Effect of method of preparation on hydrodesulphurization activity of Co- or Ni-promoted MoS₂/SBA-15 catalysts

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MS received 15 September 2013; revised 24 November 2013; accepted 27 November 2013

Abstract. Ordered mesoporous material SBA-15 was synthesized and used as a support for the preparation of molybdenum sulphide catalysts through precipitation from homogeneous solution (PFHS) technique with the Mo content varying from 2–12 wt%. The prepared catalysts were evaluated for thiophene hydrodesulphurization catalytic activities at 400°C. Catalysts prepared through PFHS method resulted in highly dispersed MoS₂ catalysts, which were inferred from powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), low temperature oxygen chemisorptions (LTOC) and BET surface area analysis. The relationship between XPS intensity ratio, oxygen chemisorption and catalytic activities is discussed in terms of highly dispersed nano particles of MoS₂ and its consequence in accommodating more promoted atoms at the edge sites.

Keywords. PFHS method; MoS₂; SBA-15; HDS; promotional effects.

1. Introduction

Environmental concerns about pollution by sulphur and nitrogen compounds and particulate matter, containing carcinogenic compounds has led to stringent specifications on petroleum products such as gasoline and diesel. Practical limitations of after-treatment devices in automobiles have shifted the responsibility of pollution control towards the petroleum refining industry. As a consequence, sulphur specifications of diesel were lowered to below 50 ppm. Most of the developed countries have sulphur specifications of diesel at around 10–15 ppm.^{1–3} Feedstock preparation for onboard fuel cells requires sulphur levels to be brought down to 0.1 ppm. Hydrotreating is a well-known unit operation in a petroleum refinery to reduce sulphur levels in naphtha, kerosene, diesel, gas oil and residue.^{1,2} In this process, employment of highly active catalysts is the most preferred choice among various options to reduce sulphur to ultra low levels. Calculations reveal that to reach such ultra low sulphur levels, activity of the catalysts needs to be increased by about seven times.²

Well-known commercial catalysts for hydrotreating operation contain Mo or W as active components, Co

or Ni as promoters and γ -Al₂O₃ as support.¹ Many approaches were followed to prepare highly active hydrodesulphurization (HDS) catalysts among which variation of support and variation of method of preparation were actively pursued.^{4,5} Rayo *et al.*⁶ studied the effect of the preparation method on the structural stability and hydrodesulphurization activity of NiMo/SBA-15 catalysts. Effects of the acid and basic treatments on the stability of SBA-15 and NiMo/SBA-15 catalysts were evidenced by different characterization techniques and they observed that large deterioration of the SBA-15 structural order at basic pH. Recent advances in the science and technology of ultra low sulphur diesel production including the effect of preparation methods for the highly active catalysts are available in a recent review.⁷ Klimova *et al.*⁸ and their group reported the highly active SBA-15 supported NiMo and CoMo catalysts and the role of citric acid.^{9,10} Various supports such as TiO₂,^{11,12} ZrO₂,¹³ carbon,¹⁴ mixed oxides such as TiO₂-ZrO₂,¹⁵ TiO₂-Al₂O₃,^{16,17} MgO-Al₂O₃,¹⁸ zeolites and mesoporous materials such as MCM-41,^{19–23} SBA-15,^{23–26} FSM-16,²⁷ HMS,²⁸ KIT-6,²⁹ and their metal-substituted or deposited analogues have been employed.^{30–32} These mesoporous materials exhibited outstanding activities for hydrodesulphurization functionality. In the earlier reports on γ -Al₂O₃-supported

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Mo catalysts prepared by precipitation from homogeneous solution (PFHS) method, several fold increase in activities were noted.³³ In order to increase the activity of the SBA-15-supported systems further, we have used PFHS technique to deposit MoS₂ nano particles inside the SBA-15 pore system. The preparation, characterization and discussion of hydrodesulphurization activities and its relation to physico-chemical properties of supported phase form the contents of this study.

2. Experimental

2.1 Preparation, characterization and activity of catalysts

SBA-15 was prepared by following the reported procedure using triblock polymer (P-123) as structure directing agent.³⁴ The calcined materials and subsequently prepared catalysts were characterized by low angle X-ray diffraction as well as wide angle XRD using GE XRD-6 diffractometer and micromeritics adsorption-desorption unit (ASAP-2010).

The SBA-15-supported Mo catalysts were prepared by following precipitation from homogeneous solution method (PFHS).^{33–35} MoS₂/SBA-15 catalyst was prepared by the PFHS method using thioacetamide as the precipitating agent. In a typical experiment, SBA-15 was suspended in a solution containing the required amount of ammonium molybdate, thioacetamide and nitric acid. The resulting mixture was heated to 90–95°C with constant stirring until the MoS₂ was deposited on SBA-15 support. After the precipitation was complete (pH 2–3), the resulting solids were filtered, washed and dried at 110°C. The promoted catalysts were prepared by precipitation of cobalt sulphide or nickel sulphide on oven-dried MoS₂/SBA-15 catalyst. This was accomplished by suspending MoS₂/SBA-15 in a solution containing requisite amounts of urea, thioacetamide, nitric acid and cobalt or nickel nitrate and then heating the mixture on a water bath until completion of the precipitation at pH 7–9. The resulting solids were filtered, washed and dried at 110°C. Catalysts prepared by PFHS method are subjected directly to HDS. For comparison purpose, catalysts supported on SBA-15 were also prepared by conventional incipient wet impregnation method¹¹ (IWIM). SBA-15 used for preparation of catalysts in both PFHS and IWIM methods are the same. The low temperature oxygen chemisorptions (LTOC) measurements were made on sulphided catalysts at –78°C in a conventional volumetric adsorption unit with a provision to sulphide the catalysts *in situ*, according to a procedure described

earlier.³⁵ BET surface area and pore size distributions were carried out using ASAP-2010 pore analyser from micromeritics (USA). A vacuum generator ESCALAB/MK11 spectrometer with Mg K α radiation (1253.6 eV) was used at 10^{–8} torr pressure along with Apple 11e (48 KB) micro computer for evaluating Mo and Si peak intensities. Binding energies are referenced against contaminant carbon present (284.6 eV). Thiophene HDS activities were carried out at 400°C on catalysts sulphided at 400°C for 2 h in a fixed bed reactor operating at atmospheric pressure.^{26,30} Briefly, about 0.2 g of catalyst sample was secured between two plugs of quartz wool inside a microreactor (Pyrex glass tube, 0.8 cm I.D.). Prior to activity measurements, catalysts were sulphided at 400°C for 2 h with CS₂ (43.6 mol%)/H₂ (40 cm³/min). After sulphidation, thiophene HDS or cyclohexene hydrogenation (HYD) was conducted at 400°C with about 40 cm³/min of hydrogen previously saturated in a saturator containing the corresponding reactant feed at room temperature, that is, 10.7 mol% of thiophene.

3. Result and discussion

3.1 Support and catalyst characterization

The support samples synthesized and calcined at 550°C for 6 h were used to prepare MoS₂-supported catalysts by PFHS. The low angle XRD patterns of SBA-15 support, 8 wt% MoS₂/SBA-15, 10 wt% MoS₂/SBA-15 are shown in the figure 1. It can be seen that the XRD pattern consists of a sharp low angle line corresponding to (100) reflection characterized by $d = 103.8 \text{ \AA}$ followed by two lines of low intensity corresponding to 110 characterized by $d = 56.4 \text{ \AA}$ and another reflection on the high angle side, corresponding to 200 reflection characterized by $d = 27.7 \text{ \AA}$.³⁴ These three lines are characteristic of hexagonal mesoporous SBA-15 structure. It can be also be seen from figure 1 that the three-peak pattern is also exhibited by 8 wt% MoS₂/SBA-15 as well as 10 wt% MoS₂ indicating that MoS₂ deposition by PFHS technique did not cause any changes in the ordered mesoporous structure. However the MoS₂-supported catalysts showed lower intensity for the 100 reflection compared to pure SBA-15. The wide angle X-ray diffraction patterns of catalysts containing various amounts (2–12 wt%) MoS₂ on SBA-15 are presented in figure 2. There is no evidence for the presence of crystalline MoS₂ in all the patterns. This observation suggests that the MoS₂ is in a highly dispersed state and the crystallite size of MoS₂ is less than 4.0 nm. The observation also indicates that the PFHS technique resulted

Figure 1. Low angle XRD pattern of (a) SBA-15, (b) 8% MoS₂-SBA-15 and (c) 10% MoS₂-SBA-15.

in depositing highly dispersed nano particles of MoS₂ inside the pores of SBA-15. The Ni as well as Co-promoted MoS₂/SBA-15 catalysts were also examined by wide angle XRD. Results related to Ni-promoted catalysts are shown in figure 3. It can be noticed in these XRD patterns that there is no evidence for any crystalline phases of cobalt sulphide, nickel sulphide or compounds of promoter atoms and MoS₂ phase.

The pure SBA-15 and MoS₂/SBA-15 catalysts were examined by BJH pore size analysis. Surface area of SBA-15 support is 650 m²/g. Corresponding adsorption-desorption isotherms for SBA-15 (A) 8 wt% MoS₂/SBA-15 (B) 10 wt% MoS₂/SBA-15 (C) are shown in figure 4. It can be noted that a H₁ hysteresis loop in the range P/P_0 0.6–0.8 is obtained in all the three cases. The pore size is about 66.3 Å. These results indicated that a narrow cylindrical pore size distribution, a characteristic of ordered hexagonal mesoporous SBA-15, is retained even after loading 10 wt% MoS₂ into the SBA-15 pores. It can also be seen that there is a small decrease in the width of hysteresis loop, indicating a decrease in pore volume and pore diameter after loading MoS₂. Landau *et al.*³⁶ analysed the surface area

Figure 2. Wide angle XRD pattern of (2–12 wt%) MoS₂ supported on SBA-15.

Figure 3. Wide angle XRD pattern of (1–5 wt%) Ni promoted 10% MoS₂-SBA-15 catalysts.

data in the case of thin layer of a metal sulphide species deposited in mesoporous materials, to suggest that normalized surface area of 0.9 indicates high dispersion of the sulphide phase inside SBA-15 pores. In the case of 10 wt% MoS₂/SBA-15, the normalized surface area is found to be 0.9 indicating a high dispersion of MoS₂ inside the SBA-15, pores up to that loading.

The BET surface areas of various catalysts as a function of MoS₂ loading are shown in table 1. The surface areas are very high and remain very high up to 10 wt % loading. However, at 12 wt% loading the surface area decreases considerably. The BET surface area data can be further analysed to obtain information about dispersion of the supported phase as a monolayer. For this purpose, the surface area for gram of support is calculated from surface area for gram of catalyst obtained from BET measurement. In the case of formation of monolayer, the surface area per gram of support remains constant with MoS₂ loading while the surface area per gram of catalyst decreases.²⁶ A plot of BET surface area per gram of catalyst as well as support is shown in figure 5 as a function of MoS₂ loading. It can be seen that the surface area per gram of catalyst

Figure 4. N₂ adsorption-desorption isotherm of (a) SBA-15, (b) 8 wt% Mo-SBA-15 and (c) 10 wt% Mo-SBA-15.

Figure 5. Variation of surface area of SBA-15-supported catalysts with Mo loading.

decreases while the surface area per gram of support remains more or less constant up to 10 wt% loading and the surface area per gram of support shows a drastic decrease at 12 wt% loading indicating a deviation from the monolayer behaviour. These results indicate that the MoS₂ loading into SBA-15 by PFHS method results in very highly dispersed MoS₂ which is probably present as a monolayer up to 10 wt% Mo loading.³⁷ Landau *et al.*³⁶ made similar surface area analysis in terms of normalized surface area (NSA) for a number of oxides. In a similar analysis of this case, a NSA of 0.9 is obtained which suggests that the MoS₂ is well-dispersed in SBA-15 pores.

XPS-binding energies and intensity ratios provide useful information about valence state and dispersion of supported phase. Samples containing various amounts of MoS₂ supported on SBA-15 by PFHS technique were examined by X-ray photo electron spectroscopy (XPS). The Si 2p and Mo 3d line binding energies indicated that oxidation state of Mo on the surface of SBA-15 is Mo⁴⁺ species. From the intensities of the lines divided by their respective photo electron cross-sections, intensity ratios of $I_{\text{Mo}}/I_{\text{Si}}$ were calculated. The $I_{\text{Mo}}/I_{\text{Si}}$ ratios

Figure 6. Variation of oxygen uptake, HDS rate and $I_{\text{Mo}}/I_{\text{Si}}$ with wt% MoS₂ loading.

Figure 7. Correlation of XPS intensity ratios ESCA with HDS activity and O₂ uptake of various wt% MoS₂ supported on SBA-15.

as mentioned earlier are a measure of dispersion of supported phase. The $I_{\text{Mo}}/I_{\text{Si}}$ ratios as a function of MoS₂ loading are plotted in figure 6. It can be seen that this ratio increases more or less linearly up to 10 wt% MoS₂ loading and then decreases at the highest loading studied (12 wt%), indicating that the dispersion of molybdenum sulphide phase increases up to 10 wt% and then decreases. This result is similar to the conclusion arrived by surface area analysis as discussed earlier.

Oxygen chemisorption at -78°C was carried out on sulphided MoS₂/SBA-15 containing 2–12 wt% MoS₂. The oxygen uptakes are shown in table 1 as a function of MoS₂ loading and corresponding graphical representation is shown in figure 6. It can be seen that the oxygen chemisorption increases linearly up to 10 wt% MoS₂ and then decreases beyond this point. It is well-known that oxygen uptake represents MoS₂ dispersion or number of anion vacancies which are the seat of catalytic activity of supported catalysts.²⁶

O₂ uptake data can be used to derive useful information about MoS₂ dispersion (O/Mo), equivalent molybdenum sulphide area (EMSA), surface coverage and crystallite size. This information calculated using oxygen uptake is shown in table 1. It can be noticed that

Figure 8. Promotional effect of Co and Ni on HDS of 10 wt% MoS₂/SBA-15 catalysts.

Figure 9. Comparison of HDS activity of MoS₂ catalysts prepared by PFHS and IWIM.

EMSA and surface coverage increases up to 10 wt% MoS₂ and the crystallite size varies in a narrow range around 2 nm up to 10 wt% MoS₂. The same parameter (crystallite size) shows a rapid increase but is still below the detection limit of XRD as shown in figure 2. In the same figure, a comparison is made with catalysts prepared by incipient wetness impregnation method (IWIM). It can be seen that the crystallite growth is rapid beyond 8 wt% MoS₂ loading for IWIM and 10 wt% MoS₂ loading for PFHS-derived catalysts. The crystallite size for PFHS-prepared 10 wt% MoS₂ catalyst is nearly half of that of IWIM. It can also be seen that the value for surface coverage for 10 wt% MoS₂ is only 10.2% which indicates that the MoS₂ selectively interacts with certain preferred sites on the surface of SBA-15. In other words, MoS₂ distributes on the surface as monolayer patches possibly using certain energetically suitable hydroxyl groups on the surface. Fixing of Mo or W on oxide surfaces using hydroxyl groups on oxide surfaces is well-known.^{38,39}

Figure 10. Comparison of HDS activity and O₂ uptake of Mo, CoMo and NiMo catalysts supported on SBA-15 and γ-Al₂O₃.

3.2 Catalytic activity studies

Thiophene hydrodesulphurization is a well-known reaction for assessing the efficiency of sulphide catalysts for C–S bond cleavage in heterocyclic sulphur molecules. In this investigation, hydrodesulphurization of thiophene was carried out at 400°C at atmospheric pressure on catalysts sulphided at 400°C. The calculated reaction rates are shown as a measure of the activity and are shown in figure 6 as a function of MoS₂ loading. It can be noticed that the HDS activity increases linearly up to 10 wt% MoS₂ loading beyond which the activity shows a decline. This observation is interesting in the light of XPS and oxygen chemisorption results which showed a similar increase up to 10 wt% MoS₂ loading and then shows a declining trend. Since XPS intensity ratios as well as oxygen chemisorption represent dispersion of MoS₂, it is clear that the activity increases up to 10 wt% and declines beyond this point due to variation of active sites, namely anion vacancies. This relationship can be clearly seen in figure 7, where both HDS and oxygen uptakes are plotted as a function of XPS intensity ratios. A good linear correlation is obtained between $I_{\text{Mo}}/I_{\text{Si}}$ and HDS or oxygen uptakes emphasizes the excellent relationship between the three parameters intimately connected to the dispersion of MoS₂.

3.3 Promotional effect

Cobalt and nickel are well-known promoters of Mo hydrodesulphurization catalysts. The effect of PFHS method on the promotional effect is studied in detail. In this investigation, Co and Ni catalysts containing 1, 3 and 5 wt% were prepared by PFHS method and corresponding IWIM catalysts are also used. Thiophene HDS activity was measured in the sulphided state at 400°C. Results of this measurement as a function of promoter content can be seen in figure 8. The rate of reaction, BET surface areas and oxygen uptakes are shown in table 2. It can be seen that the HDS rate as shown in figure 8 increases up to highest composition studied on Co as well as Ni catalysts. The oxygen uptake also shows a similar trend of variation in both Co and Ni catalysts, indicating that the increased promotional effect is due to increased dispersion of molybdenum sulphide which allows more promoter atoms to be incorporated at the sulphur edge of molybdenum sulphide crystallites. Recent STM and DFT studies by Topsoe *et al.*⁴⁰ showed that sulphur edge of hexagonal prism of MoS₂ is the position preferentially occupied by promoter atoms, which undergoes morphological changes as a result of promoter atom incorporation. Therefore, it appears that the role of PFHS method is in

Table 1. Physico-chemical characterization of MoS₂/SBA-15.

wt% “Mo”	S _A BET (m ² /g)	O ₂ uptake (μmol g ⁻¹)	EMSA (m ² /g) ^a	O/Mo × 100 (%)	%Surface coverage ^b	Crystallite size (Å) ^c	
						PFHS	IWIM ^d
2	574	30.7	17.3	29.4	2.9	12.0	13.7
4	569	38.6	21.9	18.5	3.8	19.0	19.7
6	554	41.5	27.5	15.3	4.9	22.8	23.2
8	537	69.9	39.6	16.8	7.3	21.0	23.6
10	518	94.8	53.7	18.2	10.2	19.4	37.1
12	380	67.4	34.8	10.8	9.9	35.9	50.5

^aEMSA (equivalent MoS₂ area), calculated using a factor 0.56616 obtained from pure MoS₂ BET surface area divided by oxygen uptake

^b(EMSA/BET surface area) × 100

^c $5 \times 10^4 / \rho M$, where ρ is the density of MoS₂ (4.8 g/cm³) and M is EMSA/g of MoS₂

^dCrystallite size of catalyst from incipient wet impregnation (IWIM)

preparing MoS₂ nano particles and subsequent effective incorporation of promoter atoms at the edge positions. It is well-known that in the case of IWIM prepared catalysts, a maximum occurs for both HDS and oxygen uptakes at 3 wt% promoter atoms.¹ Even at 5 wt%, in case of PFHS catalysts, the activity is still increasing and so does oxygen uptake. This clearly demonstrates that high MoS₂ dispersion provides more sulphur edges to accommodate larger number of promoter atoms at the edge positions.

3.4 Comparison of MoS₂/SBA-15 preparation by PFHS and IWIM methods

In order to assess the advantage of the PFHS method with reference to IWIM, a comparison is drawn in table 2, where MoS₂ catalysts and their promoted analogues are compared with respect to activities and oxygen uptakes. It can be seen that from the data given on SBA-15 prepared by the two methods that the dispersion as measured by oxygen uptakes can be increased

by 30–40% by this novel preparation method. In comparison with γ -Al₂O₃-supported catalysts prepared by IWIM, the dispersion is increased by four times on Mo/SBA-15 catalysts prepared by PFHS method. A similar comparison of activity parameters shown in table 2 indicates that about three times more active catalysts can be prepared by combination of SBA-15 support and PFHS preparation method.

A comparison of PFHS prepared catalysts can be better appreciated by plotting the activities of the catalysts in the same graph as a function of molybdenum loading as shown in figure 9. It can be noticed that the entire wt% of MoS₂-loading PFHS catalysts shows superior activities for thiophene hydrodesulphurization. The superiority of the catalysts is more striking at higher loadings namely at 10 wt% MoS₂ and 12 wt% MoS₂. At 10 wt% MoS₂ loading, the activity is more than doubled. Similar observation is also made in the case of oxygen uptake and the crystallite size calculated for 10 wt% MoS₂ which is half of IWIM catalysts (table 1) showing that PFHS method results in high dispersion even at high MoS₂ loading. This high dispersion also allows accommodation of more promoter

Table 2. Characterization and catalytic activity of supported Mo, CoMo and NiMo catalysts.

Catalysts	S _A BET(m ² /g)	O ₂ uptake (μmol g ⁻¹)	HDS Rate (mol h ⁻¹ g ⁻¹ × 10 ⁻³)
PFHS			
10% Mo/SBA-15	525	94.8	35.0
5% Co 10% Mo/SBA-15	425	129.5	67.6
5% Ni 10% Mo/SBA-15	415	120.4	57.3
IWIM			
8% Mo/SBA-15	322	62.2	24.0
3% Co 8% Mo/SBA-15	222	88.4	49.1
3% Ni 8% Mo/SBA-15	212	72.6	39.6
8% Mo/γ-Al ₂ O ₃	204	22.1	11.2
3% Co 8% Mo/γ-Al ₂ O ₃	138	31.8	26.8
3% Ni 8% Mo/γ-Al ₂ O ₃	141	29.0	19.1

atoms in the sulphur edge of MoS₂ crystallite which results in high activities even at high promoter loading unlike IWIM-prepared catalysts (table 2). A comparison of Mo, CoMo, NiMo catalysts prepared by PFHS technique using SBA-15 as a support with γ -Al₂O₃-supported Mo, CoMo, NiMo catalysts containing 8 wt% Mo and 3 wt% promoters is shown in figure 10. It can be clearly seen that higher activities resulted from PFHS method emphasizes the superiority of the method of preparation. A combination of SBA-15 support and PFHS preparation method can achieve three times higher activities due to increased molybdenum dispersion and accommodation of more promoter atoms in highly dispersed state. In the same graph, oxygen uptakes are also plotted which shows similar trend as activities. Since oxygen uptakes are a measure of dispersion of MoS₂, it is clear that the superiority of PFHS method lies in its ability to produce small nano particles of MoS₂.

4. Conclusion

The ordered mesoporous material SBA-15 prepared using triblock polymer is used to prepare Mo, CoMo and NiMo catalysts by PFHS technique. The support and prepared catalysts were characterized by low angle as well as wide angle XRD, BJH pore size distribution, BET surface area analysis and XPS. The low angle XRD indicated that the ordered hexagonal mesoporous structure is retained in the MoS₂ catalysts too and are conformed by BJH nitrogen adsorption-desorption measurements. The XPS measurements indicated that the dispersion as suggested by $I_{\text{Mo}}/I_{\text{Si}}$ increases up to 10 wt% Mo in these catalysts. Surface area analysis indicated that MoS₂ is dispersed as a monolayer up to 10 wt% MoS₂. Oxygen uptakes and derived small crystallite size (2.0 nm) indicated that MoS₂ is highly dispersed up to 10 wt% MoS₂. Similar results are also inferred from wide angle XRD scans of MoS₂ as well as CoMo and NiMo catalysts. All these measurements suggested that this preparation method allows loading of more MoS₂ in highly dispersed form which allows creation of more (Ni) Co-Mo-S edge sites resulting in higher activities. A comparison with γ -Al₂O₃-supported catalysts indicated that this support and preparation method combination increases the activities by about three times.

Acknowledgements

Authors SG and KS thank the Council of Scientific and Industrial Research, New Delhi, India for the Research

fellowship. We also thank ETN Reddy, Chemical Engineering Department, GVP College of Engineering for computer assistance.

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