Contents lists available at SciVerse ScienceDirect



Applied Catalysis A: General

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

# Catalytic hydrotreatment using NiMo/MAS catalysts synthesized from ZSM-5 nano-clusters

## S. Mohanty<sup>a</sup>, K. Chandra Mouli<sup>a</sup>, K.Soni<sup>a</sup>, J. Adjaye<sup>b</sup>, A.K. Dalai<sup>a,\*</sup>

<sup>a</sup> Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK S7N 5A9, Canada <sup>b</sup> Syncrude Edmonton Research Centre, Edmonton AB, T6N 1H4, Canada

#### ARTICLE INFO

Article history: Received 19 September 2011 Accepted 10 December 2011 Available online 20 December 2011

Keywords: Hydrothermal treatment ZSM-5 nano-seeds Acidity EXAFS Dibenzothiophene Hydrotreatment

## ABSTRACT

Mesostructured alumino-silcate (MAS) materials were synthesized from ZSM-5 nano-clusters and used as catalysts supports for the hydrotreatment of a model compound and real feed stock. Supports and catalysts were thoroughly characterized by using XRD, N<sub>2</sub> adsorption analysis, FT-IR, <sup>27</sup>Al MAS NMR, Raman, EXAFS and HRTEM techniques. The alumino-silicate materials exhibited different acid strength and textural properties depending on the duration of hydrothermal treatment of the zeolite seeds. Materials synthesized with low seeding time of 4 h showed properties similar to Al-SBA-15 prepared using the direct synthesis route, whereas material with high seeding time ( $t_{seed} = 24$  h) resembled ZSM-5. The EXAFS study of the sulfided catalysts revealed that sulfidation was highest in the NiMo catalyst supported on mesoporous alumino-silicate synthesized from ZSM-5 seeds with 16 h of hydrothermal treatment (MAS-16). Hydrotreating experiments were conducted using model compound (DBT) at 325 °C and 600 psi as well as real feed stock (Coker light gas oil) at industrial conditions. Catalytic activity in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) was found to be maximum for this particular catalyst (MAS-16). The same catalyst also gave higher hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) conversion than NiMo/ $\gamma$  Al<sub>2</sub>O<sub>3</sub> in the hydrotreating of Light Gas Oil.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Catalytic hydrotreating for the reduction of sulfur content in gasoline and diesel fuels has been an area of intensive research recently. Stringent environment legislations have meant that sulfur content in gasoline and diesel fuel be lowered to 10-50 ppm in most countries [1,2]. Consequently, hydrodesulfurization (HDS) catalysts with improved activity, product selectivity and longevity are needed to meet the stricter sulfur specifications of transportation fuels. Past studies have shown that the removal of refractory molecules like DBT and 4,6 DMDBT poses the greatest challenge for achieving ultra-low levels of sulfur [3]. One of the most promising approaches towards improving the performances of hydrotreating catalyst is the replacement of the conventionally used alumina by zeolites and other related acidic materials as supports for the CoMo and NiMo sulfide phases. These acidic materials have high surface areas for metal dispersion and a higher concentration of Bronsted and Lewis acid sites compared to alumina. A synergetic effect arising from the presence of both hydrogenating and strong acid sites not only accelerates the direct cleavage of the C-S bond

but also promotes alternate pathways to the removal of sulfur atom from the aromatic molecule. This effect is especially pronounced in the HDS of 4,6 DMDBT, where isomerization of 4,6 DMDBT to 3,6 DMDBT improves the rate of C—S bond scission [4,5]. Regardless of their favorable acidic properties, zeolites are essentially microporous systems (pore size <2 nm) which severely limits their applications in the field of hydrotreating bulky molecules [6,7]. As a result, there is a continuous interest in synthesizing materials that not only possesses the high surface area and strong Bronsted acid sites of zeolites but also have a more open porous system preferably with a narrow pore size distribution in the mesoporous range.

Mesoporous silica materials such as MCM-41, HMS, SBA-15 and KIT-6 with open porous channels are ideal catalyst supports for the catalytic conversions of large molecules as they can overcome the diffusion barrier for reactants and products [3,8–10]. In spite of their excellent textural properties the applications of these materials in catalytic reactions where acidity plays an important role is very limited. This restriction stems from the absence of strong Bronsted acid sites as their surface is predominantly made of silanol groups [11]. In order to overcome the disadvantages of both zeolites and siliceous mesoporous materials, various teams have synthesized materials with strong acidity in open porosity through the surfactant based assembly of zeolite nano-clusters present in the precursors that nucleate to form the final crystalline zeolite. This

<sup>\*</sup> Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777. *E-mail address:* ajay.dalai@usask.ca (A.K. Dalai).

<sup>0926-860</sup>X/\$ - see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2011.12.015

approach has been demonstrated by the successful assembly of ZSM-5 (MFI), Beta (BEA), Y (FAU) zeolite nano-clusters resulting in a mesoporous structure with strong acid sites [12–16]. The main advantage of this type of approach is the complete or nearly complete incorporation of aluminum atoms into the silica framework in a tetrahedral coordination similar to that observed in zeolites. In comparison post synthesis and direct synthesis methods for Al incorporation into silica framework of various mesoporous materials have resulted in octahedral aluminum being present as extra framework atoms.

The fine characterization and the study of the mechanistic assembly of the zeolite nano-clusters present in the precursor solution have led to the conclusion that the duration of hydrothermal treatment of the zeolite precursor solution containing the zeolite nano-clusters is a key parameter to adjust the final properties of the resulting material [17]. Zeng et al. reported the transition of MCM-41 type material synthesized from  $\beta$  zeolite seeds from an amorphous phase to a crystalline one for hydrothermal treatment durations between 6 and 16 h [18]. Similarly Frunz et al. have also studied the effect of hydrothermal treatment on the assembly of ZSM-5 seeds into a mesoporous structure using CTAB as a template. They reported first reflections of the ZSM-5 phase after 48 h of hydrothermal treatment. Interestingly all works conclude an enhanced catalytic activity for such materials in acid catalyzed reactions. The cumene cracking activity was found to be comparable to ZSM-5 and higher than ZSM-5 for the cracking of Tri iso propyl benzene (TIPB) [19]. Similarly favorable results were obtained in hydrocracking reactions and HDS of 4,6 DMDBT when these materials were used as supports for the NiW sulfide phase [20]. Based on the previous works it appeared interesting to us to evaluate the catalytic activity of these materials synthesized using different hydrothermal treatment durations in the HDS of both model compounds and real feed stock.

In our current study, Mesostructured alumino-silcate (MAS) materials were synthesized from the assembly of ZSM-5 nanoclusters using P123 as the surfactant. The synthesized materials are then used as supports for NiMo catalysts in the HDS of DBT and hydrotreating of light gas oil (LGO) obtained from Syncrude, Canada. To our knowledge, no published work has been found whereby this type of hydrotreating catalysts was screened using real feedstock. The aim of this work is to study the effect of hydrothermal treatment on the synthesis of MAS to develop highly active hydrotreating catalysts. The activities of these catalysts were then compared to NiMo catalyst supported on Al-SBA-15 and Al<sub>2</sub>O<sub>3</sub>.

## 2. Experimental

#### 2.1. Synthesis of mesoporous alumino silicates from ZSM-5

The mesoporous alumino silicate material was synthesized using the method proposed by Han et al. [21]. A typical synthesis procedure consisted of two steps: (a) preparation of the ZSM-5 nano-seed solution and (b) assembling the synthesized nano-seeds in a surfactant based approach to form the final mesoporous alumino silicate material. The chemicals used for the syntheses were tetraethoxy silane (TEOS) (>98%, Aldrich), tetrapropylammonium hydroxide (TPAOH) (1.0 M in water, Aldrich), a triblock copolymer based surfactant P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) and sodium aluminate (BDH) as the aluminum source. The zeolite precursor solution was prepared mixing 14 mL of tetrapropylammonium hydroxide (TPAOH) aqueous solution, 0.35g of NaAlO<sub>2</sub>, and 24 mL of tetraethyl orthosilicate (TEOS) with 68 mL of H<sub>2</sub>O under stirring (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Na<sub>2</sub>O/(TPA)<sub>2</sub>O/H<sub>2</sub>O with molar ratios of 1.0/50/1.0/7/1800). The clear solution thus obtained was subjected to hydrothermal treatment at 100 °C in an autoclave for various

durations. In all three precursor solution with the same chemical composition (Si/Al ratio 25) but different seeding times of 4, 16 and 24 h were prepared. Another precursor solution was prepared without any heating, but was aged for 2 h after stirring. The organization of the polymerizing silica present in the precursor solution was done using the ampiphilic triblock copolymer P123 as described by Zhao et al. [22]. 10 g of  $EO_{20}PO_{70}EO_{20}$  (Pluronic P123) was dissolved in 265 mL of H<sub>2</sub>O with 98 mL of HCl (10 M/L), followed by the addition of the precursor solution (containing 8 mmol of SiO<sub>2</sub>) obtained in step one. The mixture was stirred at 40 °C for 24 h and then transferred into an autoclave for additional reaction at 100 °C for 36 h. The product was collected by filtration, dried in air, and calcined at 550 °C for 5 h to remove the organic template. The final samples were labeled as MAS-4, MAS-16 and MAS-24 in accordance with the heating times of the precursor solution.

Al-SBA-15 and  $\gamma$  Al<sub>2</sub>O<sub>3</sub> were used as the reference materials in this study. Al-SBA-15 was prepared using the direct synthesis route as described by Yue et al. [23]. The same Si/Al ratio of 25 was maintained for Al-SBA-15 as well. Aluminum nitrate was used at the Al source in the preparation method. The  $\gamma$  Al<sub>2</sub>O<sub>3</sub> support was procured from La Roche Chemicals and was used without any further modification.

#### 2.2. Preparation of NiMo catalysts

Supported NiMo catalysts were prepared by the incipient wetness co-impregnation method using aqueous solutions of Ammoniumheptamolybdate (AHM) and nickel nitrate hexahydrate as a Mo and Ni source respectively. The nominal composition of all these catalysts was 4 wt.% Ni and 15 wt.% Mo. The impregnated catalysts were dried overnight at 100 °C and subsequently calcined at 500 °C for 4 h to get the final oxide catalyst.

## 2.3. Characterization

#### 2.3.1. ICP-MS

Quantitative estimation of Si/Al ratio was performed using inductively coupled plasma-mass spectrometer (ICP-MS). A catalyst sample (0.1 g) was dissolved in concentrated hydrofluoric acid (48–51%) at a temperature of 100-150 °C for 3 days. After cooling, samples were further dissolved in concentrated HNO<sub>3</sub> to ensure the complete dissolution of the metals. The final solution was prepared using 0.2 N HNO<sub>3</sub> and analyzed with a mass spectrometer.

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

The low-angle X-ray diffraction patterns of the samples were measured using Bruker D8 Advance Powder diffractometer with a Ge monochromator, producing a monochromatic Cu K $\alpha$  ( $\lambda$  = 1.54 Å) radiation. The scanning was made from 1.5° to 10° for the small angle measurements and 15–60° for the high angle measurements with a 2 $\theta$  step size of 0.02 and a step time of 2 s. In all cases, the generator was operated at 40 kV and 30 mA. To avoid the problem of illuminated areas at low 2 $\theta$  angles, all the samples were measured using the same sample holder.

#### 2.3.3. Measurement of $N_2$ 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 N<sub>2</sub> adsorption–desorption isotherms. Before the measurement, each 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<sub>0</sub> range from 0.01 to 0.2. The mesopore volume was determined from the N<sub>2</sub> 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 with 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.

## 2.3.4. FT-IR spectroscopy

The Fourier transform infra red (FT-IR) spectra were recorded in the range  $400-900 \,\mathrm{cm}^{-1}$  wave numbers using 64 scans and a resolution of  $4 \,\mathrm{cm}^{-1}$  with a JASCO FT-IR 4100 using pellets with spectroscopic grade potassium bromide (KBr).

The pyridine adsorption experiments were performed using a Perkin-Elmer Spectrum GX instrument. Prior to the pyridine adsorption, the samples were dried at 500 °C and maintained under vacuum ( $10^{-7}$  bar) for 3 h. Pyridine was then injected into the sample by saturating the He carrier gas for 30 min at room temperature followed by degassing and evacuation at 250 °C. Molar extinction coefficients of 1.67 cm/µmol and 2.22 cm/µmol were used to determine the absolute amount of Bronsted and Lewis acid sites [24].

#### 2.3.5. Transmission electron microscopy (TEM)

The morphologies of the materials were characterized by transmission electron microscopy (TEM). Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a carbon-coated copper grid. TEM investigations were carried out using a Philips CM20 (100 kV) transmission electron microscope equipped with a NARON energy-dispersive spectrometer with a germanium detector.

## 2.3.6. <sup>27</sup>Al MAS NMR spectroscopy

<sup>27</sup>Al MAS NMR experiments were performed on a Bruker AMX-400 FT NMR spectrometer operated at 104.2 MHz. All spectra were acquired using single-pulse excitation and spinning speeds ranging from 14 to 15 kHz. The spectra were typically obtained with a pulse width of 1.5 μs, and recycle delay of 1 s. Baselines were corrected and smoothed using the Bruker baseline correction routine. All spectra were externally referenced to aluminum nitrate solution ( $\delta$  = 0 ppm).

#### 2.3.7. Raman spectroscopy

The Raman spectra were obtained using a Renishaw Micro-Raman System 2000 Spectrometer (Spectra-Physics model 127) equipped with a He/Ne laser, operated at the argon laser wavelength of 514.5 nm. The laser spot size was approximately 1 mm with a power of 10 mW. The wavenumber accuracy was  $\pm 2 \text{ cm}^{-1}$ .

#### 2.3.8. EXAFS data collection and analysis

Mo K-edge XAS data were collected for three sulfided catalyst samples sat the Hard X-ray Microanalysis beamline (HXMA, 06ID-1) at the Canadian Light Source. The synchrotron source at the HXMA beamline is a superconducting wiggler and the beamline is equipped with a double-crystal Si(220) monochromator and Rhcoated, upstream collimating and downstream focusing mirrors. The operational current in the storage ring of CLS is 200-250 mA at 2.9 GeV. The harmonic rejection was accomplished by detuning the second monochromator crystal to 50% of the maximum intensity. XAS data for the sulfided samples were collected in fluorescence mode using a 32 element solid state germanium detector. The XAS data for the catalyst samples were collected at ambient temperature and pressure with the simultaneous measurement of a Mo reference foil spectra for energy calibration. Approximately 200 mg of the sample was pressed into the 10 mm ID quartz sample holder. The weight of the sample was calculated to have a total absorption length of about 2.0 for optimal signal to noise ratio.

The XAS spectral data collected were analyzed using Athena [25]. The data reduction of the XAS spectra included the

standard procedures for energy calibration, averaging of multiple scans, background subtraction as well as per atom normalization. Ab initio theoretical phase shifts and amplitude functions for the Mo–O, Mo–S and Mo–Mo contributions were calculated using the program FEFF version 8. Multiple shell fitting of the Mo K edge EXAFS data was done in *R*-space using the program Artemis. The fitting was done over a *k* range of 3.5-13.98 (Å)<sup>-1</sup> range. The fitting in R space ranged from 1 to 4 Å. This data and modeled regions contain approximately 18 independent points. This model is a well-constrained model as the number of independent parameters was roughly twice more than the number of parameters determined in the fit. The estimated accuracies of the EXAFS fit parameters were  $\pm 20\%$  for the coordination number (N),  $\pm 0.04$  Å for the coordination distance (*R*),  $\pm 20\%$  for the Debye–Waller factor  $\sigma_s^2$  and  $\pm 10\%$  for the inner-potential correction  $\Delta E_0$ .

#### 2.4. Catalytic activity

## 2.4.1. Catalytic hydrodesulfurization of DBT

Catalytic hydrodesulfurization of model compound DBT was performed in a 500 mL autoclave type Parr reactor at a reaction condition of  $325 \,^{\circ}$ C temperature and 600 psi pressure.

Before starting the reaction, the pelletized oxidic catalysts were sulfided exsitu by injecting sulfidation solution containing 2.9 vol.% of butanthiol in straight run atmospheric gas oil at a pressure and temperature of 8.8 MPa and 325 °C, respectively, for 24 h. The flow rate of the sulfiding solution was 5 mL/h. The H<sub>2</sub> flow rate was kept at a rate corresponding to H<sub>2</sub> sulfiding solution ratio of 600 mL/mL. 1 g of the sulfided catalyst (sieved between 0.3 and 0.5 mm) was transferred into the batch reactor containing the feed in an inert atmosphere at 25 °C.

The feed was prepared by diluting the DBT using a mixture of cis (55%) and trans decalin (45%) and dodecane (0.05 mol/L) as an internal reference. The concentration of DBT in the resulting mixture was kept 0.2 mol/L using 150 mL of decalin mixture. Reaction mass balances were found to be more than 95% in all experiments, for each reactant using dodecane as the internal reference. In a typical experiment, about 6 liquid samples of approximately 0.5 mL each were withdrawn, so that the volume feed could be considered constant throughout the experiment. The liquid product samples were diluted in ethanol (500 mL) and analyzed by GC for cyclohexyl benzene (CHB) and biphenyl (BP) using an FID detector and a DB wax capillary column at a temperature programmed from 50 to 230 °C (15 °C/min). DBT in the product was analyzed in the same GC but using a different Varian CP-Sil 8CB column using an FID detector at a temperature programmed from 80 to 280 °C (15 °C/min). Conversions were calculated according to the disappearance of reactant or the formation of products. The conversions for DBT are reported here for 6 h of reaction-on-time.

#### 2.4.2. Catalytic hydrotreating of LGO

Catalytic hydrotreating of light gas oil (LGO) feed was performed in the same 500 mL Parr reactor at reaction temperature of  $350 \,^{\circ}$ C and pressure of 1000 psi. The LGO feed had a sulfur and nitrogen content of 14,000 ppm and 1450 ppm respectively. A catalyst to feed ratio of 1:80 (wt/wt) was used in case of LGO. The reactor was flushed by nitrogen to avoid air contact with feed and sulfided catalysts before injecting H<sub>2</sub>. After flushing by N<sub>2</sub> the reactor was pressurized with H<sub>2</sub> at reactor pressure of 1000 psi. The batch reactor was kept at a constant stirring of 1000 rpm to avoid mass transfer limitations. Products were collected after 6 h of reaction time. The total nitrogen content of the liquid product was measured by combustion/chemiluminence technique following ASTM D4629 method, and the sulfur content was measured using combustion/fluorescence technique following ASTM 5463 method. Both sulfur and nitrogen were analyzed in an Antek 9000



Fig. 1. N<sub>2</sub> adsorption-desorption isotherms of (a) Al-SBA-15, (b) MAS-4, (c) MAS-16 and (d) MAS-24.

NS analyzer. The instrumental error in N and S analysis was 3%. Simulated distillation was performed using ASTM D6352 method in order to study the boiling range distribution of different product samples at different temperatures using a Varian model CP3800 gas chromatograph coupled to a Varian CP 8400 auto sampler.

## 3. Results and discussion

## 3.1. N<sub>2</sub> adsorption-desorption analysis

The N<sub>2</sub> adsorption and desorption isotherms of Al-SBA-15. MAS-4. MAS-16 and MAS-24 are shown in Fig. 1. Also, the various textural properties for these materials along with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are tabulated in Table 1. MAS-4 and Al-SBA-15 exhibit a typical Type IV with a hysteresis loop which is characteristic of regular mesoporous channels structure. The initial increase in volume of adsorption at low pressure is due to monolayer adsorption in micropores and mesopores, and the upward deviation in the 0.6–0.8  $P/P_0$  range is associated with capillary condensation inside the mesopores. An alteration in type of isotherm and relative shift in the point of inflection with increasing hydrothermal treatment duration can be observed due to a change in nature or pores. The surface area as well as the pore volume decreased continuously with increase in seeding time. The contribution of mesopores to the total surface area of the material decreases with seeding time. This effect is particularly visible in the reduction of surface area of MAS-24 as compared to MAS-16. In MAS-16 mesopores constitute almost 70% of the total surface area whereas the mesoporous area in MAS-24 is as low as 50% of the total surface area. The decline in mesopores is accompanied with a rapid growth of micropores in the materials especially in MAS-24. The increase in microporosity in MAS-24 can be ascribed to the degree of connection of the alumino-silicate network of the

#### Table 1

Textural properties of the supports and reference materials.



**Fig. 2.** XRD pattern of (a) Al-SBA-15, (b), MAS-4, (c) MAS-16 and (d) MAS-24 in small angle range plotted in cascading format.

hydrothermal gel. The alumino silicate framework after 24 h of hydrothermal treatment is nearly completely connected. The large connected alumino silicate network in MAS-24 is able to resist the capillary stress of evaporative drying and calcination. As a result the micropores are retained by the final material. In contrast, hydrothermal gel with low seeding durations ( $t_{seed} = 4$  h) possesses a very high content of silanols, which corresponds to interruption of the alumino-silicate framework. The presence of weaker silanol groups instead of a stronger alumino-silicate network allows the micropores to grow into mesopores [26].

Table 2 shows the surface area and other textural properties of the Al-SBA-15, MAS-4, MAS-16 and MAS-24 supported NiMo catalysts. The metal composition is very close to the targeted values, indicating that the support is able to hold maximum metal content on its surface which was prepared by using wetness impregnation procedure. As the seeding time increases the textual properties ( $S_{\text{BET}}$ ,  $V_{\text{P}}$ ,  $D_{\text{P}}$ ) continuously decrease due to a possible blockage of micropores which are significant in the case of MAS-24. A nonuniform dispersion of the metal phase may also be a probable reason for the reduction in surface area and pore volume in MAS-24.

## 3.2. XRD analysis

The structural arrangement of MAS and Al-SBA-15 materials were examined using XRD at low and high angles. The low angle XRD pattern of Al-SBA-15, MAS-4, MAS-16 and MAS-24 are given in Fig. 2. The reference Al-SBA-15 exhibited an intense peak at  $2\theta = 0.81^{\circ}$  and two small humps at  $2\theta = 1.42^{\circ}$  and  $1.65^{\circ}$ . The peaks are typical of ordered SBA-15 like material with p6mm symmetry [22]. In comparison with Al-SBA-15, the synthesized MAS family of materials have one broad peak around  $2\theta = 1.4^{\circ}$ . The poor

Sample	$S_{\rm tot} (m^2/g)^a$	d <sub>BJH</sub> (nm) <sup>b</sup>	PV (cc/g)	$S_{\rm micro}~({\rm m}^2/{\rm g})$	$S_{\rm meso}~({\rm m^2/g})$	S <sub>micro</sub> /S <sub>tot</sub>	Si/Al <sup>c</sup>
Al-SBA-15	887	7.1	1.58	71	816	0.08	24.8
MAS-4	759	6.5	1.36	68	691	0.09	24.7
MAS-16	683	5.4	1.03	128	455	0.18	24.4
MAS-24	478	3.3	0.53	245	223	0.51	24.6
$Al_2O_3$	267	9.2	0.72	-	-	-	-

<sup>a</sup> Calculated by the BET method.

<sup>b</sup> Calculated by BJH method.

<sup>c</sup> Determined using ICP-MS.

Table 2
---------

Textural properties and concentration of acid sites of the supported catalysts systems.

Sample	$S_{\rm tot} (m^2/g)$	d <sub>BJH</sub> (nm)	Amount of acid	Amount of acid sites (µmol/gm)	
			Lewis	Bronsted	Lewis + Bronsted
NiMo/Al-SBA-15	465	6.9	385	2	387
NiMo/MAS-4	398	6.2	453	5	455
NiMo/MAS-16	373	5.2	476	29	505
NiMo/MAS-24	202	3.4	513	43	556
NiMo/Al <sub>2</sub> O <sub>3</sub>	189	8.6	396	-	396

resolution of the 110 and 200 planes and a relative broadening of the peak width in MAS materials as compared to Al-SBA-15 may indicate that the long range ordered hexagonal symmetry is absent in materials assembled from zeolite nano-clusters. In addition, a very small peak at  $2\theta = 8^{\circ}$  can be observed only for MAS-24 which is a characteristic peak of ZSM-5. From these results it can be concluded that the duration of hydrothermal treatment of the zeolite seed solution is a very important factor in deciding the nature of the final material. At low seeding times of  $t_{seed} = 4$  h, the final material is essentially similar to mesoporous Al-SBA-15 with



Fig. 3. TEM images of (a) Al-SBA-15, (b), MAS-4, (c) MAS-16 and (d) MAS-24.



Fig. 4. XRD pattern of (a) MAS-24, (b) MAS-16, (c) MAS-4 and (d) Al-SBA-15 in high angle domain.

associated long range ordered structure exhibiting p6 mm symmetry as observed from XRD at low angles. Further, no peaks associated with crystalline structure was observed for materials with  $t_{seed}$  = 16 h. In contrast MAS-24 exhibited sharp XRD peaks similar to ZSM-5. The results from the low angle XRD are well supported by the TEM images of the MAS materials (Fig. 3). In contrast to the well-ordered 2D hexagonal arrays of mesopores in Al-SBA-15, MAS materials have very low areas of ordered structure. Hexagonal arrays are visible only but sporadically. The ill formed hexagonal mesoporous arrays to be due to the modification in the structure.

The findings of the XRD at low angles are further confirmed by the diffraction pattern observed at higher angles (Fig. 4). MAS-24 showed intense peaks similar to ZSM-5 at  $2\theta$  = 22.2° [27]. However, this peak is absent for the materials synthesized with seeding times less than 24 h. A broad peak typical of amorphous material is observed in MAS-4, indicating very little or no crystalline phase formation in the material after 4 h of hydrothermal treatment.

## 3.3. FT-IR analysis

The FTIR spectra of Al-SBA-15, MAS-4, MAS-16 and MAS-24 samples plotted in transmittance mode are shown in Fig. 5. All the MAS materials showed a band at 550 cm<sup>-1</sup> which is assigned to the double five ring (D5R) stretching present in MFI type zeolites [28]. This shows that the nano-crystal segments or nano-crystals of ZSM-5 were embedded into the framework of the mesoporous matrix. The intensity of this band is increases with seeding time and is highest for MAS-24, indicating that the alumino silicate network is predominantly present as five membered rings of Si–O–Al similar to those present in ZSM-5. The results are in good agreement with the findings of Han et al. who also reported Si–O–Al band in the 550 cm<sup>-1</sup> region for similar materials [12].

The acid strength of the supported catalyst systems was studied using the Pyridine FTIR method. Py-FTIR spectra of the protonated samples were measured in the region of 1700–1400 cm<sup>-1</sup>. According to literature, pyridine adsorbed on Lewis acid sites exhibits signals at 1450, 1596 and 1615 cm<sup>-1</sup> [29]. Bands at 1540 and



Fig. 5. FTIR spectra of (a) MAS-24, (b) MAS-16, (c) MAS-4 and (d) Al-SBA-15 in 400–900  $\rm cm^{-1}.$ 

1640 cm<sup>-1</sup> are assigned to Bronsted acid sites present in the material. Further, pyridine co-adsorbed on both Bronsted and Lewis acid sites gives rise to a band at  $1495 \text{ cm}^{-1}$  [30]. Fig. 6 clearly shows the presence of Bronsted acid sites in NiMo/MAS-24 and NiMo/MAS-16. In contrast NiMo/MAS-4 exhibits only a weak band at 1640 cm<sup>-1</sup> which corresponds to a very low concentration of Bronsted acid sites in MAS-4. The reference Al-SBA-15 however shows no peaks at 1640 or 1540 cm<sup>-1</sup>, possibly due to the absence of Bronsted acid sites. Nevertheless Lewis acid sites are present in all the four catalysts. A peak at  $1490 \,\mathrm{cm}^{-1}$  corresponding to presence of both Bronsted and Lewis acid sites is observed for all the catalysts. Table 2 lists the acid sites distribution in the four catalysts. The results are calculated after degassing of the adsorbed pyridine at 300 °C. NiMo/MAS-24 possesses more Bronsted acid sites than NiMo/MAS-16. Presence of Bronsted acid sites is fairly minimal in NiMo/MAS-4 and almost absent in NiMo/Al-SBA-15. The presence of Bronsted acid sites may be linked to the distinctive Al chemical environment present in the framework in a zeolite like Si-O-Al network. In agreement with the <sup>27</sup>Al MAS NMR results, the FTIR-Py technique demonstrates that with increase in hydrothermal treatment duration, the extent of Al incorporation into the framework through tetrahedral AlO<sub>4</sub> units increases. Indeed, the number of AlO<sub>4</sub> tetrahedron sharing an oxygen with the SiO<sub>4</sub> tetrahedron involved in the Bronsted acid site determines the Si-O(H)-Al angle deprotoantion energy and hence the acid strength [31].

## 3.4. <sup>27</sup>Al MAS NMR analysis

The <sup>27</sup>Al NMR spectra of provides evidence of the framework connectivity of the alumino-silicate network. <sup>27</sup>Al MAS NMR spectra of Al-SBA-15, MAS-4, MAS-16 and MAS-24 materials are shown in Fig. 7. The sharp peak at  $\sim$ 58 ppm is generally assigned to tetrahedral Al species present in zeolite frameworks, whereas the peak at 0 ppm is indicative of the extra framework aluminum present



Fig. 6. FTIR spectra of pyridine adsorbed spectra of (a) MAS-24, (b) MAS-16, (c) MAS-4 and (d) Al-SBA-15 after degassing at  $250\,^\circ$ C.

in an octahedral coordination. The extra framework Al peaks are only observed for Al-SBA-15 and MAS-4. In addition to the 0 ppm peak, Al-SBA-15 also gave a shoulder at  $\sim$ 10 ppm. This peak can be assigned to a hexa coordinated aluminum species with SiO groups around the AlO<sub>6</sub> structural units [32]. These results show the existence of extra framework Al-O-Si species in Al-SBA-15 and MAS-4 materials, probably generated by the dealumination of the precursor in an acidic media during the surfactant based assembly procedure. Another interesting aspect of the <sup>27</sup>Al MAS NMR spectra is the gradual shift in the position of the tetrahedral aluminum peak. The tetrahedral peak signal for Al is present in Al-SBA-15 is observed at a chemical shift  $\delta$  = 53 ppm, whereas in MAS-16 and MAS-24 the peak shifts to  $\delta$  = 57 and 58 ppm respectively. The shift in the peak position is reported in literature to be due to the difference in the locating environment of Al [12]. The 4 coordinated Al atoms in MAS materials are present as five membered ring structures similar to the pentasil unit present in ZSM-5.



**Fig. 7.** <sup>27</sup>Al MAS NMR spectra of (a) MAS-24, (b) MAS-16, (c) MAS-4 and (d) Al-SBA-15.



Fig. 8. Raman spectra of NiMo loaded on (a) MAS-24, (b) MAS-16, (c) MAS-4 and (d) Al-SBA-15.

## 3.5. Raman spectra analysis

The Raman spectra for the NiMo catalysts are presented in Fig. 8. Low frequency bands at 220 cm<sup>-1</sup> characteristic of Mo–O–Mo deformation is also observed in all the catalysts. The Mo-O-Mo linkages can be attributed to the presence of polymolybdates with similar linkages. The results are in confirmation with Mestl et al. who concluded that Mo exists as polymolybdates at intermediate loadings of 15-20 wt% on alumina silica based supports [33]. A Raman band at  $\sim$ 958 cm<sup>-1</sup> appeared in NiMo/MAS-16 and NiMo/MAS-24. This band is attributed to the vibration of Mo=O bond of the Mo species interacting with the MAS support. Another interesting feature is the appearance of bands at 820 cm<sup>-1</sup> and 996 cm<sup>-1</sup> for NiMo/MAS-4, NiMo/MAS-24 and Al-SBA-15. These bands are however not observed for NiMo/MAS-16. These bands are assigned to Mo=O stretching (820 cm<sup>-1</sup>) and Mo-O-Mo asymmetrical stretching (996 cm<sup>-1</sup>) in crystalline MoO<sub>3</sub>. A relatively weak interaction between MoO<sub>x</sub> and the supports MAS-4 and MAS-24 appears to be the reason for the formation of bulk MoO<sub>3</sub>. Thus the duration of hydrothermal treatment which directs the Al incorporation into the mesoporous framework seems to be a controlling factor for the dispersion of the MoO<sub>x</sub> species on the surface of the support.

## 3.6. EXAFS analysis

The Mo K edge EXAFS spectra and fits from the sulfided catalysts are shown in Fig. 9. The Fourier transformed Mo spectra of the samples and the fits are presented in Fig. 10. The real part of the Fourier Transformed spectra and the corresponding fits are also shown for consideration in Fig. 11. The EXAFS best fit values for all the catalysts are summarized in Table 3.

The low noise levels at high *K* values illustrate the high data quality of the spectral acquisitions. The Fourier Transformation of these samples revealed mainly 2 shells due to the Mo–S and Mo–Mo contributions. The corresponding peaks occur at 1.96 Å and 2.79 Å, both phase incorrected. Crystalline MoS<sub>2</sub> is well known to have a hexagonal structure with each Mo atom surrounded by 6 S atoms at 2.4 Å and each S atom surrounded by 6 Mo atoms at 3.16 Å [34]. From Table 3, it is evident that the S and Mo coordination in the sulfided samples is less than crystalline MoS<sub>2</sub>. The reduction in the



Fig. 9. EXAFS spectra of sulfided catalysts (line) and corresponding fits (symbols).



**Fig. 10.** Magnitude of the Fourier transform of sulfided catalysts (line) and corresponding fits (symbols). The fit range for the spectra is 1-4 Å.



**Fig. 11.** Real part of the Fourier transform of sulfided catalysts (line) and corresponding fits (symbols). The fit range for the spectra is 1-4 Å.

al	bl	e	3	
		-		

Mo K edge fit parameters of the sulfided NiMo/ZAS(X) catalysts.

Scatterer	Ν	<i>R</i> (Å)	$\Delta\sigma^2$ (Å) <sup>2</sup>	$\Delta E_{\rm o}~({\rm eV})$
NiMo/MAS-4				
0	0.77	1.98	0.002136	-3.92
S	5.37	2.4	0.004238	4.32
Mo	3.67	3.16	0.004396	3.03
NiMo/MAS-16	5			
0	0.78	1.96	0.007902	-8.99
S	5.43	2.4	0.004228	4.85
Mo	3.77	3.16	0.004565	3.63
NiMo/MAS-24	ļ.			
0	0.72	1.99	0.009163	-6.48
S	5.07	2.41	0.003724	3.43
Мо	3.79	3.16	0.004702	2.89

Mo-Mo coordination in the sulfided samples is due to the small particles size of the supported MoS<sub>2</sub> that are formed upon sulfidation. Further, a decrease in the Mo-S contribution in the catalysts with respect to MoS<sub>2</sub> is generally due to incomplete sulfidation or the presence of a Mo–O contribution in the EXAFS spectra. Indeed, the coordination parameters obtained from the fitting procedure revealed the presence of Mo–O shell at a distance of 1.96 Å. Such a Mo-O contribution has also been previously observed by Leliveld et al., who reported the presence of O shell at 1.97 Å for sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts [35]. Previous results have reported that the Mo–O contribution at 1.97 Å is typical of the first coordination shell in MoO<sub>3</sub>. The occurrence of the Mo–O bond may be attributed to the presence of unsulfided Mo species possibly from MoO<sub>3</sub>. The Mo–O coordination is highest for NiMo/MAS-24 indicating low sulfidation caused due to the presence of bulk MoO<sub>3</sub>. This is further corroborated by the low Mo-S coordination in NiMo/MAS-24 followed by NiMo/MAS-4. Thus it is clear from the Mo K edge EXAFS best fit values that the sulfidation is highest in NiMo/MAS-16 followed by NiMo/MAS-4 and NiMo/MAS-24. The results are in agreement with the Raman results of the oxide phase. The presence of bulk MoO<sub>3</sub>, due to the poor dispersion of the MoO<sub>x</sub> species in NiMo/MAS-4 and NiMo/MAS-24 does indeed hampers the complete sulfidation of the catalysts.

## 3.7. HRTEM analysis

Ta

Av ar

The HRTEM images of the sulfided catalysts are presented in Fig. 12. The formation of MoS<sub>2</sub> stacks are clearly shown in the pictures with different stack heights and lengths. MoS<sub>2</sub> crystallites with lengths between 20 and 80 Å and stacking from two to six layers are formed on the supports. The results were obtained through a statistical analysis and are presented in Table 4. Sulfided NiMo/MAS-16 shows a very well dispersed MoS<sub>2</sub> phase with mostly single or double-layered slabs of the MoS<sub>2</sub> phase. This is in confirmation with the results obtained from the EXAFS fits, that sulfidation in catalysts supported on MAS-16 results in the formation of a well-dispersed sulfide phase. Further, sulfided NiMo on MAS-24 also yields small MoS<sub>2</sub> crystallites mostly present as single layered slabs. On the contrary, multiple stacked layers of MoS<sub>2</sub> are observed in catalysts supported on Al-SBA-15 and MAS-4. The stacking of MoS<sub>2</sub> layers in Al-SBA-15 and MAS-4 is primarily due to

ible 4
verage MoS <sub>2</sub> stack length and height on the surface of the supports from HRTEN
alvsis.

Catalyst	Slab density	Avg. length (Å)	Avg. stack height
NiMo/Al-SBA-15	39	45	4.5
NiMo/MAS-4	53	41	3.6
NiMo/MAS-16	65	51	1.8
NiMo/MAS-24	19	34	2.3



Fig. 12. HRTEM images of sulfided (a) NiMo/Al-SBA-15, (b) NiMo/MAS-4, (c) NiMo/MAS-16 and (d) NiMo/MAS-24. The arrows indicate the MoS<sub>2</sub> slabs.

the weak interactions between molybdenum and the support. The linkage of the Mo atom to the support through Mo–O–Si bonds (silanol groups) instead of the relatively stronger Mo–O–Al bonds could be a possible reason for this weakened interaction. As a result stacked layers of  $MoS_2$  are formed upon sulfidation in NiMo/MAS-4 and NiMo/Al-SBA-15.

Silica based materials like SBA-15, KIT-6, MCM-41 are known to favor multiple stacked layers of  $MoS_2$  due to the low metal support interactions [36]. Single slabs of  $MoS_2$  dispersed over the MAS-16 support suggest an improvement in the metal support interaction similar to those present in alumina supports. The extensive bonding of Mo with the framework Al atoms results in Mo–O–Al linkage instead of the weaker Mo–O–Si linkages. Thus, preparation of mesoporous alumino-silicates from ZSM-5 nano-seeds seems to have a positive impact on the metal support interaction and hence the dispersion of the MoO<sub>x</sub> phase on the support. A well-dispersed MoO<sub>x</sub> phase like the one in NiMo/MAS-16, upon sulfidation resulted in single slabs of MoS<sub>2</sub> uniformly spread throughout the surface of the support.

## 3.8. Catalytic activity measurements

#### 3.8.1. Catalytic activity in the hydrotreating of the DBT

Hydrotreating activity of AlSBA-15, MAS-4, MAS-16 and MAS-24 supported catalysts is shown in Fig. 13. The MAS-16 supported NiMo catalyst showed the highest DBT conversion at all times, with DBT conversion being 30% higher than Al-SBA-15 and MAS-4 supported catalyst. DBT conversion in Al-SBA-15 and MAS-4 supported catalyst were similar. This is probably due to similar properties of Al-SBA-15 and MAS-4 since at lower durations of hydrothermal treatment; the nano-clusters do not fully exhibit zeolite like connectivity and thus have properties similar to Al-SBA-15. In contrast, the conversion of DBT over MAS-4 was higher than that of

MAS-24 despite of MAS-24 having the maximum growth of the zeolite like phase. This is probably due to the small pore size and pore volume observed in MAS-24. In addition, structural collapse of the mesophase due to the rapid growth of crystals on the walls of MAS-24 as observed from the N<sub>2</sub> adsorption and desorption isotherms could be another possible reason for the low DBT conversion. A good dispersion of the active phase combined with excellent textural properties and presence of strong Bronsted acid sites resulted in NiMo supported on MAS-16 exhibiting the highest conversion among all 4 catalysts. The product distribution analysis was done



**Fig. 13.** DBT conversions of sulfided NiMo catalysts at various times over different supports.



Fig. 14. Product distribution of BP and CHB in the HDS of DBT over NiMo/Al-SBA-15 and NiMo/MAS-4.

only for cyclohexyl benzene (CHB) and biphenyl (BP) using a GC. Biphenyl is known to be a product of the direct desulfurization (DDS) pathway whereas CHB is formed in the hydrogenation (HYD) pathway. The simplified reaction scheme for the HDS of DBT is given in Fig. 16. The selectivity for BP over CHB is highest for catalyst supported on MAS-24. This indicates that NiMo/MAS-24 favors the DDS pathway for the HDS of DBT. The acceleration of the DDS pathway may be attributed to the presence of Bronsted acid sites which act as proton donors to the metal sulfide particles and lead to a direct C-S bond cleavage. NiMo/MAS-16 with similar acid sites also yields more BP as compared to NiMo/MAS-4 and NiMo/Al-SBA-15. The product analysis for CHB, however gives different results. NiMo/MAS-4 and NiMo/Al-SBA-15 show comparable concentrations of CHB and BP in the products as compared to catalysts supported on MAS materials with higher seeding times. CHB is formed by the hydrogenation of cyclohexen-1-yl-benzene (CHEB) which is a product of direct desulfurization of THDBT [35]. The THDBT occurs as an intermediate when the HDS of DBT follows the hydrogenation route. The lower selectivity of CHB in NiMo/MAS-16 and NiMo/MAS-24 can be explained in two ways: (1) the hydrogenation pathway is less favored as compared to the DDS pathway, or (2) in presence of strong acid sites and high reaction temperatures of 320 °C, CHEB may have undergone further hydrogenation to form Iso DM decalin and alkyl-CH [37]. The strong Bronsted acid sites in NiMo/MAS-16 and NiMo/MAS-24 appear to have promoted the further hydrogenation of CHEB at 320°C. The former seems unlikely as the presence of acid sites is known to enhance hydrogenating properties as well which are ascribed to electronic effects of the acidity on metal sulfide phase [38] (Figs. 14 and 15).

In either case the DDS pathway is accelerated more than the HYD pathway over catalysts supports with longer durations of hydrothermal treatment. The presence of acidic protons in MAS-16 and MAS-24 catalysts arising from the Bronsted acid sites help in the faster scission of the C–S bond.

#### 3.8.2. Catalytic activity in the hydrotreating of the LGO

The HDS and HDN activities of MAS supported catalysts are presented relative to a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalyst. The conversion for HDS and HDN of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is standardized to 100% due to low conversions in a batch type reactor. The HDS and HDN activity of NiMo/MAS-16 is higher than NiMo supported on commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 17). However NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed better conversion than both NiMo/MAS-4 and NiMo/MAS-24. A boiling point



Fig. 15. Product distribution of BP and CHB in the HDS of DBT over NiMo/MAS-24 and NiMo/MAS-16.



Fig. 16. Simplified reaction schematic of HDS of DBT [42].

distribution comparison of catalyst supported on MAS(X) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is given in Fig. 18. The volume fraction of lighter naptha products (boiling point 90–170 °C) in NiMo/MAS-16 is more than NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The Bronsted acid sites in MAS-16 may have promoted the cracking of large hydrocarbon molecules in LGO into



Fig. 17. Hydrotreating activity of MAS supported NiMo catalysts relative to NiMo/ $\gamma$  Al<sub>2</sub>O<sub>3</sub> after 6 h of reaction time.



**Fig. 18.** Boiling point distribution of the product of LGO hydrotreating after 6 h of reaction over different catalysts.

lighter products. On the other hand  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is known to possess Lewis acid sites which do not favor cracking reactions.

From the catalytic study of HDS of DBT and hydrotreatment of LGO, it is clear that NiMo/MAS-16 is most active for hydrotreatment reactions. Large pores and a narrow pore size distribution can eliminate diffusion limitations and provides greater accessibility to the active sites for the reactant and product molecules. Previous works on HDS of bulky molecules with microporous zeolites have yielded low conversions [39]. MAS-16 with an average pore size of 5.2 nm and a surface area of  $650 \text{ m}^2/\text{g}$  is 40% more active than NiMo supported on MAS-24 in the HDS of DBT. NiMo/MAS-24 which showed the highest concentration of Bronsted acid sites suffers from low surface areas and small porous channels due to the rapid zeolite phase formation on the walls after 24h of seeding time. This leads to a lower activity in hydrotreating tests. The low surface area (predominantly microporous) causes agglomeration of the MoO<sub>x</sub> particles leading to the formation of bulk MoO<sub>3</sub> which is known to be difficult to sulfide. Further the low HDS and HDN activity in case of LGO may also be attributed to the rapid deactivation of the catalyst caused due to unwanted cracking of the feedstock leading to coke deposition on the catalysts surface [40]. Nonetheless, the low hydrotreating activity of NiMo/MAS-4 relative to NiMo/MAS-16 may be due to the difference in the chemical nature of the two supports. Indeed, MAS-4 which was found to be similar to Al-SBA-15 prepared through the direct synthesis method showed similar conversions in HDS of DBT and HDT of LGO. The deficiency of strong Bronsted sites in MAS-4 and Al-SBA-15 as indicated by the absence of the 1540 cm<sup>-1</sup> peak in FTIR-Py spectra, might have resulted in the low catalytic activity of the sulfided NiMo catalysts system. Proper distribution of acid sites in supported catalysts is known to improve the conversion in HDS of DBT and 4,6 DMDBT and the role of acidity in improving catalytic activity of hydrotreating catalyst is well cited [4,38,39]. Acidic supports facilitate an alternate hydrogenation route through spillover hydrogen atoms from the metal particles to the aromatic sulfur containing molecules [41]. Furthermore, the activity of the DDS pathway in NiMo/MAS-16 was found to be higher than NiMo/MAS-4 which was evident from the preferential selectivity towards BP in the HDS of DBT in NiMo/MAS-16. The Bronsted acid sites in MAS-16 provide protons in the close vicinity of the metal sulfide particles, leading to an accelerated C-S bond cleavage. This effect is less prominent in NiMo/MAS-4 wherein the HYD pathway

is equally favored, due to the low concentration of Bronsted acid sites. The low activity of NiMo/MAS-4 is also reflected in the HDS and HDN performance of LGO feedstock. Both the HDS and HDN conversions of NiMo/MAS-4 was found to be less as compared to NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Additionally, the EXAFS fits of the Mo K edge spectra for the sulfided catalysts revealed that sulfidation was highest for NiMo/MAS-16. The formation of a dispersed  $MoO_x$  phase due to optimum metal support interaction in MAS-16 results in proper sulfidation of NiMo/MAS-16. On the contrary, the lower sulfidation in NiMo supported on MAS-4 and MAS-24 was largely due to the presence of strong Mo–O bonds, either due to the formation of bulk MoO<sub>3</sub> or strong Mo–O–Al bonds. The latter may explain the presence of high Mo–O coordination in case of sulfided NiMo/MAS-16.

Consistent with the characterization results, sulfided NiMo catalyst supported on MAS-16 was found to be most active in the hydrotreating of both model compound and real feed stock. The high activity of the NiMo/MAS-16 can be ascribed to the following reasons: (1) excellent textural properties, (2) Optimum concentration of strong Bronsted and Lewis acid sites, and (3) formation of a well-dispersed active phase.

## 4. Conclusions

Catalytic performance of sulfided NiMo catalysts supported on mesoporous alumino silicates synthesized using the assembly of ZSM-5 seeds was evaluated in this study. The acidity of the final material could be tuned depending on the duration of hydrothermal treatment of the zeolite seed solution. The material exhibited characteristics of ZSM-5 for longer duration of hydrothermal treatment while the nature of the material was found to be similar to Al-SBA-15 for shorter periods of seeding. However the sulfided catalyst with maximum hydrotreating activity was the one with intermediate ( $t_{seed} = 16 h$ ) heat treatment duration. The high activity of this catalyst was ascribed to the combination of good textural properties and strong acid sites arising from Al in a tetrahedral coordination in ZSM-5 like environment. The metal support interaction improved in the materials synthesized with longer seeding times. As a result a well dispersed NiMoS phase with single or double layered slabs of MoS<sub>2</sub> were formed upon sulfidation of NiMo/MAS-16. This was different from sulfided NiMo/MAS-4 where an average MoS<sub>2</sub> stack height of 3.8 was observed. Raman results indicated that owing to low metal support interaction in MAS-4, bulk MoO3 is formed at 15% Mo loading. Further, EXAFS studies revealed a high Mo-O shell coordination in NiMo/MAS-4 and NiMo/MAS-24 signifying that sulfidation is low for these particular systems.

Catalytic tests showed that NiMo/MAS-16 had the highest activity in the HDS of DBT. Presence of Bronsted acid sites in the support favored the DDS pathway over the HYD pathway in the desulfurization of DBT. Availability of the acidic proton in the vicinity of the metal sulfide accelerated the direct C-S bond scission. However NiMo/MAS-24 showed low conversions due to a partial collapse in the mesoporous structure after 24h of hydrothermal treatment of the zeolite nano-clusters. NiMo/MAS-16 was found to have superior activity over NiMo catalyst supported on commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the hydrotreatment of LGO. Further, lighter products were obtained with NiMo/MAS-16 obviously due to the presence of stronger acid sites in MAS-16. It would be very interesting to evaluate the catalytic performance of these materials especially MAS-16 which combines the good properties of zeolites and SBA-15 in the hydrotreatment studies in a continuous flow reactor with real feed stock.

#### Acknowledgments

The authors are grateful to Syncrude Canada Ltd. and the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

#### References

- [1] C. Song, X. Ma, Applied Catalysis B: Environmental 41 (2003) 207–238.
- [2] A. Duan, G. Wan, Z. Zhao, C. Xu, Y. Zheng, Y. Zhang, T. Dou, X. Bao, K. Chung, Catalysis Today 119 (2007) 13–18.
- [3] U.T. Turaga, C. Song, Catalysis Today 86 (2003) 129-140.
- [4] G. Pérot, Catalysis Today 86 (2003) 111–128.
- [5] Y. Sun, R. Prins, Angewandte Chemie International Edition 47 (2008) 8478–8481.
- [6] J. Blanchard, M. Breysse, K. Fajerwerg, C. Louis, C. Hédoire, A. Sampieri, S. Zeng, G. Pérot, H. Nie, D. Li, in: N.Z.a.P.N.J. Cejka (Ed.), Studies in Surface Science and Catalysis; Molecular Sieves: From Basic Research to Industrial Applications, Proceedings of the 3rd International Zeolite Symposium (3rd FEZA), Elsevier, 2005, pp. 1517–1524.
- [7] M. Breysse, C.E. Hédoire, C. Louis, G. Pérot, in: Masakazu Anpo, Makoto Onaka, Hiromi Yamashita (Eds.), Studies in Surface Science and Catalysis; Science and Technology in Catalysis 2002, Proceedings of the Fourth Tokyo conference on Advance Catalytic Science and Technology, Elsevier, 2003, pp. 115–120.
- [8] R. Nava, J. Morales, G. Alonso, C. Ornelas, B. Pawelec, J.L.G. Fierro, Applied Catalysis A: General 321 (2007) 58–70.
- [9] G.M. Dhar, G.M. Kumaran, M. Kumar, K.S. Rawat, L.D. Sharma, B.D. Raju, K.S.R. Rao, Catalysis Today 99 (2005) 309–314.
- [10] K. Soni, B.S. Rana, A.K. Sinha, A. Bhaumik, M. Nandi, M. Kumar, G.M. Dhar, Applied Catalysis B: Environmental 90 (2009) 55–63.
- [11] A. Prabhu, L. Kumaresan, M. Palanichamy, V. Murugesan, Applied Catalysis A: General 360 (2009) 59-65.
- [12] Y. Han, S. Wu, Y. Sun, D. Li, F. Xiao, J. Liu, X. Zhang, Chemistry of Materials 14 (2002) 1144–1148.
- [13] Y. Liu, T.J. Pinnavaia, Journal of Materials Chemistry 12 (2002) 3179-3190.
- [14] Y. Liu, T.J. Pinnavaia, Journal of Materials Chemistry 14 (2004) 1099-1103.
- [15] Y. Liu, W. Zhang, T.J. Pinnavaia, Journal of the American Chemical Society 122 (2000) 8791–8792.
- [16] Y. Liu, W. Zhang, T.J. Pinnavaia, Angewandte Chemie-International Edition 40 (2001) 1255–1258.
- [17] B. Zebib, S. Zeng, J. Krafft, J. Lambert, J. Blanchard, H. Nie, D. Li, M. Breysse, in: N.Z.a.P.N.J. Cejka (Ed.), Studies in Surface Science and Catalysis; Molecular

Sieves: From Basic Research to Industrial Applications, Proceedings of the 3rd International Zeolite Symposium (3rd FEZA), Elsevier, 2005, pp. 517–524.

- [18] S. Zeng, J. Blanchard, M. Breysse, Y. Shi, X. Su, H. Nie, D. Li, Applied Catalysis A: General 294 (2005) 59–67.
- [19] L. Frunz, R. Prins, G.D. Pirngruber, Microporous and Mesoporous Materials 88 (2006) 152–162.
- [20] S. Zeng, J. Blanchard, M. Breysse, Y. Shi, X. Su, H. Nie, D. Li, Applied Catalysis A: General 298 (2006) 88–93.
- [21] Y. Han, F. Xiao, S. Wu, Y. Sun, X. Meng, D. Li, S. Lin, F. Deng, X. Ai, The Journal of Physical Chemistry B 105 (2001) 7963–7966.
- [22] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548-552.
- [23] Y. Yue, A. Gedeon, J. Bonardet, J. D'Espinose, J. Fraissard, N. Melosh, Chemical Communications (1999) 1967–1968.
- [24] C.A. Emeis, Journal of Catalysis 141 (1993) 347-354.
- [25] B. Ravel, M. Newville, Journal of Synchrotron Radiation 12 (2005) 537-541.
- [26] A. Morsli, M.F. Driole, T. Cacciaguerra, R. Arletti, B. Chiche, F. Hamidi, A. Bengueddach, F. Quignard, F. Di Renzo, Microporous and Mesoporous Materials 104 (2007) 209–216.
- [27] Y. Cheng, L. Wang, J. Li, Y. Yang, X. Sun, Materials Letters 59 (2005) 3427-3430.
- [28] P.A. Jacobs, E.G. Derouane, J. Weitkamp, Journal of the Chemical Society–Chemical Communications (1981) 591–593.
- [29] T. Barzetti, E. Selli, D. Moscotti, L. Forni, Journal of the Chemical Society–Faraday Transactions 92 (1996) 1401–1407.
- [30] T.R. Hughes, H.M. White, Journal of Physical Chemistry 71 (1967) 2192-2201.
- [31] L. Grajciar, C.O. Arean, A. Pulido, P. Nachtigall, Physical Chemistry Chemical Physics 12 (2010) 1497–1506.
- [32] D.A. Atwood, M.J. Harvey, Chemical Reviews 101 (2001) 37-52.
- [33] G. Mestl, T.K.K. Srinivasan, Catalysis Reviews: Science and Engineering 40 (1998) 451–570.
- [34] R.G. Dickinson, L. Pauling, Journal of the American Chemical Society 45 (1923) 1466–1471.
- [35] R.G. Leliveld, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, Journal of Catalysis 165 (1997) 184–196.
- [36] Z.-. Huang, W. Bensch, L. Kienle, S. Fuentes, G. Alonso, C. Ornelas, Catalysis Letters 122 (2008) 57–67.
- [37] D. Zhang, A. Duan, Z. Zhao, C. Xu, Journal of Catalysis 274 (2010) 273–286.
- [38] W.J.J. Welters, V.H.J. de Beer, R.A. van Santen, Applied Catalysis A: General 119 (1994) 253–269.
- [39] D. Solís, A.L. Agudo, J. Ramírez, T. Klimova, Catalysis Today 116 (2006) 469–477.
- [40] I.E. Maxwell, Catalysis Today 1 (1987) 385-413.
- [41] S.D. Lin, M.A. Vannice, Journal of Catalysis 143 (1993) 539–553.
- [42] C. Linares, M. FernÃindez, Catalysis Letters 126 (2008) 341-345.