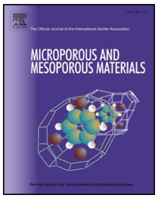
Microporous and Mesoporous Materials 265 (2018) 1–7

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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



Synthesis of mesoporous Ti-inserted SBA-15 and CoMo/Ti-SBA-15 catalyst for hydrodesulfurization and hydrodearomatization

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ARTICLE INFO

Keywords:
Cobalt molybdenum catalyst
Ti- SBA-15
Hydrodesulfurization
Hydrodearomatization
Microwave hydrothermal method

ABSTRACT

Ti-inserted ordered mesoporous silica SBA-15 (Ti-SBA-15) synthesized by original microwave-assisted method as a support was used to prepare CoMo catalysts to develop a new catalyst with high hydrodesulfurization (HDS) and controlled hydrodearomatization (HDA) activities. The activity tests of catalysts were carried out by using a pressurized fixed-bed flow reactor. 4,6-Dimethyldibenzothiophene (4,6-DMDBT), 1-methylnaphthalene, and phenanthrene were used as model reactants in HDS and HDA, respectively. CoMo/Ti-SBA-15 catalyst showed about 1.35 times of HDS activity and half of HDA activity of CoMo/SBA-15 catalyst. The results of XRD, FT-IR and ^{29}Si-NMR reveal that titanium was successfully inserted into silica framework of SBA-15, and the SBA-15 mesoporous structure was maintained after insertion of titanium. The reduction of molybdenum from Mo^{6+} to Mo^{4+} readily occurred with incorporation of titanium, resulting in an increase in Mo^{4+} species and CoMoS phase on sulfided catalysts. This enhanced the HDS activity of CoMoTiSBA15 catalyst. Moreover, the presence of Ti^{3+} on CoMo/Ti-SBA-15 was observed, suggesting that TiMoS was formed and played a role as new active sites. CoMoS active slabs with shorter length and higher stacking layer were formed on CoMo/Ti-SBA-15 comparing with CoMo/SBA-15, resulting in the low HDA activity of the former.

1. Introduction

Recently, production of valuable Benzene-Toluene-Xylene (BTX) from light cycle oil (LCO) produced in the fluidized catalytic cracking (FCC) process, i.e. selecting hydrotreating, has been focused. In hydrotreating of LCO by using conventional alumina supported catalyst, poly-aromatic compounds are also completed hydrogenated to saturated hydrocarbon as well as the removal of sulfur and nitrogen compounds that cause high consumption of hydrogen. Therefore, it is necessary to develop a special catalyst with high activity of hydrodesulfurization (HDS) and controlled activity of hydrodearomatization (HDA) that only convert polyaromatic compounds to monoaromatic compounds.

Al_2O_3 is the most widely used support material but due to its strong metal-support interaction (MSI), the catalytic activity was limited [1]. Another metal oxides or mixed metal oxides materials such as TiO_2 [2], SiO_2 [3], Al_2O_3- TiO_2 [4], Al_2O_3- SiO_2 [5] or mesoporous zeolites such as MCM-41 [6], HSM [7], SBA-15 [8] and their modified material with substitution of foreign metals, i.e., MHS-Ti [9,10], Al-HMS [11] were used as catalyst supports to overcome the disadvantage of Al_2O_3 and improve the common catalytic activity. Among these new support, titania was reported as a support with higher HDS activity and higher hydrodenitrogenation (HDN) selectivity than alumina [12–15] but the specific surface area of titania is very low and expensive that could not be suitable for industrial usage. The mesoporous silica materials like SBA-15 have larger pores, thicker pore walls and higher hydrothermal stability [16] but SBA-15 showed low support-metal interaction that a special method like ultrasonic deposition had to be used to achieve a better dispersion of sulfide metal spices [8,17]. Therefore, combining of titania and SBA-15 is expected to develop a support that can not only overcome low support-metal interaction of SBA-15 and low surface area of titania but also enhance active metals dispersion [18]. The supports synthesized by grafting titanium [19,20] on SBA-15 or insert titanium into SBA-15 structure methods were reported by a few researching groups [21,22]. Chemical grafting and incipient wetness impregnation methods are conventionally used to graft titanium on zeolite support surface [23] while hydrothermal method is often applied for inserting titanium into SBA-15 framework [24,25]. Moreover, Zhan et al. also proposed a chemical vapor deposition for grafting titanium on SBA-15 [26]. The most suitable synthesis method for HDS catalyst is via direct hydrothermal procedure using titanium isopropoxide as titanium resource that reported by Laniecki et al. [27]. However, there is extremely less compelling evidences of how titanium be grafted or inserted and discussion on controlling of adding titanium amount. There

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https://doi.org/10.1016/j.micromeso.2018.01.026
Received 26 October 2017; Received in revised form 12 January 2018; Accepted 16 January 2018

Table 1
Textural and structural characteristics of prepared supports and catalysts.

Catalysts	CoO[a] (wt%)	MoO_3[a] (wt%)	Ti[a] (wt%)	Surface area[b] (m^2/g)	d_p[c] (nm)	V_p[d] (cm^3/g)	NO adsorption amount (mmol/g)
SBA-15	–	–	–	733	6.18	0.78	–
20Ti-SBA-15	–	–	2.9	718	5.41	0.82	–
CoMo/SBA-15	3.4	16.8	–	305	6.18	0.34	6.20
CoMo/Ti-SBA-15	3.6	16.7	2.4	236	4.76	0.33	7.17

[a] Chemical composition determined by XRF.
[b] Specific surface area.
[c] Average pore diameter.
[d] Pore volume.

is also less report about identification of state of titanium in/on SBA-15. Besides, the synthesizing methods of these supports are complex and take long time of about over 48 h. Moreover, to our best knowledge, there are few reports on applying of Ti-SBA-15 in hydrotreating catalysts. Ti-SBA-15 supported CoMo catalyst was reported to have more activity in HDS of dibenzothiophene than the Ti-free one because the incorporation of titanium into SBA-15 framework providing better dispersion for the oxide and sulfide metal species and enhanced the direct desulfurization route (DDS) [28]. However, the effect of insertion of titanium into SBA-15 to the control of hydrogenation, especially HDA, have not yet been discussed until now.

In the present study, we considered to develop a new catalyst with high HDS and controlled HDA activity. Firstly, we introduced Ti-inserted ordered mesoporous silica SBA-15 (denoted as xTi-SBA-15 in which x = Si/Ti molar ratio) was prepared by an original and simply microwave-assisted hydrothermal method that dramatically shortened the synthesis time. The CoMo supported on Ti-SBA-15 and Ti-free catalysts were synthesized in order to investigate the relationship between active slabs structure and catalytic activity.

2. Experimental

The SBA-15 and Ti-SBA-15 synthesized time was 24 h shortened by using following original microwave-assisted method. In case of synthesis of 20Ti-SBA-15 (Si/Ti molar ratio = 20), firstly 21 g silica source tetraethylorthosilicate (TEOS), 1.1 g titanium source, titanium isopropoxide $Ti(OCH_2CH_3)_4$, and 10 g directing agent Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Mw = 5800) purchased from Aldrich were mixed and rotated with 20 g anhydrous ethanol as solvent until completely soluble. Above solution was added into rotary evaporator and stirred for 3 h at 40 °C until anhydrous ethanol was completely vaporized. Then the solution was moved to a pressure tight glass-tube and 40 g water was added for hydrolysis and aging by microwave-hydrothermal method using a microwave reactor (μReactor, Shikoku Instrumentation Co.) with following conditions: 1 h, 90 °C and 200 W. The crystallized product was washed with hot distilled water and dried overnight at 60 °C. Lastly, the powder was calcinated at 450 °C for 6 h and then sieved to yield 425–800 μm particles by extrusion molding method. The 10Ti-SBA-15 was synthesized with the same method.

The 20Ti-SBA-15 supported cobalt and molybdenum catalyst were prepared by conventional incipient wetness impregnation [29], dried in air at 120 °C for 2 h, and then calcined at 450 °C for 12 h in air. Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Kishida Chem. Co., purity > 99.9%) and cobalt nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$ (Kishida Chem. Co., purity > 99.9%) were used as precursors to achieve a loading amount of 16.6 wt% MoO_3 and 3.3 wt% CoO, in which MoO_3 was introduced first. Synthesized catalyst is denoted as CoMo/Ti-SBA-15.

Supports and CoMo supported catalyst were characterized by means of BET, XRF, XPS, TEM and ^{29}Si-NMR as reported before [30–32]. Besides, prepared supports were characterized by small-angle X-ray diffraction (Smartlab, Rigaku) using Cu Kα radiation at 45 kV and 200 mA. Data were collected from $2\theta = 0.5°$ to $5.0°$ with scan speed of 0.5°/min and step size of 0.02°/s. FT-IR spectra of synthesized supports were recorded on an IRPrestige-21 instrument (Shimadzu Co.) by attenuated total reflection (ATR) method at a resolution of 4 cm^{-1} with 64 scans in the wavenumber range of 400–4000 cm^{-1}. NO pulse chemisorption was performed using ChemBET Pulsar TPR/TPD instrument (Quantachrome Instruments). 200 mg of the catalysts was used for each experiment. After sulfidation, the sample was further heated to 400 °C under a helium flow for surface cleaning and cooled to 40 °C for pulse adsorption. 10% NO/He gas were subsequently introduced using calibrated injection valve (250 μL NO $pulse^{-1}$). Prior to analysis or reaction, the prepared catalyst was activated by sulfidation with a mixture of 5 vol% H_2S in H_2 (50 mL/min) at 400 °C for 3 h.

4, 6-dimethyldibenzothiophene (4, 6-DMDBT), phenanthrene and 1-Methylnaphthalene (1-MN) which have been purchased from Sigma-Aldrich (> 97% purity), Wako Pure Chem. Ind. (> 97% purity) and Acros Organics (> 98% purity), respectively, were chosen as model feedstocks to evaluate the HDS and HDA activities of the catalysts. Decalin (Kishida Chem. Co.) was the commercial GR grade and used as solvent for all feedstocks. The activity tests were carried out using a high-pressure fixed-bed continuous-flow stainless steel reactor (i.d. 8 mm), operated in the down-flow mode, under the 300 mL/min flowing H_2 at pressure of 5 MPa, with a weight hourly space velocity (WHSV) of 39 h^{-1} at 260–320 °C. After reactions, the products qualitative was performed using a gas chromatograph–mass spectrometer (GC–MS-QP5050A, Shimadzu Co.). The quantitative of products were conducted using a gas chromatograph (GC-2025, Shimadzu Co.) equipped with a flame ionization detector (FID) and a DB-1 column (Agilent, 60 m × 0.25 mm i.d., 0.25 μm).

3. Results and discussion

3.1. Synthesis and characterization of Ti-SBA-15 support

The textural properties of prepared supports are shown in Table 1. Due to the insertion of titanium, the surface area and pore size of SBA-15 support decreased slightly from 733 to 718 m^2/g and 6.18 to 5.41 nm, respectively. The nitrogen adsorption-desorption isotherms and pore size distributions of various supports were shown in Fig. 1. The curves are type IV and the pore sizes are the same that in good agreement with previous study [33]. It can be revealed that substation of titanium did not changed textural properties of SBA-15 support. However, the relative pressure range was quite wide from $p/p_o = 0.5$ to 1.0 indicated that the pore size was slightly reduced as shown in Table 1. Besides, TiO_2 did not be detected by XRF measurement and the amount of titanium was loaded as expect, which are 2.9 and 2.4 wt% for 20Ti-SBA-15 support and CoMoTiSBA15 catalyst, respectively.

Powder small-angle XRD measurement was carried out to investigate the nature of mesoporous structure of zeolite supports. The XRD patterns of calcined SBA-15, 20Ti-SBA-15 are presented in Fig. 2. Both samples showed the same three peaks as following: an intense peak at $2\theta = 0.8°$ and two very weak peaks at $2\theta = 1.7°$ and 2.1°, which are attributed to the (100) and (110), (200) diffraction planes, respectively. The two latter peaks are too weak to be observed. These