



## Effect of Ti loading on the HDS and HDN activity of KLGO on NiMo/TiSBA-15 catalysts

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### ABSTRACT

TiSBA-15 with high surface area and large pore diameter with variable Si/Ti molar ratios of 20, 40, and 80 were synthesized and used as supports for NiMo catalysts. TiSBA-15 supports and NiMo/TiSBA-15 catalysts were extensively characterized by using XRD, N<sub>2</sub> adsorption analysis, FT-IR, Py-FTIR, Raman, TPR, SEM and TEM techniques. Results from XRD and IR measurements confirm the hexagonally ordered mesoporous structure and incorporation of Ti into the framework of SBA-15 support, respectively. TPR analysis confirmed that Ti incorporation resulted in better dispersion and more homogeneous distribution of octahedral Ni and Mo species on the support compared to NiMo/SBA-15. Hydrotreating experiments were conducted using coker light gas oil (KLGO) under industrial conditions of temperature, pressure, LHSV, and gas to oil ratio of 330–370 °C, 8.8 MPa, 2 h<sup>-1</sup>, and 600 mL/mL, respectively. NiMo/TiSBA-15 catalysts showed very high catalytic activities of hydrodesulfurization and hydrodenitrogenation of KLGO than the NiMo catalysts prepared by using SBA-15 and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as support.

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### 1. Introduction

Catalytic hydrotreating (HDT) is one of the most important processes in the petroleum-refining industry from technical, economic, and environmental points of view. The hydrotreating process has been used for over 60 years to reduce the polluting compound content (sulfur, nitrogen, aromatics, etc.) in fossil fuels and to fulfill the applicable legal norms of gas emissions. The recent environmental regulations on sulfur and nitrogen specifications for transportation fuels are very stringent, and will be increasingly so [1]. A problem currently facing by the petroleum industry is that a significant part of the reserves consists of heavier fractions with a high content of contaminants such as sulfur, nitrogen, (poly)-aromatics, and metals [2,3]. Heavier crudes and bitumens tend to be richer in both sulfur and nitrogen. While hydrotreating is relatively effective in removing sulfur down to low concentrations, hydrodenitrogenation (HDN) is much harder to accomplish. The current technology for nitrogen removal mainly relies on sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts.

The demand for lower sulfur and nitrogen content in fuels requires the synthesis of more active catalysts [4]. This has led to a worldwide search for better catalysts for hydrotreating of these compounds. One approach includes the improvement of existing

sulfide catalysts and the investigation of new compositions such as carbide, nitride, phosphides, heteropoly acid and another approach is to find a suitable support [5–9]. Many studies have shown that one of the major factors affecting the activity of a catalyst is the interaction between the active components of the catalyst and the support. Development of novel supports seems to be an interesting and practical option because the support nature and characteristics play an important role in the catalytic activity. So far, different materials have been tried as supports for Mo (or W) active phases promoted by Ni (or Co). It was found that the support can influence catalyst reducibility or sulfidability, structure and dispersion of the deposited metal oxides, as well as the morphology of the sulfided active phases [10].

Many studies described the influence of the support on the performance of hydrotreating catalysts such as molecular sieves [11,12], amorphous and ordered mesoporous silica-aluminas [13], zirconia [14], titania [15], niobia [16] and other metal and mixed oxides [17,18]. In recent years, the mesoporous silicate materials with ordered pore structure such as MCM-41, SBA-15, KIT-6, and FSM-16 [19–23] materials, which have large pore diameters and higher surface areas than the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> attracted widespread attention as new potential materials for the preparation of supported hydrotreating catalysts. There are several reports available on developing high performance supported hydrotreating catalysts on HMS, MCM-41 and SBA-15 materials. Principally, the HMS material prepared by a neutral template

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pathway offers certain advantages for the preparation of supported hydrotreating catalysts over the MCM-41 material that is synthesized by electro-statically template [20]. This advantage could be because the HMS material shows higher thermal and hydrothermal stability than the MCM-41 material. Unfortunately, the HMS material has low mechanical and thermal stability in comparison with the  $\gamma$ - $\text{Al}_2\text{O}_3$  [20,21]. Several solutions have been reported in open literature to enhance the stability of mesoporous materials. In this regard, SBA-15 material was synthesized having high thermal, hydrothermal and mechanical stability, and its textural properties are better than those of the HMS, MCM and traditional  $\gamma$ -alumina supports. Pure siliceous SBA-15 materials have already been tested as supports for unpromoted and promoted catalysts. Vradman et al. [24] reported the excellent performance of NiW/SBA-15 catalyst in the deep hydrodesulfurization (HDS) of petroleum feedstocks. Sampieri et al. [25] reported the preparation of Mo/SBA-15 catalysts with various Mo loadings (9, 14 and 20 wt.%) by thermal spreading of  $\text{MoO}_3$ . These catalysts showed higher catalytic activity in dibenzothiophene HDS than the reference Mo/ $\text{Al}_2\text{O}_3$  catalyst, and the activity was found to increase with the Mo loading up to 14 wt.% Mo. Murali Dhar et al. [21] evaluated the catalytic activity of Mo/SBA-15 catalysts with 2–12 wt.% Mo loadings, prepared by a standard incipient wetness impregnation method, in HDS of thiophene and hydrogenation (HYD) of cyclohexene. It was also observed that SBA-15-supported catalysts were 2–2.5 times more active compared to  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported formulations.

The modification of the mesoporous SBA-15 by incorporating heteroelements (Ti, Al, Zr, etc.) provides the silica framework additional structural stability in comparison with the counterpart heteroelement-free molecular sieves [19,20,26]. In particular, the Al and Ti-containing SBA-15 material has thicker pore walls and acceptable hydrothermal stability [27]. Kumaran et al. [28] synthesized Mo, CoMo, and NiMo catalysts supported on Al-containing SBA-15 materials with different Si/Al ratios (10–40). Aluminum (III) incorporation in the support increased Mo dispersion and catalytic activities in thiophene HDS and cyclohexene HYD. Murali Dhar et al. [29] prepared SBA-15 materials modified with various amounts (10–50 wt.%) of  $\text{ZrO}_2$  nanoparticles by the urea hydrolysis method and tested them as supports for Mo, CoMo, and NiMo catalysts. Their catalytic activities for thiophene HDS and cyclohexene HYD were evaluated as a function of  $\text{ZrO}_2$  content in SBA-15. It was noted that both HDS and HYD activities increased up to 25 wt.% of zirconia and decreased with further increase in  $\text{ZrO}_2$  loading. Nava et al. [27] studied the effect of Ti-loading on CoMo/SBA-15 catalysts for HDS of DBT and reported that the Ti-containing catalysts were more active than the Ti-free counterpart and traditional alumina-supported catalysts. Gutierrez et al. [30] prepared NiMo catalysts using SBA-15 as supports modified with titanium (IV) or zirconium (IV) oxides. These catalysts showed high performance in HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT), one of the most refractory sulfur compounds.  $\text{TiO}_2$  and  $\text{ZrO}_2$  loading in the support produced an increase in the activity. Improvement of the catalytic activity was attributed to an increase in the dispersion of Ni and Mo species due to their strong interaction with titania and zirconia-containing supports compared to pure SBA-15 support.

To our knowledge, there are no reports about the use of heteroatom-modified SBA-15 materials in hydrotreating of KLGO as feed derived from Athabasca bitumen. In the present work, with the aim of searching for new, highly effective catalysts for deep hydrotreating, a series of NiMo/TiSBA-15 catalysts with different Si/Ti ratios (20, 40 and 80) were prepared and KLGO HDS and HDN activity on these catalysts were studied in detail. The heteroatom Ti present in the support improves the interaction of the support with the active metal deposited and improves the dispersion.

## 2. Experimental section

### 2.1. Catalyst preparation

TiSBA-15 supports with different Si/Ti ratios were synthesized using poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) as a structure-directing agent, titanium isopropoxide and tetraethyl orthosilicate as titanium and silica sources, respectively [31]. The molar gel composition of the mixture is  $\text{TEOS}:0.012\text{--}0.05 \text{ Ti}(-\text{O}^i\text{Pr})_4:0.016 \text{ P123}:0.46 \text{ HCl}:127 \text{ H}_2\text{O}$ . In a typical TiSBA-15 synthesis, 9.28 g of pluronic P123 was added to 228.6 g of water. After stirring for a few hours, a clear solution was obtained. Thereafter, 4.54 g of HCl (37%) was added and the solution was stirred for another 2 h. Then, 20.6 g of tetraethyl orthosilicate and the required amount of the Ti source were added, and the resulting mixture was stirred for 24 h at 40 °C. The solid products were recovered by filtration, washed several times with water, and dried overnight at 100 °C. The resulting gel was transferred to the polypropylene bottle and kept in an air oven at 100 °C for 48 h. The solid product was recovered by filtration, washed with water several times, and dried overnight at 100 °C. Finally, the product was calcined at 540 °C to remove the template. The samples were labeled TiSBA-15 (x), where x denotes the Si/Ti ratio.

The NiMo/TiSBA-15 (2.5 wt.%Ni and 13 wt.%Mo) catalysts with different Si/Ti ratios (80, 40 and 20) were prepared through incipient wetness co-impregnation method by using appropriate concentration of ammonium heptamolybdate and nickel nitrate. The impregnated samples were dried at 120 °C for 5 h and then calcined at 500 °C for 5 h in air. The NiMo/SBA-15 and NiMo/ $\gamma$ - $\text{Al}_2\text{O}_3$  were also prepared at same concentration for comparison purpose.

### 2.2. Characterization

#### 2.2.1. ICP-MS

The elemental compositions of the calcined NiMo/SBA-15 and NiMo/Ti-SBA-15 catalysts with different Si/Ti ratios were measured by ICP-MS. A catalyst sample (0.1 g) was dissolved in concentrated hydrofluoric acid (48–51%) at a temperature of 100–150 °C for three days. After cooling, samples were further dissolved in concentrated  $\text{HNO}_3$  to ensure the complete dissolution of the metals. The final solution was prepared using 0.2 N  $\text{HNO}_3$  and analyzed with a mass spectrometer.

#### 2.2.2. Measurement of $\text{N}_2$ adsorption–desorption isotherms

The BET surface area, pore volume, and pore size distribution of the samples were measured with a Micromeritics ASAP 2000 instrument using low temperature  $\text{N}_2$  adsorption–desorption isotherms. Before measuring, the sample was degassed in vacuum at 200 °C. The surface area was computed from these isotherms using the multi-point Brunauer–Emmett–Teller (BET) method based on the adsorption data in the partial pressure  $P/P_0$  range from 0.01 to 0.2. The value of 0.1620  $\text{nm}^2$  was taken for the cross-section of the physically adsorbed  $\text{N}_2$  molecule. The mesopore volume was determined from the  $\text{N}_2$  adsorbed at a  $P/P_0 = 0.4$ . The total pore volume was calculated from the amount of nitrogen adsorbed at  $P/P_0 = 0.95$ , assuming that adsorption on the external surface was negligible compared to adsorption in pores. The pore diameter and pore volume were determined using the (BJH) method. In all cases, correlation coefficients above 0.999 were obtained.

#### 2.2.3. X-ray diffraction (XRD) analysis

The low-angle X-ray diffraction patterns of the samples were measured using a Bruker D8 Advance Powder diffractometer with a Ge monochromator producing a monochromatic  $\text{Cu K}\alpha$  radiation.

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