2-reduction strategy
Nickel precursors
KIT-6
Adsorption
Fuels

ABSTRACT

In the present contribution, a single step H_2-reduction strategy was developed for the first time to fabricate nickel-based KIT-6 (Ni-KIT-6) for adsorptive desulfurization of fuels. As-synthesized KIT-6 was used as a support and nickel nitrate, nickel chloride and nickel acetate as a nickel precursor was directly introduced into as-synthesized KIT-6. Ni^0-based KIT-6 was obtained by single-step H_2-reduction strategy which not only remove template and decompose nickel precursors to NiO but also reduce NiO to Ni^0. This strategy is much more convenient and facile than reported strategies for Ni-based mesoporous silica KIT-6. Characterization results show that Ni-KIT-6 with nickel content up to 30 wt.% was highly dispersed due to silanols and confined space in as-synthesized KIT-6. The percentage content (54%) of Ni^0 in the as-synthesized KIT-6 is higher than Ni-based calcined KIT-6 (38%). Interestingly, Ni-based as-synthesized KIT-6 prepared using nickel nitrate as a precursor exhibited stronger nickel-KIT-6 interaction, higher Ni^0 content and dispersion than those prepared with nickel chloride and nickel acetate precursors. We also demonstrate here that the shielding effect of capping anions and hydration degree of different nickel precursors significantly affect the dispersion of nickel species even using as-prepared KIT-6 as a support. As a result, Ni-KIT-6(NO_3^-) captured 0.195 and 0.12 mmol g^{-1} of sulfur from model fuel and FCC gasoline, respectively. Thus, single step H_2-reduction strategy may have potential applications to be applied for fabrication of other nickel based mesoporous silicas for adsorptive desulfurization technology.

1. Introduction

In the last few years, deep desulfurization of transportation fuels in a petroleum refining industry received great importance

---

* Corresponding authors at: State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China (F. Subhan).
E-mail addresses: fazle@awkum.edu.pk (F. Subhan), zfyancat@upc.edu.cn (Z. Yan).

http://dx.doi.org/10.1016/j.cej.2016.05.041
1385-8947/

because of stringent environmental regulations imposed by governments around the globe to lower down the existing sulfur levels [1–3]. The existence of sulfur species in commercial fuels not only harm environment but also dangerous for other utilities [4–7]. Among different alternatives, hydrodesulfurization (HDS) is one of a major process employed in refineries worldwide for desulfurization of transportations fuels to make it environmental friendly. However, HDS need elevated temperature (>300 °C) along with high hydrogen pressure (>4 MPa) for capturing thiols and sulfides instead of thiophene derivatives than other process for sulfur removal employed elsewhere [3,8–11]. Therefore, adsorptive desulfurization (ADS) emerged as a best industrial option to produce sulfur free fuels under mild operation conditions and overcome the deficiencies of the existing HDS.

Adsorbents/materials play a crucial role in adsorptive desulfurization, and hence many attempts by different research groups have been made towards the development of particularly high performance nickel based adsorbents based on various supports [12–16]. However, two factors are considered crucial for high activity of such materials i.e., support with high surface area because it accommodate maximum amount of nickel species and appropriate method disperse well the nickel species on supports. Thus, there is a great need of appropriate method and a support for nickel dispersion to increase the sulfur removal capacity from fuels. Other than various supports reported in literature, mesoporous silica with different pore structures are promising and has attracted considerable attention for different fields including sulfur adsorption [3,17,18].

KIT-6, mesoporous silica, has received great interest since it discovery for metal/guest species dispersion. The excellent properties for metal dispersion and sulfur removal were obtained due to its three-dimensional structure [19]. Park et al. reported Ni based KIT-6, which presented larger total sulfur adsorption capacity (3.3 mg/g) than (2.3 mg/g) of Ni/SBA-15 for diesel fuel [12]. The higher adsorption in the case of Ni based KIT-6 was attributed to the structure of mesoporous silica support. However, in those previous fabrication strategies, calcined mesoporous KIT-6 were employed as support instead of as-synthesized and the loading process were consisted of KIT-6 calcination to remove template, dispersion of nickel by IWI impregnation, followed by second calcination to convert Ni $(NO_3)_2$ to NiO and finally reduction of NiO to Ni^0 by high temperature H_2-reduction treatment to generate Ni^0-based mesoporous silicas for sulfur removal as shown in Scheme 1A. These 4 steps approaches are rather complicated and consume a lot of time, energy and hard to be industrialized. Thus, the demand for a facile and single step strategy for nickel dispersion over KIT-6 with maximum Ni^0 active sites is highly required.

Using as-synthesized mesoporous silica SBA-15 as a support, Liu and his co-workers introduced high amount of copper precursor for adsorptive desulfurization of fuel [20]. High amount dispersion of copper and sulfur adsorption capacity of Cu-SBA-15 was correlated with the confined space and silanol groups in template possessing SBA-15. However, to the best of our knowledge, reports on the effective role of silanols and microenvironment for nickel dispersion in as-synthesized mesoporous silica KIT-6 via single-step H_2-reduction strategy are very scarce, if any.

Herein, we report for the first time single-step H_2-reduction strategy to fabricate nickel based KIT-6 adsorbents (Scheme 1B). Three different nickel precursors were loaded into as-prepared KIT-6, and Ni^0-based KIT-6 was prepared through single-step H_2-reduction strategy which not only remove template of mesoporous support and decompose nickel precursors to NiO but also reduces NiO to Ni^0. Our results show that the shielding effect of capping anions along with hydration degree of nickel precursors highly affect the dispersion degree of nickel species even using as-prepared KIT-6 as a support and adsorption capacities were strongly correlated with nickel dispersion from different nickel precursors. Thus, one-step H_2-reduction strategy synthesized highly active nickel based materials for desulfurization of fuels with minimum consumption of time and energy and with the effective use of the confined spaces and silanols in mesoporous silicas.

2. Experimental

2.1. Materials

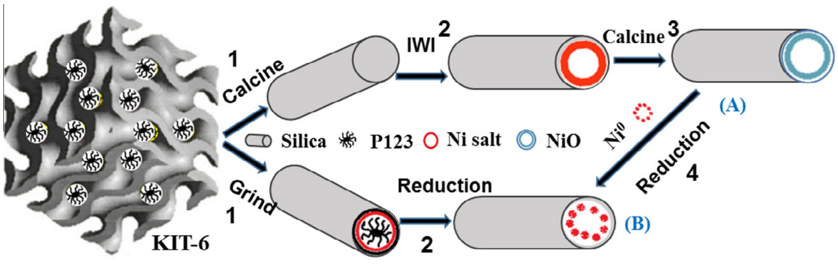
Thiophene with percentage purity of 99% was obtained from Aladdin Reagent Limited Company (Shanghai, China). $Ni(NO_3)_2\cdot 6H_2O$ (98%) was purchased from Shanghai Hengxin Chemical Reagent Co., Ltd. $NiCl_2\cdot 6H_2O$ (98%), $Ni(CH_3COO)_2\cdot 4H_2O$ (98%), n-Octane (98%) and TEOS (28.4%) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai China). Pluronic P123 (EO20PO70EO20, Aldrich) was purchased from Germany.

2.2. Preparation of as-prepared KIT-6

KIT-6 was synthesized hydrothermally as reported in literature [21]. In this procedure, 4 g of Pluronic P123 as a template was first dissolved in 144 mL distilled water. Then, 144 mL of HCl (35%) was added by continuous stirring at temperature of 35 °C for 4 h, followed by dropwise addition of n-butanol (4.95 mL) and continued stirring for an additional 1 h. Finally, TEOS (9 mL) was introduced and stirred at 35 °C for one day. The hydrothermal treatment at 100 °C for 24 h was performed in Teflon lined SS autoclave. The as-synthesized white material named as KIT-6 was recovered by filtration and subsequently dry at 100 °C for 12 h. Calcination of as-prepared KIT-6 was carried out in air at 550 for 8 h.

2.3. Preparation of Ni-KIT-6 and Ni/KIT-6 samples

In fabrication process before one step H_2-reduction strategy, three different nickel precursors as a nickel source were incorporated into as-synthesized KIT-6 *via* solid-state grinding at room temperature for 0.5 h, followed by drying overnight at 100 °C. The as-synthesized samples using Ni $(NO_3)_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$



Scheme 1. Synthesis of Ni-based KIT-6 via (A) Conventional method and (B) One-step H_2-reduction strategy.