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Physico-chemical characterization and catalysis on mesoporous Al-HMS supported molybdenum hydrotreating catalysts

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Abstract

HMS and Al-HMS materials were synthesized by neutral templating pathway and Mo, CoMo, NiMo catalysts were prepared using them as the support. On Al-HMS material (Si/Al = 35) as the support, Mo concentration varied from 2 to 14 wt.%. The promotional effects were studied on 10 wt.% Mo/Al-HMS using 1–5 wt.% Co and Ni. All these catalysts were characterized by surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR) and oxygen chemisorption methods. The catalytic activities for HDS, HYD and HDO were evaluated on sulfided catalysts. The oxygen chemisorption and catalytic activities as a function of Mo loading indicated that a correlation exists between these two parameters for all these reactions. A comparison with γ-Al$_2$O$_3$ supported catalysts indicated that these catalysts exhibit higher activities. The results on HMS, Al-HMS supported catalysts indicated that HMS mesoporous structure has a unique ability to impart higher activities in the supported MoS$_2$ phase through metal support interactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Al-HMS support; Mesoporous materials; CoMo catalysts; Oxygen chemisorption; Hydrotreating; HDS; HYD; HDO

1. Introduction

It is well known that support plays an important role in determining the structure and activity of supported catalysts [1–3]. In the case of hydrotreating catalysts, γ-Al$_2$O$_3$ is the support that is generally used in commercial applications [2]. In recent years, in order to meet stringent environmental regulations, deep or ultra-deep desulfurization catalysts with four to five times higher activity than the present level are required [3]. In order to realize such high activities several approaches have been applied among which variation of the support is a very important one.

In search of better supports for Mo and W a wide variety of materials have been examined with

reference to hydrodesulfurization (HDS) and related reactions. These include clays [4], zeolites [5,6], oxides like SiO$_2$ [7], TiO$_2$ [8], ZrO$_2$ [9], MgO [10] and carbon [11]. Several combinations of mixed oxides like SiO$_2$–Al$_2$O$_3$ [12], SiO$_2$–TiO$_2$ [13], SiO$_2$–ZrO$_2$ [14], ZrO$_2$–TiO$_2$ [15,3] TiO$_2$–Al$_2$O$_3$ [16–19] have been studied with great interest. In recent times the attention is shifted to the use of zeolites like Y, USY and mesoporous materials like MCM-41, HMS [5,6], etc. as supports to hydroprocessing catalysts. Y zeolites are well known in hydroprocessing formulations because of their resistance to poisoning by nitrogen compounds [20,21]. Recently, it has been demonstrated that formation of bifunctional catalysts by combining NiMo or CoMo on γ-Al$_2$O$_3$ with a zeolite allows removal of very refractory sulfur compounds like 4,6-dimethyl dibenzothiophene [22]. MCM-41 is also reported to exhibit higher activities for conversion

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of benzothiophene and petroleum residues [23]. Song and Reddy [24] demonstrated that CoMo/MCM-41 is substantially more active than Co-Mo/Al$_2$O$_3$ catalysts at high molybdenum loadings. Hexagonal mesoporous silica supports containing Ti were tested for naphthalene hydrogenation (HYD) using NiMo, PNiW as active components [5]. To the best of our knowledge Halachev et al. [6] and Chiranjeevi et al. [25] are only references on using Al-HMS materials as support for HDS and related reactions. In order to further understand the potential of HMS material as a support for MoS$_2$, a systematic study of dispersion and catalytic functionalities is undertaken.

2. Experimental

The HMS and Al-HMS materials were synthesized following procedures similar to that of Pinnavia and co-workers [26] and Mokaya and Jones [27,28] via neutral templating pathway using hexadecyl amine as the surfactant. In a typical preparation of Al-HMS material, a gel composition of SiO$_2$: 0.0285, Al$_2$O$_3$: 0.25, hexadecyl amine: 8.3, IPA: 100 H$_2$O was used. In a typical preparation, required amount of Al-isopropoxide was mixed with 35 ml of isopropanol (IPA) (step I). Required amount of hexadecyl amine was mixed with 100 ml of water + 20 ml of IPA and was stirred for 30 min (step II). The required amount of TEOS was mixed with solution from step I and 40 ml water and stirred for 30 min (step III). The step III solution + step II solution was mixed with 40 ml of water and stirred for 2 h (step IV). The final pH of the solution was 9.3. The step IV solution was aged for 20 h at room temperature to obtain a crystalline product. The solid product was separated by filtration, dried at 110 °C over night and calcined at 540° for 6 h. The calcined mesoporous materials were characterized by X-ray diffraction (XRD) using GE XRD-6 diffractometer and micromeritics ASAP-2010 adsorption–desorption unit. The Al$_2$O$_3$ support was prepared by homogeneous precipitation method using urea at 90 °C.

The molybdenum supported catalysts were prepared by incipient wetness impregnation method using appropriate concentrations of ammonium hepta molybdate using Al-HMS (Si/Al = 35) or HMS material as a support. The Co and Ni promoted catalysts were

prepared by impregnating the promoter on an oven dried Mo supported catalysts. The impregnated catalysts were dried in air at 100 °C over night and all the catalysts were calcined at 500 °C for 5 h.

The oxygen uptakes were measured at −78 °C in a conventional high vacuum system on a catalyst sulfided at 400 °C for 2 h using a CS$_2$/H$_2$ mixture at a flow rate of 40 ml/min, according to the double isotherm procedure reported by Parekh and Weller [29] for reduced molybdenum catalysts. The same system was used for the BET surface area measurements. The thiophene HDS, cyclohexene HYD and furan hydrodeoxygenation (HDO) reactions were carried out at 400 °C on a catalyst sulfided at 400 °C for 2 h in a flow of a CS$_2$/H$_2$ mixture, in a fixed-bed reactor operating at atmospheric pressure and interfaced with a six-way sampling valve for product analysis [30]. First order rates were evaluated according to the equation $x = r(W/F)$ where r is rate in moles per hour per gram, x the fractional conversion, W the weight of the catalyst in grams and F is flow rate of the reactant in moles per hour [8,30]. The conversions were kept (below 15%) to avoid diffusional limitations.

3. Results and discussion

In this investigation HMS and Al-HMS materials were synthesized by neutral templating pathway and Mo catalysts and their promoted analogues were prepared using them as the support. For the purpose of comparison, γ-Al$_2$O$_3$ supported catalysts were prepared according to the same impregnation procedure and catalytic activities were evaluated under the same conditions. Using Al-HMS material (Si/Al = 35) as the support various catalysts were prepared by varying the Mo loading between 2 and 14 wt.%. All the supports and catalysts were characterized by the BET surface area, XRD and temperature programmed reduction (TPR) in oxide state and oxygen chemisorption in the sulfided state. The catalytic activities were evaluated for thiophene HDS and cyclohexene HYD. The results on Mo/Al-HMS materials are considered in more detail. HMS and γ-Al$_2$O$_3$, supported catalysts are used for the purpose of comparison. A detailed characterization of the support, active phase and relationship between physico-chemical properties and catalytic activities for

Table 1
BET surface area and oxygen chemisorption data of MoS$_2$/Al-HMS catalysts

Mo (wt.%)	BET surface area (m^2/g)	Oxygen uptake (μmol/g cat.)	O/Mo $\times$ 100	EMSA (m^2/g)[a]	% surface coverage (θ)[b]	Crystallite size (Å)[c]
2	852	30	28.7	16.9	1.98	12.2
4	824	48	23.0	27.1	3.28	15.3
6	804	64	20.4	36.2	4.5	17.2
8	789	88	21.1	49.8	6.3	16.7
10	760	97	18.6	54.9	7.2	18.9
12	701	85	13.5	48.1	6.86	25.9
14	643	67.4	9.2	38.1	5.92	38.2

[a] EMSA (equivalent MoS$_2$ area), calculated using a factor 0.56616 obtained from pure MoS$_2$ BET surface area divided by oxygen uptake.
[b] (EMSA/BET surface area) $\times$ 100.
[c] $5 \times 10^4 / \rho M$, where ρ is the density of MoS$_2$ (4.8 g/cm^3) and M is EMSA/g of MoS$_2$.

HDS, HYD and HDO are presented in the following discussion.

3.1. Characterization of supports and Mo supported on HMS and Al-HMS materials and their promoted analogues

3.1.1. Surface area and XRD studies

Results of characterization of the supports by BET surface area, XRD, N$_2$ adsorption–desorption derived pore size distribution, are identical with literature reported values conforming that the synthesis resulted in hexagonal mesoporous silica [26,27,31,32]. The Mo supported Al-HMS material or HMS material and their Co and Ni promoted analogues were characterized in the oxide state by BET surface area measurements, XRD and TPR studies and in the sulfided state by oxygen chemisorption. It can be seen from the Table 1,

that all these catalysts based on mesoporous materials are of high surface area in the range of 600–800 m^2/g. The surface area of γ-Al$_2$O$_3$ supported catalysts is around 130 m^2/g.

The total surface area measured as functions of Mo loading viz. surface area per gram of support and per gram catalysts are shown in Fig. 1. Total surface areas can be utilized to derive information about dispersion of Mo or its monolayer formation. In the case of monolayer formation of an oxide or sulfide species on a support, addition of Mo to fixed weight of support results in constant surface area per gram of support while surface area per gram of catalyst decreases. By analyzing surface area data Massoth [33] has shown that in Mo and CoMo catalysts supported on γ-Al$_2$O$_3$, the molybdenum oxide exists as monolayer in the oxide and as well as the sulfide state. Liu and Weller [34] have shown that in reduced CoMo/γ-Al$_2$O$_3$ catalyst
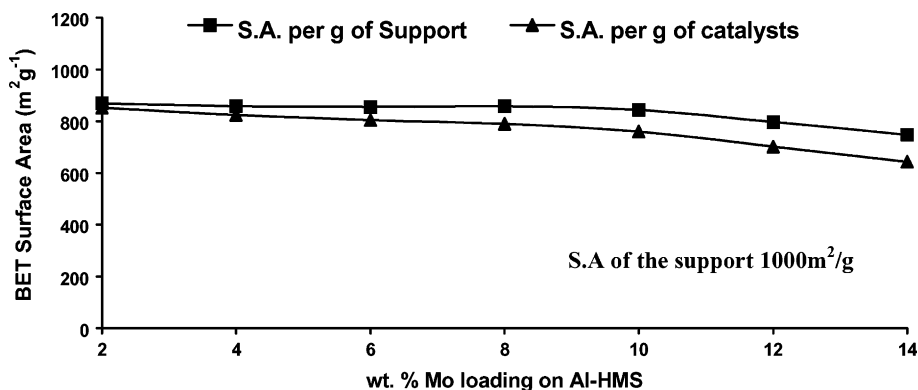

Fig. 1. Variation of surface area per gram of support and per gram of catalyst as a function of Mo loading.

molybdenum exists as microcrystallites. Rao and Murali Dhar [35] showed that WO_3 exist as a monolayer on WO_3/ZrO_2. Chiranjeevi et al. [25] showed that on Al-HMS material, WO_3 exists in highly dispersed state. In this investigation similar analysis of surface areas is shown in Fig. 3. It can be seen that surface area per gram of catalysts decreases with the loading up to 14 wt.%. However, the decrease is sharp after 10 wt.% Mo. Surface area for per gram of support remains constant up to 10 wt.% Mo and then start to decrease. These results indicate that MoO_3 is in highly dispersed state on Al-HMS support and probably of monolayer dimensions. The XRD results also agree with the conclusion in that the X-ray diffractogram did not reveal any clear indications for the presence of crystalline MoO_3 up to the highest loading studied on Mo catalysts and all the CoMo, NiMo catalysts prepared using HMS and Al-HMS materials.

3.1.2. Temperature programmed reduction (TPR)

The TPR studies were carried out in the temperature range 100–1100 °C at a heating rate of 10 °C/min on samples containing 0, 4, 6, 8, 10, 12 wt.% Mo. The reduction profiles of the above said samples are shown in Fig. 2. It can be seen that the reduction profile of Al-HMS material is featureless indicating that the support contribution to the reduction profiles is negligible. In the case of 4 wt.% Mo a peak at 700 °C and a small shoulder at higher temperature can be noted.

The reduction profiles of 6 wt.% Mo present a clear two peak pattern with a peak at 660 and 900 °C. The two peak pattern continues up to the highest loading studied. At 12 wt.% loading there is a small shoulder at 660 °C. The low temperature peak shifts to further lower temperatures with the increase of Mo loading. The high temperature peak behavior is quite different. The peak temperatures decrease up to 10 wt.%, i.e. the loading where so-called completion of the monolayer of molybdenum on the support is noted and then increases at the highest loading. The temperature where the reduction starts, shifts to lower temperatures with molybdenum loading. The reduction profiles therefore indicate that at least two types of species which have different reducibilities are present. It is also clear that with the increase of molybdenum loading, easily reducible species are formed. The two peak pattern is generally explained by the presence of tetrahedral monomeric molybdenum species that are difficult to reduce and polymeric octahedral species that are relatively easily reducible. The assignment of low temperature peak as due to reduction of polymeric MoO_3 to MoO_2 is more or less accepted in literature [36]. However, high temperature peak at low loading has predominant contribution from monomeric species. But at high loadings the high temperature peak has contributions from monomeric MoO_3 reduction, and contribution from reduction of MoO_2 to Mo, formed from MoO_3 crystallites. It is known that MoO_3
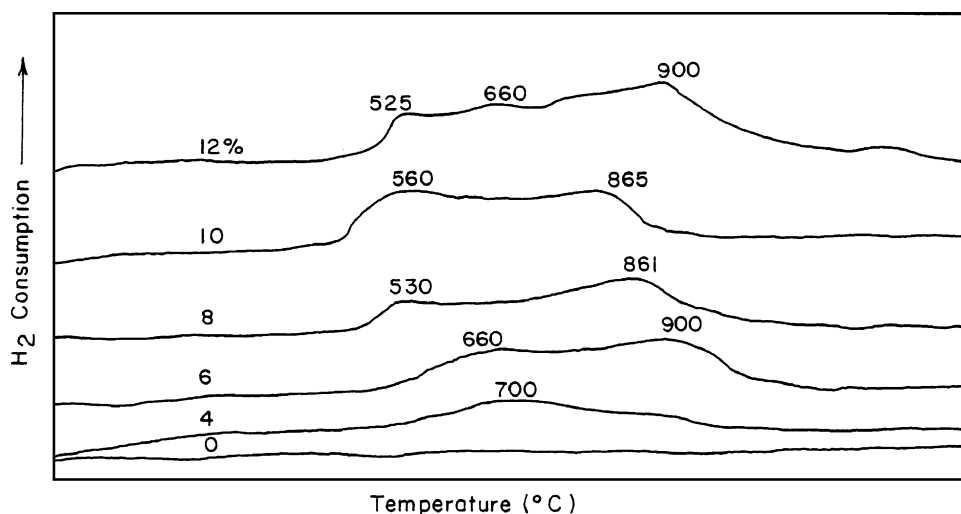

Fig. 2. TPR patterns of Mo/Al-HMS catalysts as a function of Mo loading.
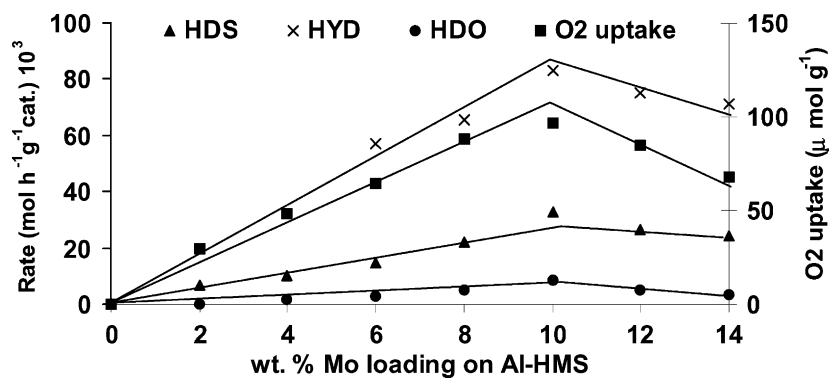
Fig. 3. Variation of oxygen uptake and catalytic activity with Mo loading.

reduction inhibited by water, results in high temperature peak [36]. Regalbuto and Ha, analyzed large amount of literature on TPR of Mo catalysts arrived at similar conclusions on γ-Al_2O_3, SiO_2 supported catalysts [36].

3.1.3. Oxygen chemisorption

Oxygen uptakes on in situ sulfided MoS_2/Al-HMS catalysts evaluated at $-78\,^{\circ}C$, as a function of Mo loading are shown in Table 1 and Fig. 3. It can be seen that oxygen uptake increases with molybdenum loading up to 10 wt.% and then decreases with further increase of Mo loading. It is well known that oxygen chemisorbs on anion vacancies of sulfided catalysts and is a measure of the dispersion of Mo. Therefore, the increase up to 10 wt.% Mo and decrease then afterwards is related to the changes in dispersion of MoS_2. Using oxygen uptakes it is possible to calculate MoS_2 dispersion (O/Mo), equivalent Mo sulfide surface area (EMSA), surface coverage of MoS_2 (θ) on Al-HMS and crystallite size. The corresponding data is given in Table 1. It can be seen that O/Mo, EMSA, and θ, increases with the molybdenum loading up to 10 wt.% Mo and then start decreasing. The crystallite size remains more or less constant up to 10 wt.% Mo and increases with further increase of Mo loading. The crystallite sizes are small and range between 12 and 38 Å. The small crystallite sizes indicate that Mo is well dispersed on the Al-HMS support, even at the highest loading studied. The absence of any clear indication for the presence of MoO_3 in the XRD pattern in the oxide precursors also supports the conclusion. It can be noted that the surface coverages are very

small which suggests that Mo interacts with certain selected regions of support surface. The low O/Mo ratios indicate that oxygen also interacts with certain selected sites on the MoS_2 surface. Overall oxygen chemisorption studies indicate that MoS_2 is well dispersed on Al-HMS material and the maximum dispersion is obtained around 10 wt.% Mo, supporting the conclusion derived from BET surface area analysis and XRD studies. The increasing EMSA, more or less constant crystallite size below 10 wt.% Mo loading, low surface coverage by MoS_2 suggests that the Al-HMS support surface is covered by patches of MoS_2 of monolayer dimensions.

3.1.4. Catalytic activities

The catalytic activities for HDS of thiophene, HYD of cyclohexene and HDO of furan were evaluated on sulfided catalysts as a function Mo loading. The rates of reactions plotted as a function of Mo loading are presented in Fig. 5 for all the three reactions. In the same graph oxygen chemisorption is also plotted for comparison purposes. It can be seen that the rates for all the three reactions increase up to 10 wt.% Mo and then decreases at higher loadings. It is interesting that oxygen uptakes also follow similar trend. It is well known that oxygen chemisorbs on anion vacancies on MoS_2 and WS_2 catalysts. It is also well documented that anion vacancies are the seat of HDS and related reactions. It is also generally accepted that oxygen chemisorption on sulfided catalysts is a measure of dispersion of the sulfide. Therefore, the increase and decrease of activities for the three reactions is related to molybdenum dispersion and
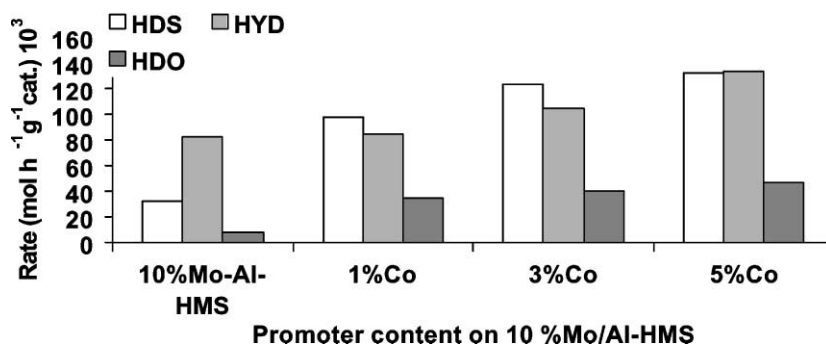
Fig. 4. Effect of promoter content on catalytic activity.

variation of anion vacancies. There appears to be a correlation between catalytic activities and oxygen uptakes in the case of all the three reactions. Since the correlation is obtained in the case of all the three reactions it appears that oxygen chemisorption is not specific to any one of the functionalities on these catalysts.

3.1.5. Promotional effects

Promotion of HDS activity of MoS_2 and WS_2 catalysts by Co and Ni is well known [1]. The promoter concentration is varied from 1 to 5 wt.% on both in the case of Ni and Co. The variation of rates for the three reactions as a function of cobalt concentration is shown in Fig. 4. It can be seen that activity increases with promoter concentration up to the highest loading studied in the case of all the three reactions. The promoted activities are comparable in the case of HDS and HYD but are lower in the case of HDO. The differences in promotional effects for the three reactions by the same promoter active component and support combination suggests that the active sites for the three reactions are different in a subtle way although all the reactions involve anion vacancies. Ni promoted catalysts showed exactly similar behavior as cobalt promoted catalysts. As is well known in the case of γ-Al_2O_3 supported catalysts HDS is better promoted by cobalt and HYD is promoted better by nickel in the case of Al-HMS supported catalysts also.

3.1.6. Comparison of MoS_2/Al-HMS and their promoted analogues with γ-Al_2O_3 supported ones

In order to assess the support effect on catalytic functionalities and also to know how these catalysts perform in comparison with standard composition of active phase and promoters on γ-Al_2O_3, a comparison of MoS_2/Al-HMS and MoS_2-γ-Al_2O_3 under exactly similar conditions is made. The promoted analogues and commercial catalysts also included in the comparison. The activity data and oxygen uptakes are given in the Table 2.

It is interesting to compare the activities of CoMo/Al-HMS with that of CoMo/γ-Al_2O_3. It can be seen that CoMo/Al-HMS exhibit outstanding activities for the two principal hydrotreating reactions. The HDS activity of CoMo and Ni-Mo catalysts is three to five times higher than that of the standard CoMo composition on γ-Al_2O_3. Similarly HYD activity is more than four times higher than standard composition, 3% Co-8% Mo/γ-Al_2O_3. It can be seen that these catalysts exhibit outstanding activities compared to 3% Co-8% Mo/γ-Al_2O_3, which is a standard composition in commercial catalysts. It can be seen from the Table 2, that Mo/Al-HMS, CoMo-Al-HMS, NiMo/γ-Al_2O_3 are more active than corresponding γ-Al_2O_3 supported catalysts for all the three reactions. It can be clearly noticed from Fig. 5 that the oxygen chemisorption and catalytic activities show similar trend of variation. Therefore, it appears that increase of dispersion of MoS_2 and increase of anion vacancies are indeed intimately connected with the increase of catalytic activities. The catalytic activities of HMS and Al-HMS supported catalysts is to be taken with the point in mind that this observation only indicates about their potential as supports for HDS and related reactions but the prospects about commercial utility cannot be ascertained until and unless high pressure studies with more relevant model compounds such

Table 2
Characterization and catalytic activity of supported Mo, Ni and Co promoted catalysts

Supported catalysts	BET surface area (m^2/g)	O$_2$ uptake (μmol/g cat.)	Reaction rates ((mol/h/g cat.) × 10^3)	
			HDS	HYD
10% Mo/HMS	605	93	16.4	36.3
3% Ni-10% Mo/HMS	517	102	62.3	72
3% Co-10% Mo/HMS	461	108	75.3	48
8% Mo/γ-Al$_2$O$_3$[a]	204	22.1	11.2 (10.9)	25.4 (26.3)
3% Ni-8% Mo/γ-Al$_2$O$_3$[b]	141	29.0	19.1 (22.5)	29.1 (35.3)
3% Co-8% Mo/γ-Al$_2$O$_3$[b]	138	31.8	26.8 (25.7)	24.7 (43.5)
10% Mo/Al-HMS	760	97	32.5	83
3% Ni-10% Mo/Al-HMS	655	116	85.4	127
3% Co-10% Mo/Al-HMS	662	113	124.0	105

[a] Values in parenthesis are for 8% Mo/γ-Al$_2$O$_3$ (178 m^2/g).

[b] For commercial catalysts of comparable composition.
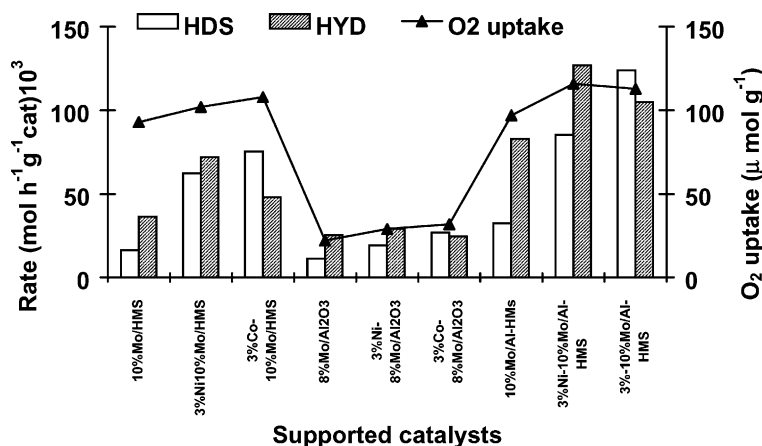
Fig. 5. Catalytic activities of Mo, CoMo, NiMo catalysts prepared using HMS, Al-HMS and γ-Al$_2$O$_3$ supports.

as alkyl dibenzothiophene and real feeds confirm the above observation. The fact that both Mo and W [25] supported Al-HMS, HMS materials display high activities suggest that these materials deserve further examination. Purely siliceous HMS supported catalysts also show considerably higher activities than γ-Al$_2$O$_3$ supported catalysts. The higher activity of Al-HMS catalysts compared to HMS supported catalysts suggest that incorporation of Al indeed increases the activity of MoS$_2$. The fact that HMS, Al-HMS and MCM-41 [37] supported CoMo, NiW catalysts show significantly higher activities suggests that the hexagonal mesoporous structure has the unique ability to impart higher activities in MoS$_2$ and WS$_2$.

4. Conclusions

Hexagonal mesoporous silica and its Al substituted analogues were synthesized by neutral templating pathway. The characterization by XRD and adsorption–desorption methods indicated that these materials are indeed HMS type of materials. Mo and promoted catalysts derived from these materials were examined by surface area, XRD and TPR in oxide state and in the sulfided state by O$_2$ chemisorption and model reactions. The surface area and XRD measurements indicated that MoS$_2$ is well dispersed on HMS and Al-HMS materials. The TPR measurements indicated that the surface is populated

by species that display different reducibilities and two of these species may be monomeric tetrahedral MoO_3 and polymeric octahedral MoO_3 species. However, interpretation of high temperature peak is complicated. The oxygen chemisorption studies also indicated that MoS_2 is well dispersed on this support and maximum dispersion is obtained at 10 wt.% Mo on Al-HMS materials. The crystallite sizes obtained from oxygen chemisorption confirmed these conclusions. The surface coverage by MoS_2, equivalent molybdenum sulfide area, crystallite size indicated that MoS_2 attaches to selected regions of the support surface as patches of monolayer dimensions. The variation of catalytic activities as a function of Mo loading indicated that maximum activity is obtained at 10 wt.% Mo loading. The similarity in variation of catalytic activities and oxygen chemisorption indicated that oxygen uptakes correlates well with catalytic activities. Since the correlations were obtained in all the three cases it appears that oxygen chemisorption is not specific to any one of the functionalities but measures general state of dispersion of MoS_2. The promotional studies indicated that the three functionalities originate from different set of sites containing the anion vacancies. A comparison of Al-HMS supported MoS_2 catalysts with γ-Al_2O_3 catalysts indicated that the former exhibit outstanding activities.

Acknowledgements

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