Preparation, Characterization, and Catalytic Evaluation of Metal Containing MCM-41-Based Hydrodesulfurization Catalysts

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Abstract: In this study, the preparation of nickel and cobalt incorporated MCM-41 (metal-MCM-41) with Si/Al = 10, Si/Mo = 10 and Si/Co and Si/Ni as 50 was done. Then molybdenum was impregnated on Ni-MCM-41 and Co-MCM-41 by incipient wetness impregnation method. MCM-41 based catalysts were characterized by XRD, surface area, pore volume, pore-size distribution, and temperature programmed reduction (TPR). The catalysts were evaluated for hydrodesulfurization of model compounds thiophene and benzothiophene in pulse reactor at atmospheric pressure and at different temperatures. HDS of dibenzothiophene dissolved in dodecane, was also performed in a batch autoclave reactor at high pressure and temperature. The results of hydrodesulfurization activity indicate that when impregnated with molybdenum the prepared metal-MCM-41 showed higher activity as compared to commercial catalyst. Mo-CoMCM-41 showed highest conversion per mole of metal in hydrodesulfurization of thiophene and benzothiophene. For comparison purposes, a sample of NiMo-Y zeolite catalyst was also prepared and evaluated.

Keywords: Hydrodesulfurization, MCM-41, Catalyst preparation, Characterization.

1. INTRODUCTION

In recent years, the development and use of “environmentally friendly” fuels has had high priority through out the world. The increasing stringency of sulfur specifications has motivated intensive research in the field of hydrodesulfurization (HDS). Environmental Protection Agency has adopted a tough set of diesel emissions standards aimed at drastically reducing the sulfur content of diesel fuel to improve air quality. Ultra low sulfur diesel and the new emissions-reducing technology that it facilitates will help make the air cleaner and healthier for everyone. Recently, the breakthrough discovery of the M41S family [1,2] exemplified by the MCM-41 bearing hexagonal-close-packed channels, has led to a host of studies aimed at creating novel composite materials and tailoring the catalytic properties by incorporating transition metals such as Al, Ti, Zr, V, Cr, Ga, Fe, Mo, and Mn into the silica based mesostructures.

M41S family of materials have opened new possibilities for preparing catalyst with uniform pores in mesoporous region (2 – 50 nm) that can be easily accessed by bulky molecules that are present in crude oils. Possibility to introduce different atoms in these mesoporous materials can generate catalytically active centers together with high surface areas. Tunable pore size and pore size distribution enables one to use these materials in acid base and redox catalysis as well as high surface area supports for acid, bases, metal oxides and transition metal complexes.

Chemical and structural feature of MCM-41, when metals are incorporated into the structure network for desulfurization, will facilitate diffusion of polyaromatic sulfur compounds within its mesopores and capable of preventing undesirable cracking and probably isomerizing polyaromatic sulfur compounds to more reactive variants. Several studies are conducted on metal supported MCM-41 based hydrodeslufurization catalysts [3-9]. Incorporation of transition metal ions in the framework of mesoporous materials are also remained the subject of several studies [10-14]. However, bimetallic HDS catalysts in which one metal is incorporated in to the framework of the MCM-41 and the other promoting metal is supported on the metal containing MCM-41 are not reported to the best of our knowledge. The objective of this study was to investigate the preparation of metal incorporated MCM-41 mesoporous materials, characterization, and evaluation of catalysts for HDS activity using sulfur containing model compounds.

2. EXPERIMENTAL

2.1. Synthesis of MCM-41 Based Catalysts

Synthesis of MCM-41 was followed by the procedure described by Kim and co-workers with some modifications [15]. The synthesis steps for preparing catalysts are given in Figure **1**.

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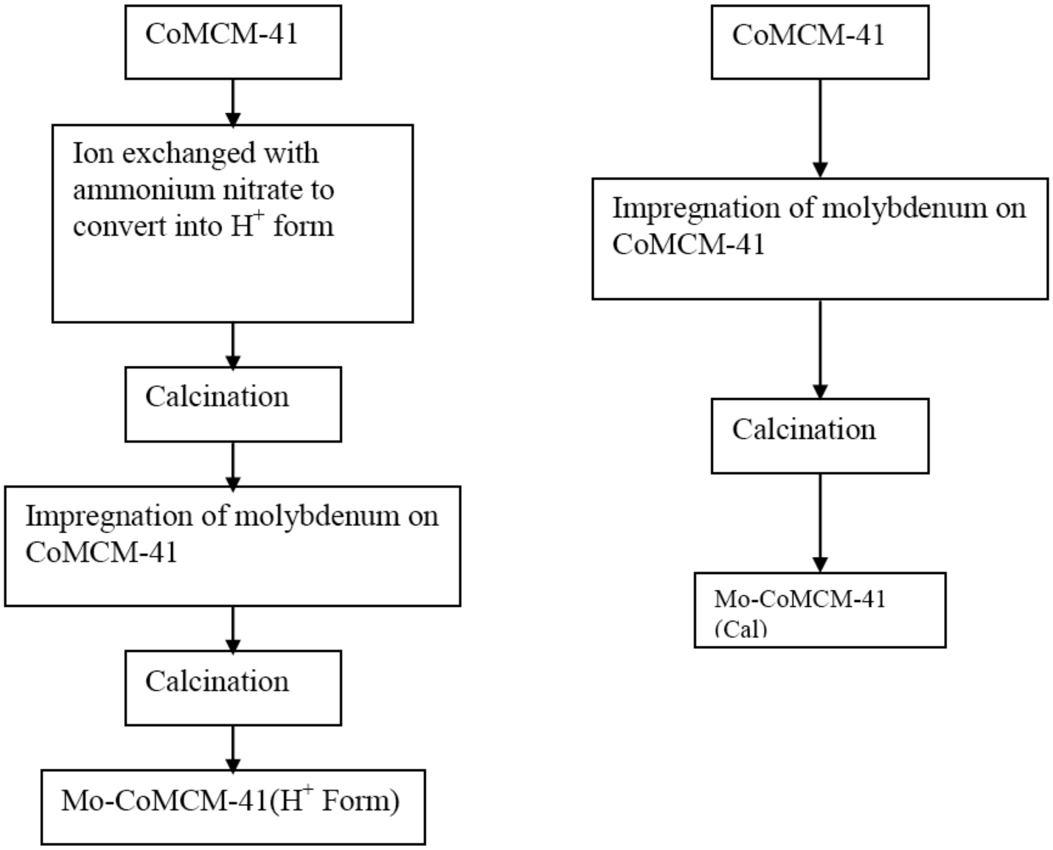

Figure 1: Synthesis steps in ion exchanged and calcined samples.

In a typical synthesis of metal containing MCM-41 the following procedure was adopted. Three solutions, A, B, and C were prepared. Solution A was prepared by dissolving 12.5 g of cetyl trimethyl ammonium bromide in 38 ml of distilled water. To this solution metal precursor (cobalt nitrate, nickel nitrate or hex ammonium heptamolybdate) was dissolved to achieve the required amount of metal ions incorporated into the MCM-41 framework structure. Solution B was prepared by diluting 1 g of NaOH in to 13.5 g of distilled water. To this solution 1.55 g of NaAlO2 was added and thoroughly mixed to get a clear solution. Whereas solution C was prepared by dissolving 3.83 g NaOH in 100 ml of distilled water and 33.5 g of silica sol (Ludox HS-40). These three solutions were mixed by adding solution A to B and then solution C was added dropwise. A homogenous gel was prepared by the addition of three solutions under constant stirring.

After the preparation of the homogeneous gel, it was transferred into a Teflon bottle, which is then heated, up to 97 ^{o}C for 4 days. During these 4 days pH is maintained at 10.5. Upon the reaction being completed, the reactor was cooled down, and the mixture was separated by filtration with extensive washing in order to remove any unwanted species such as sodium ions, chloride, nitrate etc.

After filtration, the solid sample was dried over night in air flowing oven at 100 °C and then the template was removed by calcining in muffle furnace at heating rate of 2 °C/min from room temperature to 550 °C. The sample was kept at 500 °C for 6 hours and then cooled to room temperature.

The metals; cobalt, nickel, and molybdenum were supported on metal containing MCM-41using their appropriate precursors by incipient wetness impregnation method. In this method, a solution of a metal salt of sufficient concentration to give the desired loading was added to the support. The support in this was one of the metal containing MCM-41 already synthesized. The volume of the solution was barely enough to wet the support. Then the sample was aged, usually for about one hour, dried, and calcined. Each metal incorporated MCM-41 is impregnated with other metal with desired loading. The details of samples prepared with metal loadings are given in Table **1**.

Table 1: Metal Impregnated on Synthesized Catalysts

No.	Catalyst	Wt% of Metal Incorporated			Wt% of Metal Impregnated		
		Co	Ni	Mo	Co	Ni	Mo
1	Mo-NiMCM-41 (cal)		1.6				2.5
2	Mo-NiMCM-41 (H Form)		1.4				2.5
3	Mo-CoMCM-41 (cal)	1.6					2.5
4	Mo-CoMCM-41 (H Form)	1.5					2.5
5	Ni-MoMCM-41 (cal)			2.5		1.6	
6	Ni-MoMCM-41 (H Form)			1.7		1.6	
7	Co-MoMCM-41 (cal)			2.5	1.6		
8	Co-MoMCM-41 (H Form)			1.7	1.6		
9	Mo-Ni/Y zeolite					1.6	2.5
10	Comm. Cat.					2.7	12.3

MCM-41 based samples are designated as follows:

Metal Incorporated MCM-41:

MoMCM-41 means Molybdenum incorporated MCM-41 and similar convention for NiMCM-41 and CoMCM-41.

Metal impregnated on metal incorporated MCM-41:

Co-MoMCM-41 means cobalt is impregnated on the molybdenum incorporated MCM-41. Some catalyst samples were ion exchanged before impregnation and some were not.

To make catalysts catalytically active, the calcined as-synthesized samples were ion exchanged with 0.1 M ammonium nitrate solution. Ion exchange process is as follows:

1. 10 g of catalyst was added to 150 ml of ammonium nitrate solution in a beaker and solution was stirred continuously.
2. Fresh ammonium nitrate solution was used after every 24 h.
3. After 3 days the sample was filtered and dried it in oven overnight at 100 °C.
4. The sample calcined with temperature program similar to template removal except that final temperature was increased till 500 ^{o}C and maintained for 1 hour.

2.2. Catalyst Characterization

X-ray powder diffraction (XRD) analyses were performed with a computer controlled Jeol JDX-3530 diffractometer, operating in 2-theta/theta geometry, equipped with a scintillator detector. Data were collected stepwise in the 1 to 20° 2θ range, with step size 0.020° 2θ and 1.00 second/step accumulation time; CuKα (λ=0.154178 nm) radiation was used.

The chemical composition of the catalysts was determined by atomic absorption spectrometer (Perkin Elmer Analyst 100).

The BET surface area, pore volume and pore size distribution were obtained from nitrogen adsorption-desorption isotherms measured at 77 K by a Quantachrome, NOVA-1200 porosimeter, using the BJH method. All samples were pretreated under nitrogen flow at 350 °C for 1h prior to nitrogen adsorption.

Temperature-programmed reduction (TPR) experiments were carried out in a system supplied by Ohkura Riken Co. Ltd., (Model TP-2000). The measurement was carried out using a mixture of 10% H_2/Ar under a constant heating rate of 10 °C/min from room temperature to 1000 °C. The samples were pretreated in air from ambient temperature up to 400 °C for 1h. The detailed procedures for pretreatment and subsequent TPR experiments are given elsewhere [16].

2.3. Catalyst Evaluation

2.3.1. Pulse Micro-Reactor

Pulse micro reactor was supplied by Okhura Riken, Japan. It consists of two identical, parallel units, A and B. Each unit comprises a gas inlet, injection port, micro-reactor, and gas chromatograph (GC). A well design control panel was also attached with the system to control and monitor reactor temperature, pressure and flow rates. The micro reactor was filled with 0.1 gm of catalyst. Quartz wool was inserted at both ends of the reactor tube to make sure that catalyst bed is located at the middle of the tube. Before starting run catalyst was pretreated for 6 hours. The pretreatment was done by hydrogen/hydrogen sulfide mixture (5% H_2S, 60 ml/min). During pretreatment the reactor temperature was programmed to increase from room temperature to 400 °C. Nitrogen gas was introduced to purge the system. Reactant (0.3 μl) was injected into port by using a syringe, and its conversion was measured by an on-line gas chromatograph. Pure thiophene and 50% solution of benzothiophene in benzene were used as reactants.

2.3.2. Batch Autoclave Reactor

For batch autoclave reaction studies the prepared catalysts were formed into pellets and then crushed to the size range of 0.2 – 0.6 mm. All catalyst samples were presulfided ex-situ before the activity tests. For presulfiding, about 1.25 g of catalyst was taken in a small tubular reactor. The reactor was purged with nitrogen at a rate of 60 cm^3/min and at atmospheric pressure for 30 minutes. A mixture of 5% hydrogen sulfide and 95% hydrogen was used for sulfiding the catalysts. The temperature of the reactor furnace was increased to 200 ºC in about 1 h and maintained at 200 ºC for 1 h. The temperature was further increased to 400 ºC in about one hour and maintained at 400 ºC for 2 h to complete the presulfiding. The reactor was then cooled to room temperature under flowing nitrogen. The catalyst was removed and stored in an airtight bottle. *Ex-situ* presulfiding may affect the outer surface of the catalyst that was exposed to air during transfer for storage and loading to the reactor. But this also common practice for loading presulfurized catalysts in a commercial operation. Also the feed contained enough sulfur to keep the catalyst in sulfided state. The feedstock used for the batch autoclave reactor experiments was 0.25 wt% dibenzothiophene dissolved in dodecane. 75 grams of feed and 3% of the presulfided catalyst was taken into the batch autoclave reactor of a capacity of 300 ml. The reactor vessel containing the feedstock catalyst was then placed in the furnace along with the appropriate attachments. Nitrogen gas was purged to remove air. The reactor was then pressurized by hydrogen to 67 kg/m^2 at room temperature. The temperature of the reactor was increased at a rate of 5 ºC/min. When the inside temperature of the reactor reached the target value, the hydrogen pressure was adjusted to the desired value. From this time onwards, the reaction time was counted. Total reaction time was 3 ½ hours. System was allowed to cool down to room temperature and then it was purged by nitrogen after removing the product gas sample. Liquid product was analyzed by gas chromatograph of Shimadzu 14-B equipped with FPD (flame photo-ionization detector) sulfur detector.

3. RESULTS AND DISCUSSION

3.1. Characterization

The results obtained for the chemical composition of the catalysts by atomic absorption were in agreement with the amounts of metals loaded. This confirmed the validity of our catalyst preparation procedures.

The d spacing and unit cell parameter of synthesized catalysts, measured by XRD analyses are given in Table **2**. The d spacing and corresponding a_o for MCM-41 and Ni and Co containing MCM-41 are in the close range. On the other hand Mo incorporated MCM-41 showed higher d spacing and a_o. This could be attributed to the larger atomic size of the Mo as compared with Co and Ni.

Table 2: XRD Parameters of Synthesized Catalysts

B	**d_{100} (Å)**	**$^*a_o$ (Å)**
MCM-41	40.7	47.0
NiMCM-41	42.0	48.5
CoMCM-41	39.4	45.5
MoMCM-41	55.8	64.5

$^*a_o = 2d_{100}/\sqrt{3}$.

Figure **2** shows XRD patterns of synthesized MCM-41 and metal incorporated MCM-41 catalysts. The pattern show higher order pore structure similar to typical hexagonal lattice reported in the literature [17]. The pattern shows four low angle peaks in the region 2θ = 1.5° – 10°, corresponding to hkl values of (100), (110), (200), and (210) reflections. Similar XRD patterns were observed in the case of Co and Ni incorporated MCM-41. However, Mo containing sample showed lower level of crystallinity. This is in accordance with the reported literature when Mo was tried to incorporate in the structure of MCM-41 [18]. The previous reported work also shows that when Al was incorporated in the pure siliceous MCM-41 resulted in low order pore structure [19]. Similarly incorporation of metal (Ni, Co or Mo) in the framework of MCM-41 resulted in low ordered pore structure. In addition to the metal (Ni, Co or Mo), aluminum was also added to these MCM-41 based samples to increase the acidity of MCM-41, which again would have added to the effect of decreasing the crystallanity. The results of BET surface area, pore volume and average pore radius (BJH, desorption) are given in Table **3**.

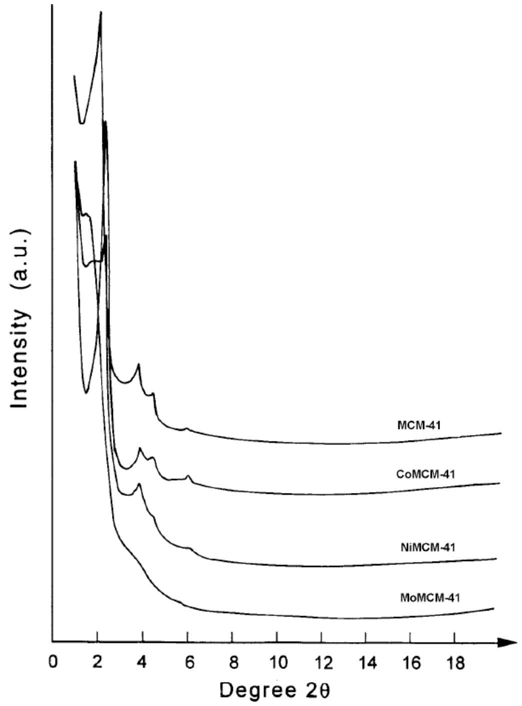

Figure 2: XRD pattern of MCM-41 and metal incorporated MCM-41 catalysts.

As observed from Table **3** average pore radius of all MCM-41 based catalysts are high compared to zeolite based catalyst with MCM-41 based catalyst in the range of 22 -58 Å while zeolite from 7 - 15 Å. Surface area of MCM-41 and metal incorporated MCM-41 (NiMCM-41, CoMCM-41, MoMCM-41) and metal impregnated on metal incorporated MCM-41 is high as compared to zeolite and zeolite impregnated catalyst, with MCM-41 based catalysts in the range of 250-900 m^2/gm and zeolites 190-400 m^2/gm. Similarly pore volume of MCM-41 based catalysts ranging from 0.4-1.4 cc/gm and for zeolites 0.15-0.28 cc/gm. Clearly from above it can be concluded that MCM-41 based catalysts are far superior as compared to zeolites in terms of surface area, pore volume, and pore radius. The surface area of commercial catalyst is also in comparison with the prepared catalysts.

Table 3: BET Surface Area, Pore Volume and Average Pore Radius of Catalysts

Catalyst	Average Pore Radius (A^{o})	Pore Volume (cc/gm)	Surface Area m^2/gm
MCM-41	22.5	0.99	883
NiMCM-41	27.0	0.81	459
CoMCM-41	25.3	0.82	457
MoMCM-41	43.8	0.94	430
Co/MoMCM-41 (H Form)	58.0	1.37	472
Mo/CoMCM-41 (H Form)	39.8	0.44	223
Mo/NiMCM-41 (H Form)	40.9	0.54	264
Ni/MoMCM-41 (H Form)	57.0	1.12	409
Co/MoMCM-41 *(cal)	58.3	1.25	430
Mo/CoMCM-41 *(cal)	36.0	0.45	251
Mo/NiMCM-41 *(cal)	29.6	0.40	268
Ni/MoMCM-41 *(cal)	58.6	0.99	341
Y Zeolite	7.0	0.28	428
Mo-Ni/ Y zeolite	15.9	0.15	193
Comm. Catalyst	40.0	0.56	288

* Calcined; non ion exchange form.

After incorporating metals in MCM-41 like Ni, Co, Mo the surface area reduces by a large extent from 883 m^2/g for MCM-41 to 459, 477 and 453 m^2/g respectively. Incorporation of aluminum in the structure also adds to the decrease in the surface area as discussed by Luan and his co-workers [20]. Decrease in surface area of metal incorporated MCM-41 indicates less crystallanity, which was confirmed by XRD. CoMCM-41 and NiMCM-41 when impregnated with molybdenum, surface area reduces to almost half, which can be because of the blockage of the pores by the big atomic size molybdenum. There are some minor changes observed in surface area and pore volume when MoMCM-41 was impregnated with Ni and Co. For instance, BET surface area of MoMCM-41 (430

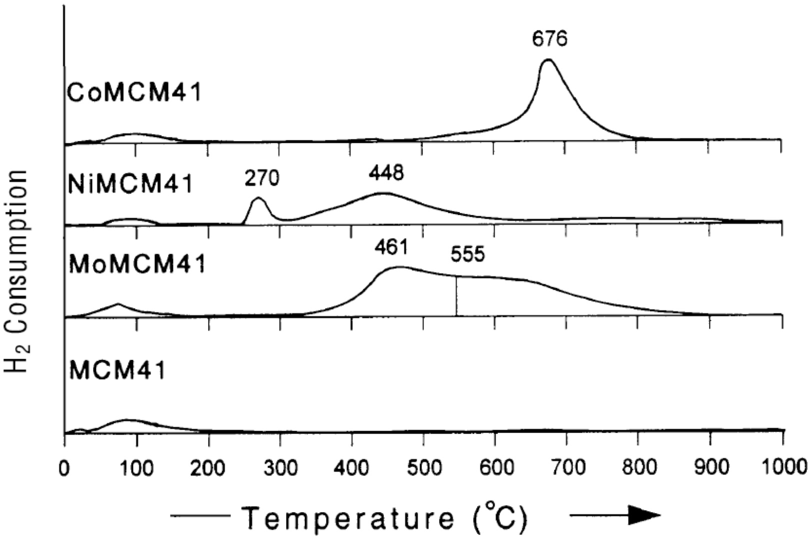

Figure 3: TPR profiles of MCM-41 and metal incorporated MCM-41 catalysts.

m^2/g) remained same when Co was impregnated. However, it was decreased in the case of Ni/MoMCM-41 (341 m^2/g). On the other hand, an increase was observed for ion-exchanged (H$^+$-Form) samples. These variations could be attributed to additional calcinations step involved in the preparation of H$^+$-from of the catalysts. Average pore radius for molybdenum incorporated MCM-41 (MoMCM-41) is more as compared to nickel and cobalt incorporated MCM-41 as atomic radius for molybdenum is high. Due to bigger atomic radius molybdenum faces difficulty in getting incorporated in the structure.

The TPR profiles of MCM-41 catalyst and metal incorporated MCM-41 (Ni, Co, Mo) are shown in Figure **3**. It has been reported by Arnoldy and Moulijn that at least four oxidic Co phases could be distinguished which differ widely in their reducibility and which could be divided into eight sub phases [21]. It has been reported that the peak of cobalt in CoMCM-41 at 676 °C is the reduction of surface phase of Co^{2+} ions. Recent studies reporting Co supported on silica suggest the possibility of formation of cobalt hydrosilicate being reduced in the region of 500 °C to 800 °C [22-23]. It is also reported that peak I (270 °C) of NiMCM-41 can be assigned to reduction of traces of the higher Ni (III) oxide, while peak II (448 °C) results from much more reduced Ni (II) species. Ni (II) can be either a surface nickel silicate or NiO present as very small, difficultly reducible particles [24]. Arnoldy and co-workers reported that first peak at low temperature is reduction peak of octahedrally surrounded Mo^{+6} multilayer, and second peak at higher temperature is attributed to reduction of tetrahedrally and octahedrally surrounded Mo^{+6} monolayer species [25].

It was observed that during ion exchange some of the metal ions specifically molybdenum was leached out. That was evident from TPR spectra by showing lower reduction peak area and latter confirmed by atomic absorption analysis. A substantial loss of Mo (32 wt%) was observed in case Mo-MCM-41. The active metal loss also affected the HDS activity of the catalyst that will be discussed in next section. However, in the case of Co- (6.2 wt %) and Ni-MCM-41 (12.5 wt%) the metal losses were relatively lower. The results of elemental analyses are summarized in Table **4**.

Table 4: Elemental Analysis of Fresh Catalysts for Different Metal Incorporations

No.	Catalysts	Metal Loaded (Wt%)			Metal Wt % Loss
		Ni	Co	Mo	
01	CoMCM-41 (H Form)	-	1.5	-	6.25
02	CoMCM-41 (Calcined)	-	1.6	-	
03	NiMCM-41 (H Form)	1.4	-	-	12.5
04	NiMCM-41 (Calcined)	1.6	-	-	
05	MoMCM-41 (H Form)	-	-	1.7	32.0
06	MoMCM-41 (Calcined)	-	-	2.5	

Table 5: Pulse Reactor Results for HDS Activity of Metal Impregnated on Metal Incorporated MCM-41 Catalyst

Run No.	Catalysts	HDS Activity (% Conversion of thiophene)				
	Temperature (°C)	250	275	300	325	350
1	Mo-NiMCM-41-2	17.23	25.31	33.06	40.84	48.05
2	Mo-NiMCM-41-4 *(H)	14.82	23.21	32.10	35.27	41.45
3	Mo-CoMCM-41-2	17.32	25.77	29.58	37.05	44.14
4	Mo-CoMCM-41-2 (H)	17.00	25.33	31.49	36.67	43.31
5	Co-MoMCM-41-2	3.01	5.26	7.45	9.21	11.03
6	Co-MoMCM-41-3 (H)	1.02	1.72	3.00	3.97	5.52
7	Ni-MoMCM-41-2	11.98	19.51	23.21	28.59	34.30
8	Ni-MoMCM-41-1 (H)	1.45	2.25	4.03	7.00	9.90
9	Commercial Catalyst	8.72	10.34	11.17	13.83	19.14

* H denotes H Form of metal containing MCM-41 before second metal was impregnated.

3.2. Catalyst Evaluation

3.2.1. Pulse Micro Reactor Evaluation

Thiophene HDS reaction was conducted in pulse reactor to evaluate the metal impregnated on metal incorporated MCM-41-based catalysts. The results are summarized in Table **5**. The results show higher conversion of thiophene in case of catalysts prepared by impregnating Mo on Co- or Ni-MCM-41 as compared with the reverse order of these metal impregnated. Commercial catalyst also showed lower activity for thiophene hydrodesulfurization reaction. The H-form of MoMCM-41-based catalyst showed lower activity as compared with non ion exchange form. As discussed earlier, this was the consequence of Mo being leached out during ion exchange to produce H-form of MoMCM-41.

Similar results were obtained for the conversion of benzothiophene conducted in pulse reactor. Figure **4** shows the results of HDS activity of catalyst presented as conversion of benzothiophene per mole of active metals.

Convectional HDS catalysts contain the catalytically active metals in oxidic form, *i.e.*, MoO_3/WO_3 and CoO/NiO. Upon sulfidation in the presence of H_2, MoO_3 or WO_3 are converted to sulfides having the metal in 4-valant state: MoS2 or WS2, respectively. Cobalt and nickel can form different sulfides depending on the amount of metal and sulfidation temperature. In

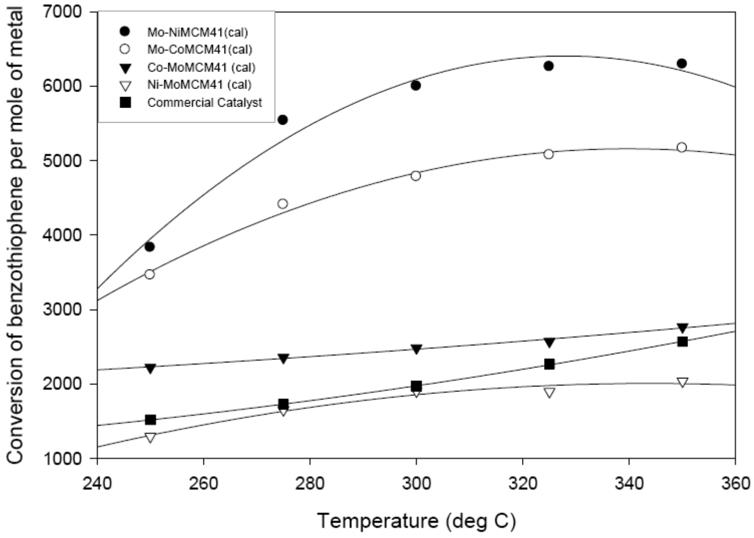

Figure 4: Benzothiophene HDS activity per mole of active metals.

Co(Ni)Mo/Alumina catalyst, most of the Co or Ni is adsorbed on the edge of MoS2 crystallite, forming a structure usually referred to as the Co(Ni)-Mo-S phase. This is believed to be the most active site in which Co or Ni act as a promoter. Similar structure is expected to be formed in case of Co/Ni promoted Mo-MCM-41 catalysts investigated in this study.

The higher activity of Mo impregnated catalysts could be attributed towards the better dispersion of Mo as observed by TPR profiles of theses catalysts (not presented here). Good dispersion of molybdenum on nickel impregnated MCM-41 catalyst was also indicated by Kilmova and co-workers and also observed high HDS activity [19]. However, in their study the nickel was impregnated instead of incorporating into the structure of MCM-41. The commercial catalyst showed lower HDS activity for benzothiophene and the results are comparable with Co-MoMCM-41 catalyst.

3.2.2. Batch Reactor Evaluation

It is well known that dibenzothiophene (DBT) and its derivatives are the most refractory of all sulfur compounds present in heavy oil fractions. Since, zeolites provide limited accessibility for larger molecules like DBTs therefore, MCM-41 based HDS catalyst could be used as alternative to the conventional catalysts. Batch auto clave reactor test with DBT were conducted for the promising catalysts. Based on the pulse reactor results Mo-NiMCM-41, and Mo-CoMCM-41 and for comparison purposes Y zeolite based and commercial catalysts are evaluated by batch reactor. The results of batch reactor catalyst evaluation are given in Table **6**.

Table 6: Batch Reactor Evaluation Results

Catalyst	Product Sulfur (ppm)	Conversion (%)
Commercial Catalyst	750	70.0
Mo-NiMCM-41	810	67.6
Mo-CoMCM-41	770	69.2
MoNi-Y zeolite	1770	29.2

*2500 ppm dibenzothiophene in dodecane as feed and 0.5 wt% catalyst; Reaction temperature 360 °C; Time 1 hour.

The results show comparable conversion of DBT for MCM-41 based catalysts and the commercial catalyst. However, when the activity was calculated on the bases of active metals in the catalysts the conversion was found to be much higher for MCM-41 based catalysts. The results are in line with the study of Corma et. al., where it was shown that in case of MCM-41 based catalysts, the large surface area, uniform pore size distribution, and larger pore size to allow diffusion of larger molecules produces better HDS performance than either amorphous or USY zeolite based catalysts [26]. Similar results were obtained by Song and Reddy [27], where they showed that when cobalt and molybdenum were impregnated on MCM-41, the activity was increased for hydrodesulfurization of DBT in n-tridecane. The results are presented in Figure **5**. Y zeolite based catalyst showed lowest conversion of DBT. This could be attributed to the lower surface are of the catalyst and smaller pore size of Y zeolite that could pose diffusion limitation for DBT.

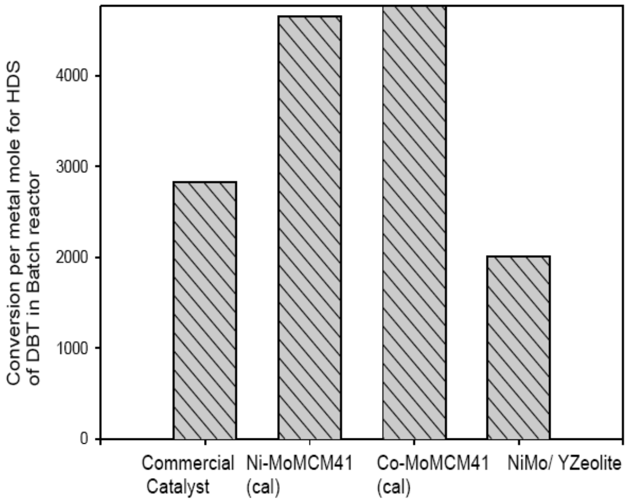

Figure 5: Conversion of DBT per mole of active metals in batch reactor.

4. CONCLUSION

From this study the following conclusions could be drawn:

1. Metal containing MCM-41 has been successfully synthesized. Molybdenum incorporated MCM-41 has high activity in pulse reactor as compared to nickel and cobalt for thiophene and benzothiophene HDS. During ion exchange metal is getting leached out from metal incorporated MCM-41.Molybdenum is getting leached out the most as compared to cobalt and nickel incorporated MCM-41 molecular sieves.

2. Mo-NiMCM-41 and Mo-CoMCM-41 has shown high activity for thiophene and benzothiophene HDS in pulse reactor as compared to commercial catalyst.

3. MCM-41 based catalyst have shown high conversion per metal mole as compared to commercial catalyst in batch reactor as the conversion for DBT was almost the same with more than 3 times of metal content in commercial catalyst

4. Mo-Ni/Yzeolite showed very less conversion for DBT in dodecane as compared to MCM-41 based catalyst and commercial catalyst.

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