

Mesoporous Al-SBA-15 as a support for NiMo sulfide catalysts for hydrotreating of gas oil

V. Sundaramurthy¹, I. Eswaramoorthi¹, A.K. Dalai^{1*} and J. Adjaye²

¹Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, S7N 5A9, Canada

²SynCrude Edmonton Research Centre, Edmonton, AB, T6N 1H4, Canada

*ajay.dalai@usask.ca

Introduction

γ -Al₂O₃ supported NiMoS is widely used in oil refineries for the hydrotreating of petroleum derived feedstocks. The improvement of above catalysts is mandatory in view of the greater concern over environmental pollution by automobiles and consequently more stringent limitations to sulfur contents in gasoline and diesel fractions. In recent years, in order to improve the activity of hydrotreating catalysts, many approaches like changing the active component, preparation method and support have been followed. Among these approaches, variation of support is an important one. Different materials have been studied as supports for hydrotreating catalysts, such as metal oxides, carbon, zeolites, mesoporous materials like MCM-41, SBA-15, mixed metal oxides. Among the different supports, MCM-41 and SBA-15 have attracted attention in recent years due to their ordered mesoporous with controlled pore size and high surface area. MCM-41 supported CoMo and NiMo catalysts are reported to exhibit substantially more active than corresponding γ -Al₂O₃ catalysts. However MCM-41 type materials have poor stability, which represents a serious limitation to their practical applications. SBA-15 type materials have larger pores, thicker pore walls and higher hydrothermal stability compared to MCM-41. Purely siliceous SBA-15 has been tested as support for NiW [1], CoMo and NiMo [2] sulfides and their hydrotreating activity has been explored using model compounds such as dibenzothiophene [1] and thiophene [2]. SBA-15 supported catalysts showed superior activity that conventional γ -Al₂O₃ support with model compounds. No report is available on hydrotreating of real feeds using SBA-15 supported catalysts. In this investigation, hydrotreating activity of NiMo supported on aluminum substituted SBA-15 (Al-SBA-15) was studied using light gas oil at industrial conditions.

Materials and Methods

Al-SBA-15 was synthesized by conventional hydrothermal method using Pluronic P123, tetraethyl orthosilicate and aluminum sulphate as template, silicon source, and aluminum respectively. The gel composition is 50 SiO₂: 1 Al₂O₃: 0.16P123: 0.46HCl. The gel is autoclaved at 120°C for 72 h. The filtered solid product was washed, dried and calcined at 500°C to remove the template molecules. Al-SBA-15 supported Ni Mo catalysts containing 7, 12, 17 and 22 wt.% Mo with Mo/Ni ratio of 0.2 (designated as cat-1, cat-2, cat-3 and cat-4) were prepared by a sequential pore filling impregnation procedure using ammonium heptamolybdate and nickel nitrate as a source for Mo and Ni respectively. The hydrotreating experiments were performed in a trickle bed reactor using 5 ml of catalyst. The feed used is light gas oil (LGO) derived from Athabasca bitumen. The experiments were done at 1300 psig pressure and 4.5 h⁻¹ of WHSV. The sulfidation of the catalyst was done first at 193°C and then at 343°C for 24 h using sulfidation solution containing 2.9 vol.% of butane thiol in a straight run atmospheric gas oil. Prior to the activity studies, the catalyst was precocked at 370°C with LGO for 3 days to get steady state activity.

Results and Discussion

Textural characteristics and Mo and Ni contents of the support and catalysts are listed in Table 1. Elemental chemical analysis of catalysts indicates that most of the Mo and Ni precursors are deposited on the support during the impregnation. The surface area and pore volume of the support decreased with Ni and Mo loading, due to the pore blocking of Al-SBA-15 with impregnated materials. X-ray diffraction of NiMo/Al-SBA-15 catalysts revealed no peaks other than that of amorphous silica (figure not shown), indicating high dispersion of Ni and Mo on the Al-SBA-15 surface. The TPR profiles of NiMo/Al-SBA-15 show that Ni as well as Mo species reduced at much lower temperature than that of NiMo/Al₂O₃, indicating higher dispersion of Mo and Ni on former catalyst. The surface sites on the sulfided NiMo/Al-SBA-15 catalysts were characterized by DRIFT spectroscopy of adsorbed CO. The CUS located on MoS₂ site and Ni promoted MoS₂ sites (NiMoS phase) are characterized by a band at 2094 and 2065 cm⁻¹ respectively. Both these sites are increasing with increase of Mo loading and optimum sites concentration are obtained with 17 wt.% of Mo (cat-3).

Table 1. Physico-chemical properties and HDN and HDS activities of NiMo/Al-SBA-15

Sample	Mo (wt.%)	Ni (wt.%)	Pore volume (cc/g)	Surface area (m ² /g)	Conversion (wt.%)	
					N	S
Al-SBA-15	-	-	1.36	709	-	-
Cat-1	6.7	1.5	1.15	612	41	88
Cat-2	11.2	2.3	0.96	540	68	90
Cat-3	16.8	3.1	0.85	504	83	92
Cat-4	21.3	4.2	0.72	462	79	93
Cat-5	12.2	2.4	0.59	196	81	94

The HDN and HDS activities of NiMo/Al-SBA-15 catalysts at temperature, pressure and WHSV of 370°C, 1300 psig and 4.5 h⁻¹ respectively are presented in Table 1 along with the conventional γ -Al₂O₃ supported NiMo catalyst (cat-5). It is observed that the HDN and HDS activities of Al-SBA-15 supported catalysts are significantly increased with increasing Mo content up to 17 wt% and beyond that there is no significant increase in both HDN and HDS activities. It indicates that 17 wt% Mo is the optimum for the better activity of NiMo/Al-SBA-15 catalyst. The HDN and HDS activities of this optimum Al-SBA-15 supported NiMo catalyst are comparable with the conventional Al₂O₃ supported catalyst in real feed at industrial conditions.

Significance

This finding demonstrates the excellent potential of high loading NiMo/Al-SBA-15 sulfide catalysts for hydrotreatment of gas oils derived from Athabasca bitumen.

References

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