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Characterisation and Evaluation of γ-Al_2O_3 Supported Hydroprocessing Catalysts Prepared through the Precipitation from Homogeneous Solution (PFHS) Method[1]

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Unpromoted and cobalt- or nickel-promoted γ-Al_2O_3 supported molybdenum sulfide catalysts were prepared by the precipitation from homogeneous solution (PFHS) method in a single step. These catalysts were characterised by surface area measurements, X-ray diffraction, and electron spin resonance spectroscopy. Studies were made on the effect of Mo loading on oxygen chemisorption, variation of O/Mo, equivalent metal sulfide area (EMSA) and surface coverage, variation of hydrodesulfurisation (HDS) and hydrogenation (HYD) activity, and correlation of oxygen uptake with HDS and HYD rates. These catalysts do not need presulfidation prior to HDS reaction and have higher activity, better characteristics than the catalysts prepared by conventional methods.

INTRODUCTION

Because of its favourable surface characteristics, almost all of the commercial hydrotreating catalysts use γ-Al_2O_3 as the support (*1*, *2*). Studies on γ-Al_2O_3 supported hydrotreating catalysts have revealed that the active phase is well dispersed on the surface of the support due to a strong interaction between the support and the active phase (*3*). Thus, one reason for the use of γ-Al_2O_3 for the large-scale preparation of Co–Mo and other HDS catalysts is its capacity to impart remarkable structural stability to the finished catalysts through its pronounced interaction with the active phase (*4*). The pronounced metal–support interaction prevents agglomeration and sintering of the particles of the active component on alumina catalysts. On the other hand, the HDS reaction is promoted to a larger extent than the HYD reaction on the Co–Mo catalysts (*5*, *6*). The activity of the catalysts mainly depends on the method of preparation and nature of the support. Usually the γ-Al_2O_3 supported hydroprocessing catalysts were prepared by an impregnation method. The calcined precursors are presulfided during the HDS process. A single-step method for preparing supported sulfide catalysts has not been reported so far. Recently the PFHS method has been identified as a good means of making better controlled catalysts (*7*–*11*). Very recently we applied the PFHS method for preparation of a novel type of unpromoted MoS_2/γ-Al_2O_3 catalyst (*12*). In the present study, a series of molybdenum sulfide catalysts with molybdenum loading ranging from 2 to 15 wt% on a γ-Al_2O_3 support are prepared by the PFHS method. The details of the preparation are described elsewhere (*13*). These catalysts were characterized by low-temperature oxygen chemisorption (LTOC) at −78°C, XRD, and ESR studies. Those properties are shown to be correlated with the activity of the materials as

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catalysts for hydrodensed hydrodesulfurisation of thiophene and hydrogenation of cyclohexene.

EXPERIMENTAL

Commercial γ-Al_2O_3 of Harshaw Al-111-61E with surface area 234 m^2g^{-1}, P.V. 0.65 cm^3 g^{-1}, pore radius 5.6 nm was used as a support in the preparation of catalysts. γ-Al_2O_3 supported unpromoted molybdenum sulfide catalysts and promoted catalysts, cobalt sulfide–molybdenum sulfide, nickel sulfide–molybdenum sulfide, were prepared by the PFHS method using thioacetamide hydrolysis in a single step (*12–14*). LTOC at −78°C was studied on these catalysts using a static method (*15*). The surface areas of the catalysts were measured by the BET method using an N_2 adsorption technique, in a high vacuum unit made (constructed) of glass. All the XRD results were recorded on a Phillips PW-1051 diffractometer by using Ni-filtered CuK_α radiation. ESR spectra were recorded on a JEOL FE-3X X-band spectrometer with 100-kHz modulation at ambient temperature. Thiophene hydrodesulfurisation (HDS) and cyclohexene hydrogenation were chosen as the model reactions for testing the hydrogenolytic and hydrogenation functionalities of the catalysts. A differential flow microreactor, operating under normal atmospheric pressure and interfaced to a gas chromatograph (CIC make, India) by a six-way gas sampling valve, was used to measure the activities of the catalysts. In a typical experiment about 0.2 g of catalyst sample was secured between two plugs of quartz wool inside the borosilicate glass reactor of 10-mm i.d fitted with a thermowell and an electrically heated vertical furnace. High purity H_2 was passed through two saturators containing thiophene or cyclohexene maintained at appropriate temperatures to achieve the desired partial pressure. All the conversion rates were measured under steady state conditions with the help of the equation (*16*) $X = r(W/F)$. The conversions are kept below 15%. The ratio of rate constants (k_{HYD}/k_{HDS}) were determined from the corresponding initial rates assuming first-order dependence. Butene and butane, the HDS products of thiophene, were analysed by gas chromatograph with a 2-m stainless steel column (2-mm i.d) packed with 10% OV-17, maintained at 80°C. Cyclohexane was the predominant product of cyclohexene HYD. These products were analysed by a gas chromatograph with a 20% PEG-1500, 2-m stainless steel column, maintained at 60°C. A carrier gas (N_2) flow of 20 cm^3 min^{-1} was maintained and a Flame Ionisation Detector (FID) was used in both cases.

RESULTS AND DISCUSSION

X-ray Diffraction

MoS_2/γ-Al_2O_3 catalysts with varying Mo loading have been examined by X-ray diffraction technique. The X-ray diffractograms of the samples are shown in Fig. 1. It can be seen from the diffractograms that only γ-Al_2O_3 lines are observable (at d = 1.977, 1.395, 2.39) up to 8 wt% Mo. In the range 10–15 wt% Mo loading, however, lines attributable to crystalline MoS_2 are observed (d = 6.16, 1.83). The absence of any lines due to MoS_2 in catalysts having Mo loading in the range 2–8 wt% indicates that molybdenum sulfide is well dispersed and may be in the form of a monolayer. From this observation, it can be said that the interaction of MoO_3 and MoS_2 with the support are similar in this composition range. The appearance of crystalline MoS_2 beyond the 8 wt% level as observed in these PFHS catalysts indicates that MoS_2 interaction beyond 8 wt% is weak with the γ-Al_2O_3 support.

Surface Area

The BET surface areas of the fresh catalysts and the ones preheated in vacuum at 400°C for 2 h and also the catalysts reduced in flowing hydrogen at 400°C for 2 h are shown in Table 1. The fresh catalysts are the ones in which the MoS_2 is precipitated

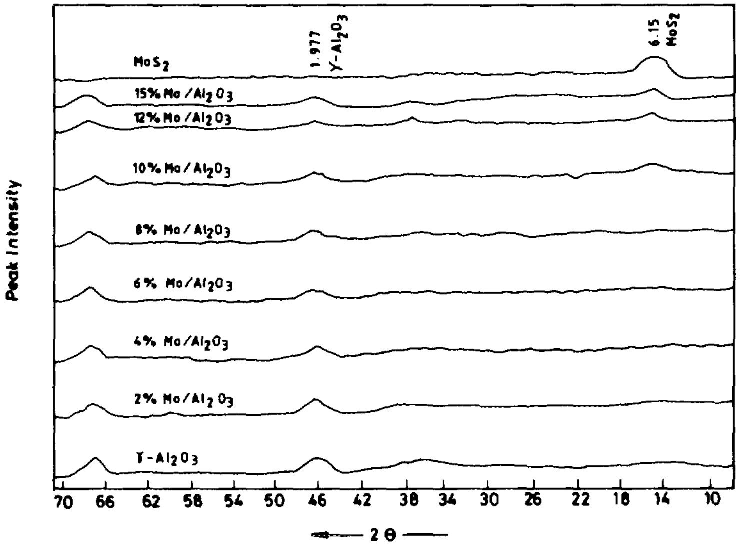

FIG. 1. X-ray diffractograms of MoS_2, MoS_2/γ-Al_2O_3, and γ-Al_2O_3 samples.

on the support in liquid medium by the PFHS method and then dried at 110°C in an air oven. It can be seen that the BET surface areas of all the catalysts decrease with the increase of Mo loading. The surface areas of fresh catalysts are low compared to ones that are preheated or reduced at 400°C. There is essentially no difference in the surface areas of preheated and reduced catalysts. The low surface areas of fresh catalysts may be attributed to the blockage of pores by free sulfur, thioacetamide, etc. During heat treatment or reduction it appears that most of the blocking material is removed. The BET surface areas are very useful in understanding whether there is a monolayer formation of active component on the support. In the case of monolayer formation, addition of Mo to a fixed weight of γ-Al_2O_3 results in constant surface area

TABLE 1

Surface Areas and LTOC Data of MoS_2/γ-Al_2O_3 Catalysts

Mo loading (wt%)	BET surface areas (m^2 g^{-1})			O_2 uptake (μmol g^{-1})		% Dispersion[a]	EMSA[b] (m^2 g^{-1})	% Surface coverage[c]
	Fresh	Preheated	Reduced	Preheated	Reduced			
2	193	214	216	5.3	14.0	13.43	9.5	4.4
4	180	206	208	8.5	24.8	11.90	16.8	8.1
6	176	203	206	12.0	36.0	11.51	24.4	11.8
8	170	200	200	15.0	47.0	11.27	31.8	15.9
10	167	200	196	12.2	42.0	8.06	28.5	14.5
12	165	190	191	10.0	38.0	6.08	25.7	13.5
15	162	185	187	4.5	30.0	3.84	20.3	10.9

[a] Calculated as O/Mo × 100.

[b] Calculated using a factor 0.6774 × O_2 uptake.

[c] Calculated as EMSA/BET surface area of reduced catalyst × 100.

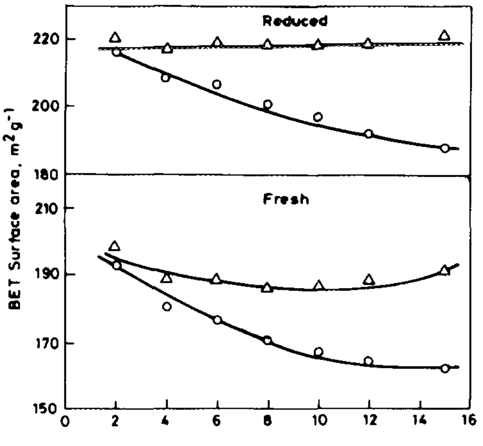

FIG. 2. Variation of BET surface area as a function of molybdenum loading: (△) surface area per gram of support and (○) surface area per gram of catalyst.

per gram of support but decreased surface area per gram of catalyst. An attempt is made in this investigation to see if these criteria are applicable to the catalysts prepared by the PFHS method also. Figure 2 depicts the variation of surface area per gram of support as well as per gram of catalyst as a function of Mo loading, both in the case of fresh as well as reduced catalysts. In the case of fresh catalysts the surface area per gram of support is not constant, which is likely due to blocking of the pores by free sulfur. In the case of reduced catalysts the surface area per gram of support is invariant with loading. The surface areas per gram of catalyst decrease with loading. From these results, it can be said that molybdenum sulfide is distributed on the support surface as monolayer. No change in specific surface area of the catalysts expressed per gram of the support is observed even beyond the full monolayer coverage. Remembering that bulk MoS_2 phase is formed in this region (from XRD), it appears that these crystallites cover only a negligible surface area of alumina. It is also indicated from O_2 chemisorption that they grow on top of the monolayer phase MoS_2 crystallites preferentially growing mostly along the plane perpendicular to the alumina surface. This is quite reasonable because the crystallites are formed in the first place due to lack of interaction between alumina and the molybdenum sulfide phase.

Electron Spin Resonance Spectroscopy

ESR studies are quite fruitful in understanding the changes occuring in the sulfide upon reduction in unpromoted as well as promoted Mo/Al_2O_3 catalysts (*17–20*). In this investigation, an examination of fresh catalysts and catalysts reduced at 400°C for 2 h is made. In addition, pure molybdenum sulfide catalysts prepared by PFHS are also examined along with their reduced counterparts and the features characterised by g factors, g_1, g_2, and g_3 are shown in Table 2. The g values $(h\nu)/\beta H$ of the reduced catalysts and fresh catalysts are also shown in the same table and spectra of unsupported MoS_2 are shown in Fig. 3 (inset). The g_{av} value of the feature identified as g_1 is 2.015; this agrees with values assigned to MoS_3 (*21*). The g_2 value can be ascribed to $g_\perp$ of Mo^{5+} in sulfur environment whose $g_\parallel$ appears as a kink over the feature that gave g_1 values. The g_3 value may be assigned to Mo^{5+} in oxygen environment, which might have been due to oxidation of MoS_2 by air. The spectrum of reduced MoS_2 shows only

TABLE 2

ESR Parameters of Fresh and Reduced $MoS_2/\gamma\text{-}Al_2O_3$ Catalysts

Mo loading (wt%)	Fresh		Reduced	
	g_1	g_2	g_1	g_2
2	2.010	1.965	2.018	1.922
4	2.010	1.964	2.018	1.922
6	2.010	1.967	2.020	1.923
8	2.010	1.967	2.019	1.923
10	2.015	1.964	2.019	1.922
12	2.014	1.965	2.019	1.920
15	2.012	1.965	2.019	1.924

Note. Pure MoS_2: g_1 = 2.015; g_2 = 1.972, 2.017; g_3 = 1.927.

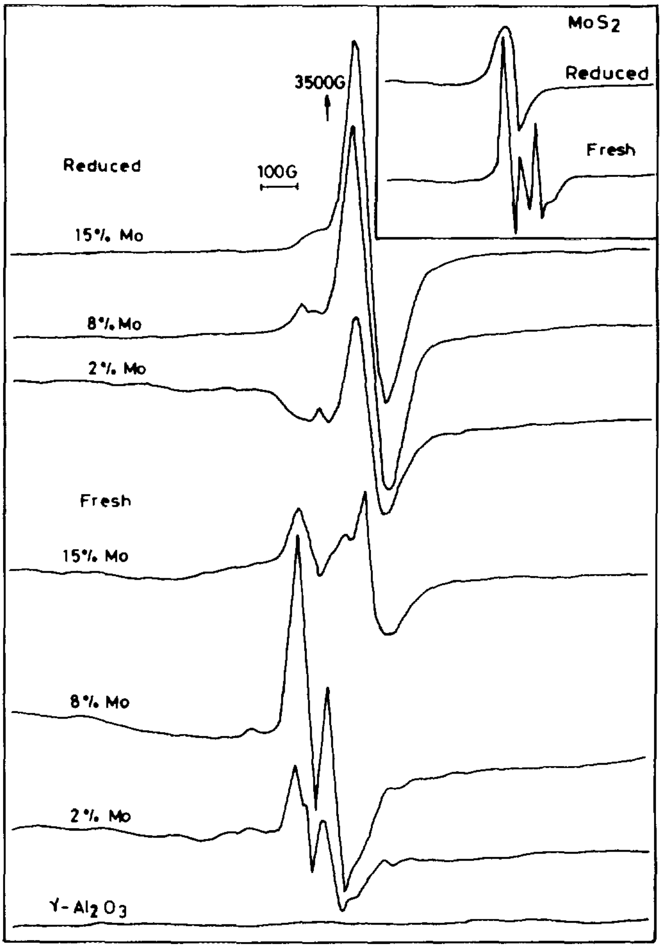

FIG. 3. ESR spectra of reduced and fresh MoS_2/γ-Al_2O_3 catalysts.

one single line with *g* value of 1.986. The value is in agreement with the Mo^{5+} in sulfur environment.

Some selected ESR spectra of the γ-Al_2O_3 supported MoS_2 fresh catalysts and the ones reduced at 400°C for 2 h are shown in Fig. 3. It can be seen that the same features as observed in unsupported MoS_2 are also observed in supported catalysts. After reduction, however, all the spectra contain one main peak whose *g* value is around 1.93. Based on the assignment made by others (*17, 18, 22*), this line can be assigned to Mo^{5+} containing majority of ligands as oxygen. This particular feature is only found in the supported catalysts, and since the samples are not exposed to oxygen at any stage, the oxygen environment present might be due to interaction with the hydroxyl groups of γ-Al_2O_3.

The intensity of the two peaks in fresh and reduced catalysts characterised by a *g* value of 1.923 is plotted as a function of molybdenum loading in Fig. 4. It passes through a maximum at around 8 wt% Mo, where the activities and oxygen chemisorption plots also showed a maximum, indicating that Mo species can interact with the support hydroxyl groups of γ-Al_2O_3 up to around 8 wt% and that beyond that molyb-

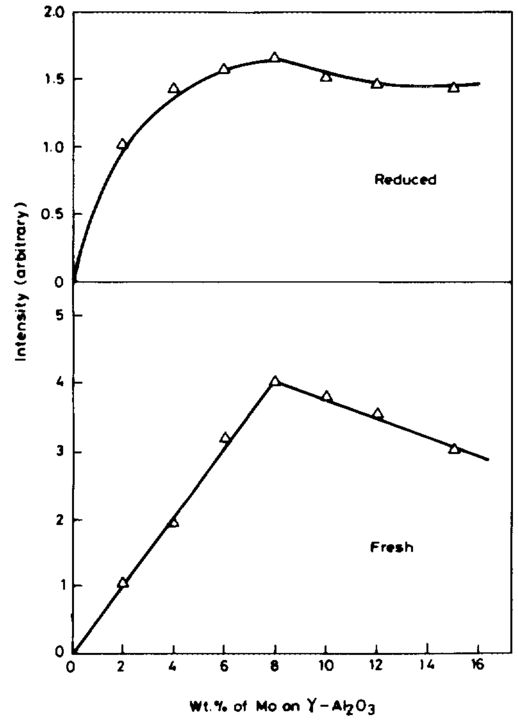

FIG. 4. Variation of ESR signal intensity with Mo loading.

denum is getting reduced to valencies lower than Mo^{5+}. This behaviour is understandable, and it is known that support stabilises the Mo^{5+} whereas in the absence of support interaction, molybdenum species gets reduced to lower valency states which are not detectable by ESR measurement.

Effect of Molybdenum Loading on Oxygen Chemisorption

The molybdenum loading was varied from 2 to 15 wt% on the γ-Al_2O_3 support. The effect of variation of Mo loading on O_2 uptake at −78°C is shown in Fig. 5 for the catalysts which are subjected to two types of pretreatment. In the first case the temperature of catalyst samples was raised to 400°C at a heating rate of 8°C min^{-1} and the catalysts were evacuated at the same temperature for 2 h at 10^{-6} Torr in order to clean the catalysts' surface. The results were published earlier (*12*). In the second case the samples were reduced at 400°C in a flow of hydrogen (40 cm^3 min^{-1}) for 2 h and then evacuated at the same temperature for 1 h at 10^{-6} Torr. It can be seen from Fig. 5 that oxygen chemisorption increases linearly with the Mo loading up to 8 wt% and then decreases above this Mo level in both the preheated and reduced catalysts. Numerous investigators (*23–25*) have correlated the oxygen chemisorption to the various functionalities like HDS, HYD, HDO,

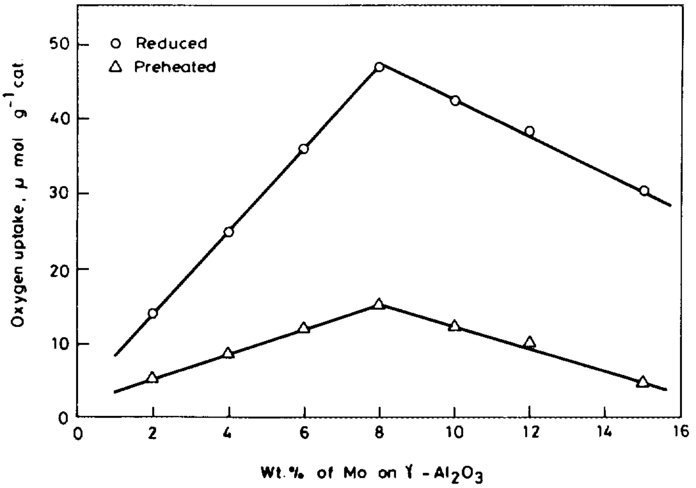

FIG. 5. Oxygen uptake at −78°C as a function of Mo loading on γ-Al_2O_3.

etc., of the active phase of the catalyst. The O_2 uptake exhibited a linear relationship with each functionality. It is generally believed that the coordinatively unsaturated sites (CUS) or vacancies created by the removal of sulfur during reduction treatment are responsible for O_2 uptake and the different functionalities of the catalysts. From Fig. 5, the monotonic decrease of oxygen chemisorption (beyond 8 wt% Mo) must be due to the formation of large MoS_2 crystallites with increasing Mo loading on alumina surface. The O_2 uptake values of the reduced catalysts are much higher (about three times) than those of the preheated catalysts up to the monolayer loading (8 wt%). Above this the reduced catalysts adsorb oxygen three to six times more than the preheated catalysts (Fig. 5 and Table 1). It is obvious that the MoS_2 species of the active phase get reduced to a greater extent in hydrogen and the number of active sites or anion vacancies created are higher than those created by removal of sulfur under vacuum at 400°C.

Variation of O/Mo with Molybdenum Loading

The dispersion of the active phase is plotted against Mo loading in Fig. 6, and the values are given in Table 1. The dispersion of MoS_2 varies marginally from 13.3 to 11.4% up to the monolayer level (8 wt%) and decreases sharply beyond this level. The only small change in the dispersion of MoS_2 up to 8 wt% may be attributed to the pronounced metal support interaction. The O/Mo values obtained in PFHS method are comparable with those obtained by others. A comparison can be made between the dispersion characteristics of the present catalysts and those of conventional catalysts studied by Nag (*26*). The LTOC on the present catalysts has increased with Mo loading up to 8 wt% above which it has decreased, in contrast to LTOC on conventional catalysts on which it has increased up to 8 wt% Mo above which it has levelled off. The dispersion of active phase in the conventional catalysts (*26*) has decreased continuously with Mo loading, while in present catalysts the dispersion decrease is less sharp up to monolayer level (8 wt% Mo) above which it has decreased abruptly. The difference may be attributed to the basic difference in the method of preparation of the catalysts. However, it may be noted that for the same metal loading range, the PFHS catalysts have slightly higher O/Mo values than the corresponding conventional catalysts. This coupled with oxygen uptakes obtained on the samples prepared by PFHS method suggests that molybdenum is better dispersed in these catalysts. In the present catalysts the surface metal ion would naturally have the maximum sulfur coordination, since the molybdenum sulfide is precipitated by the sulfidation of Mo ions by HS^- species generated *in situ* in solution during catalyst preparation. The CUS on the PFHS catalysts are created by the reduction of a sulfide phase supported on γ-Al_2O_3, while they are created by simultaneous reduction and sulfidation of an oxidic phase on γ-Al_2O_3 surface in conventional catalysts. It is supposed that the surface state of the oxide precursor in conventional catalysts remains essentially intact even after sulfidation (*26*). It may be assumed that in the PFHS catalysts also the surface phase configuration does not change during

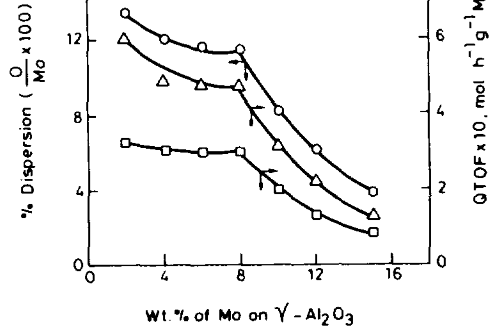

FIG. 6. Effect of Mo loading on QTOF and dispersion.

reduction and the active sites are created by the removal of sulfur atoms, and the sites are of the same type created on conventional catalysts (*26–28*).

Equivalent Metal Sulfide Area (EMSA) and Surface Coverage

Equivalent metal sulfide area (EMSA) of the catalyst is the area of the active phase (MoS_2) in the catalyst. The knowledge of this parameter is essential since the HDS activity of a catalyst depends on the extent of the area available. EMSA of a catalyst is calculated by multiplying the ratio of BET surface area to O_2 uptake of pure unsupported MoS_2 (conversion factor) by LTOC values of supported MoS_2 (*29*). In view of divergent values of the conversion factor (*30, 31*), the following methodology for the calculation of the factor is adopted in the present work. A bulk molybdenum sulfide was prepared by the PFHS method; BET surface area and oxygen uptake measurements were made on the sample in the same way as on supported catalysts. The reduced sample with BET surface area of 13 m^2g^{-1} gave an O_2 uptake value of 19.2 μmol g^{-1}. Thus the calculated factor came out to be 0.6774 $m^2/\mu mol\ O_2$, which is slightly higher than the factor (0.5662) given by Fierro *et al.* (*29*).

The surface coverage values calculated from the EMSA values of the PFHS catalysts are given in the last column of Table 1. It is clear that the PFHS catalysts have higher effective areas (20%) of the active MoS_2 phase ranging from 9.5 to 31.8 $m^2\ g^{-1}$ calculated with a factor of 0.6774 $m^2/\mu mol$ O_2 when compared to the values derived using Fierro's (*29*) factor. The surface coverage of the catalysts has changed from 4.5 to 15.9%. The EMSA value of 31.8 $m^2\ g^{-1}$ is high, and 15.9% of the surface is covered by MoS_2 at Mo loading corresponding to a monolayer (8 wt%). An explanation for a low coverage of 15.9% could be that the monolayer exists as patches or aggregates of MoS_2 attached to the support by strong chemical bonds. This chemical interaction is possible on a small fraction of the total surface of the support having reactive OH groups. The saturation of a monolayer occurs when this active surface is completely covered by MoS_2. Further addition of the active component leads to multilayer growth and consequent formation of bulky MoS_2 aggregates, while a large fraction of carrier surface still remains uncovered (*32, 33*). The obvious reason for the increase of EMSA with Mo loading is the spreading of the active phase on the γ-Al_2O_3 surface up to the formation of monolayer. Above this molybdenum loading the increase in the MoS_2 aggregate size and the increase in thickness of the MoS_2 layer on the pore walls bring about a drastic decrease in EMSA of the active phase with increasing Mo loading. This is also in agreement with X-ray diffraction results which indicate the growth of MoS_2 beyond monolayer region. The EMSA and surface coverage values of the PFHS catalysts can be compared with the corresponding values of the conventional catalysts (*34*). The EMSA values of the conventional catalysts have changed from 6.1 to 18.9 $m^2\ g^{-1}$ and the corresponding surface coverages changed from 3.35 to 12% only while the surface area of the support used was the same. The EMSA and surface coverage values of the present catalysts are higher than those of the conventional catalysts by about 30 to 40% at corresponding Mo loading on the support having essentially the same surface area. The higher active phase areas of PFHS catalysts should be attributed to the effectiveness of the PFHS method, in which small MoS_2 particles of uniform size are likely to be formed.

Variation of HDS and HYD Activities with Molybdenum Loading

The thiophene HDS and cyclohexene HYD rates on the MoS_2/γ-Al_2O_3 catalysts are presented in Table 3. It can be seen from the table that both HDS and HYD activities of the catalysts increase linearly up to 8 wt% Mo loading and then decrease at

TABLE 3

Thiophene HDS and Cyclohexene HYD Rates of Mo/γ-Al_2O_3 Catalysts and Their QTOFs

Mo loading (wt%)	HDS rate × 10^3 (mol h^{-1} g^{-1} cat)			HYD rate × 10^3, mol h^{-1} g^{-1} cat		QTOF (at 400°C) mol h^{-1} g^{-1} Mo	
	350°C	400°C		350°C	400°C	HDS	HYD
		Preheated	Reduced				
2	7.5	12.0	12.0	4.0	6.5	0.60	0.33
4	12.1	17.5	19.0	9.0	12.5	0.48	0.31
6	17.5	26.0	27.5	12.0	17.5	0.46	0.29
8	22.0	33.0	36.0	15.5	23.8	0.45	0.30
10	18.4	27.0	32.5	14.2	20.0	0.33	0.20
12	16.1	22.0	29.0	13.0	16.0	0.24	0.15
15	8.0	10.0	22.5	10.0	12.5	0.15	0.08

higher Mo loading just in the same fashion as LTOC or EMSA with the loading. This result is expected since the activity of the catalyst mainly depends on its EMSA. It is also evident that the HYD rates are lower than the HDS rates, unlike those found in conventional heptamolybdate impregnated preparations. There is not much difference between the HDS activities of the preheated and reduced catalysts at 400°C at lower loadings and the difference increases with Mo loading. The reason for the difference in the activities lies in the difference in pretreatment conditions of the catalysts which results in an increase of anion vacancies in the case of reduced catalysts. An increase in reaction temperature from 350 to 400°C increases the HDS and HYD activities of the catalysts.

A comparison of the HDS activities of the PFHS catalysts with those of the conventional catalysts would reveal interesting characteristics. Though the PFHS catalysts have EMSA which are higher by about 30% than those of conventional catalysts, they have exhibited HDS activities which are 10 times higher than the activities of the catalysts studied by Nag and co-workers *(25)* with the corresponding loadings on the same support. The exceptionally high activities of the PFHS catalysts may be attributed to the new method of preparation of these catalysts. Precipitation of MoS_2 *in situ* would have created small crystallites with a greater number of CUS similar to edges and corners which are potential active sites for HDS reaction. During the presulfiding process, the conventional oxidic precursors might have not been completely converted into sulfide, a part of the oxide layers in the bulk remaining intact. The PFHS catalysts contain the Mo–S–Mo bonds throughout the bulk and on the top layer of the active phase. The sulfur atom being a greater electron donor than an oxygen atom, it would have increased electron density on the molybdenum ions on the surface of the catalysts created during reduction. This higher electron density might have resulted in the enhanced electron donation to the thiophene molecule causing greater C–S bond rupture. This would result in increasing the activity per site for the HDS reaction. The fact that oxygen chemisorption is increased by only 40% while the activity increased about 10 times when compared to conventional preparation shows in addition to increased dispersion that the activity per site has also increased. The activity of the catalyst can also be expressed as quasi-turnover frequency (QTOF). The QTOF values of the

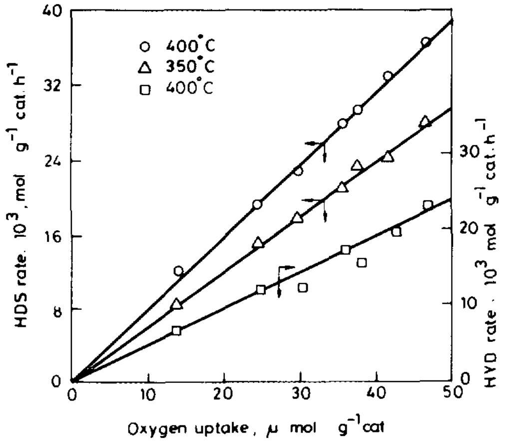

FIG. 7. Correlation between O_2 uptake and HDS and HYD activity on $MoS_2/\gamma\text{-}Al_2O_3$ (reduced catalysts).

present PFHS catalysts for HDS and HYD reactions are presented in Table 3 and are plotted against Mo loading in Fig. 6. It is not surprising that the shapes of the three plots have a rather noticeable resemblance, indicating that the trend of change of the activities of the two reactions and the dispersion of the active phase is the same with the Mo loading.

Correlation of Oxygen Uptakes with HDS or HYD Rates

The oxygen uptakes measured on catalysts reduced at 400°C are plotted as a function of HDS and HYD rates in Fig. 7. It can be seen in all cases that a linear relationship passing through origin is obtained. The linear correlation suggests that HDS and HYD activities are proportional to the oxygen uptakes obtained at −78°C. This relationship is true for HDS activity obtained at 350°C, as well as 400°C. At these two temperatures essentially the same relationship is obtained except that the slopes are different, indicating that the activity per site is increased at higher temperature. The intrinsic activities or turnover frequencies (TOF) of the HDS and HYD reactions are shown in Fig. 8. The intrinsic activities for HDS are higher and after an initial decrease remain invariant with molybdenum loading. HYD intrinsic activities are lower than those of HDS. These activities increase with loading and pass through a maximum at about 8 wt% Mo and then decrease up to 12 wt% Mo and thereafter remain constant. An examination of TOF variation with

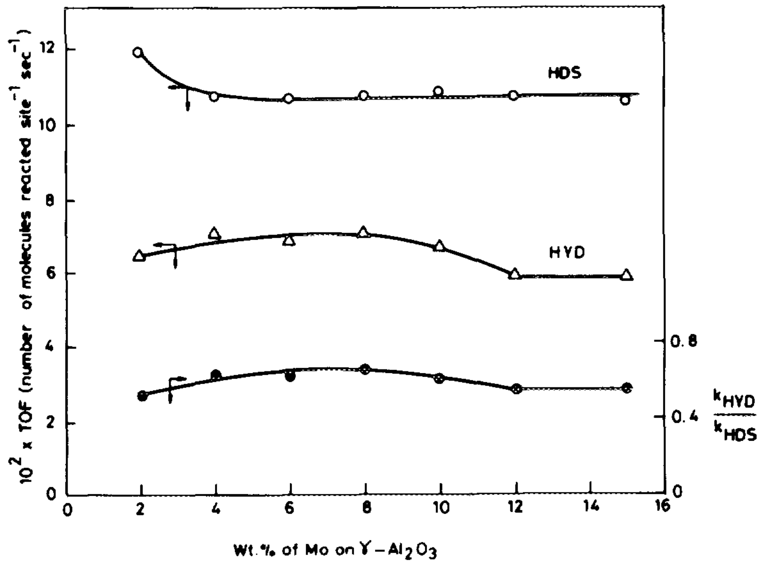

FIG. 8. Variation of selectivity and intrinsic activity of HDS and HYD with Mo loading.

loading of the two functionalities indicates these variations to be distinctly different. This independent variation suggests that the HDS and HYD may be taking place on different sites. In the same plot variation of k_{HYD}/k_{HDS} is shown as a function of Mo loading. It can be seen that the selectivity for HYD varies with the loading passing through a maximum (at 8 wt% Mo) and reaches a value comparable with that of lower loading. PFHS catalysts have higher HDS to HYD ratio than the conventional catalysts. The k_{HYD}/k_{HDS} for pure MoS_2 is 0.79, whereas for γ-Al_2O_3 supported catalyst it is 0.6. In pure MoS_2 the HYD is less than HDS by about 24%, whereas in supported catalyst it is less by about 40%. Therefore, it appears that the decrease of relative selectivity is caused by a disproportionate increase of HDS. The effect of the support is to increase HDS activity relative to HYD.

Effect of Cobalt and Nickel on the Activity of MoS_2/γ-Al_2O_3 Catalysts

The effect of promoters Co or Ni added by the PFHS method on MoS_2/γ-Al_2O_3 prepared by the same method is studied with the help of BET surface area, O_2 uptake, and the HDS and HYD activities. The catalyst with 8 wt% Mo/Al_2O_3 is selected for this purpose as MoS_2 forms monolayer at this loading. The nickel and cobalt are varied between 0 and 5 wt%. Various properties of these catalysts as a function of Co and Ni loading on 8-wt% Mo are given in Table 4a. The properties of 8-wt% Mo/γ-Al_2O_3 conventional catalysts (prepared by impregnation method) with the same promoter loadings which are studied under the same conditions are given in Table 4b. The properties of few commercial catalysts with Mo loading from 8 to 10 wt% and with similar promotor concentrations are given in Table 4c for the purpose of comparison. Prior to the reaction the conventional catalysts and commercial catalysts are sulfided for 2 h at 400°C.

As can be seen clearly, the BET surface areas of both PFHS and conventional catalysts decrease considerably on the deposition of promotors. This decrease in BET surface areas is expected, as the promotors are deposited as sulfides after impregnating

TABLE 4

BET Surface Areas, Oxygen Uptake, Thiophene HDS, and Cyclohexene HYD Activities of Various Catalysts

Catalyst	Composition (wt%)			BET surface area ($m^2\ g^{-1}$)	O_2 uptake ($\mu mol\ g^{-1}$ cat)	EMSA ($m^2\ g^{-1}$)	HDS rate × 10^3 ($mol\ h^{-1}\ g^{-1}$)	HYD rate × 10^3 ($mol\ h^{-1}\ g^{-1}$)
	Mo	Co	Ni					
a. Prepared by precipitation from homogeneous solution method								
Mo/Al_2O_3	8	—	—	200	47.0	31.8	33.0	23.8
Co-Mo/Al_2O_3	8	3	—	184	50.0	33.9	37.3	20.0
Co-Mo/Al_2O_3	8	5	—	182	58.0	39.3	46.5	28.0
Ni-Mo/Al_2O_3	8	—	3	187	51.2	34.7	34.1	17.8
Ni-Mo/Al_2O_3	8	—	5	187	56.2	38.1	43.4	23.6
b. Prepared by impregnation method								
Mo/Al_2O_3	8	—	—	178	32.3	21.9	10.9	26.3
Co-Mo/Al_2O_3	8	3	—	164	35.2	23.8	26.4	29.4
Co-Mo/Al_2O_3	8	5	—	161	37.2	25.2	28.6	23.0
Ni-Mo/Al_2O_3	8	—	3	169	39.0	26.4	22.7	33.4
Ni-Mo/Al_2O_3	8	—	5	158	42.0	28.5	24.2	38.5
c. *Commercial catalysts*								
Harshaw (HT-400)	9.86	2.52	—	200	35.7	24.2	25.7	43.5
Ketjenfine-124	7.73	3.26	—	267	33.5	22.7	24.7	44.1
Harshaw (HT-500)	9.93	—	2.51	210	36.2	24.5	21.3	47.0
Ketjenfine-802	7.67	—	4.09	273	47.0	31.8	22.3	35.3

the dry MoS_2/γ-Al_2O_3 catalysts in their respective aqueous nitrate solutions. The oxygen uptakes on catalysts reduced at 400°C for 2 h have increased by 10–12 μmol g^{-1}, indicating an approximate increase of 10–30% in EMSA when compared to unpromoted catalysts. Roughly the same increase in O_2 uptakes and hence the EMSA are observed in the case of conventional catalysts prepared from oxidic precursors. The O_2 uptakes of commercial catalysts also (Table 4c) fall in the same range as those of conventional catalysts. Some small variation on the commercial catalysts is expected due to composition changes, and differences in the support and the preparation method.

It is clear that the HDS activities of the PFHS catalysts are higher than their HYD activities (Table 4a), while the conventional Co–Mo/γ-Al_2O_3 catalysts (Table 4b) exhibit almost equal HDS and HYD activities. The HYD activities of conventional Ni–Mo/γ-Al_2O_3 catalysts are also higher than their HDS activities. The HYD activities of the commercial catalysts (Table 4c) are much higher than their HDS activities. The HDS rates of the PFHS catalysts and also conventional catalysts steadily increase with increase in promotor concentration. The HDS rate of 8-wt% Mo/γ-Al_2O_3 catalyst prepared by the PFHS method has increased from 33×10^{-3} to 46.5×10^{-3} mol h^{-1} g^{-1} when cobalt concentration is increased from 0 to 5 wt%, while for Ni-promoted catalysts the rate has increased up to 43.4×10^{-3} mol h^{-1} g^{-1} catalyst. The conventional catalysts have exhibited much lower HDS activities than the PFHS catalysts.

Structure of Mo/γ-Al₂O₃ and Co(Ni)–Mo/γ-Al₂O₃ Catalysts

The complex physico-chemical behaviour of sulfided Co(Ni)–Mo/γ-Al_2O_3 catalysts under actual reaction conditions have contributed greatly to the difficulty in understanding their structure vis-à-vis catalytic properties. Several structural models in which the role and chemical state of cobalt or nickel promotors in the sulfided catalysts have been proposed but none of these models was found to be adequate (*35–37*). Topsøe *et al.* (*4*) and Wivel *et al.* (*38*) proposed a Co–Mo–S model for the active phase in Co–Mo catalysts, on the basis of combined Mössbauer emission spectroscopy (MES) and thiophene HDS activity. This phase has been observed for both supported and unsupported catalysts (*38–40*). The Co–Mo–S phase may have a monolayer dispersion (*41*). According to this model, the dispersed phase of MoS_2 crystallites comprised of one slab or "sandwich." The edges and corners of these patches contain coordinatively unsaturated (CUS) molybdenum ions which have been identified as the active sites for hydroprocessing reactions. Co–Mo–S structures are similar to MoS_2 structures (*42*) with Co atoms located at edges of MoS_2 slabs. The Co–Mo–S type phases are also found to be present in catalysts such as Ni–Mo (Ni–Mo–S) (*43*). Candia *et al.* (*44, 45*) proposed the existence of a low-temperature (type I) and a high-temperature (type II) form of Co–Mo–S. They suggested that high-temperature sulfiding partially eliminates Mo–O–Al linkages, transforming the low-temperature type I to the more active high-temperature type II Co–Mo–S phase. Moreover, it has been found that type II phase has a higher HDS but a lower HYD performance than type I phase.

To understand if a free Co phase exists in HDS catalysts and contributes significantly to both activity and O_2 uptake of the catalysts, a few experiments were designed. Such experiments on a reduced 5-wt% Co/γ-Al_2O_3 catalyst (PFHS) indicated that free Co phase adsorbs an insignificantly low quantity of oxygen. Thiophene HDS activity study of this catalyst showed very low activity, which is very very small when compared to the high activity of Co–Mo–S catalysts.

In view of the fact that the PFHS catalysts exhibited higher HDS and lower HYD activities, it can be inferred that type II Co(Ni)–Mo–S phase may exist predominantly.

CONCLUSIONS

The precipitation from homogeneous solution (PFHS) technique can be used successfully to prepare supported and promoted hydroprocessing catalysts. LTOC can precisely determine the Mo level at which the formation of the monolayer is completed on the catalysts prepared by this method. These catalysts have the following characteristics:

1. The molybdenum is better dispersed.
2. The CUS are generated by the reduction of the sulfide phase.
3. The formation of monolayer is attained at 8 wt% Mo on γ-Al_2O_3.
4. The EMSA and surface coverage values are higher than those of the conventional catalysts by about 30 to 40%.
5. The PFHS catalysts are much more active than the catalysts prepared by the conventional impregnation technique and commercial catalysts.
6. The exceptionally high HDS activities of these catalysts may be attributed to the new method of preparation of these catalysts.

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REFERENCES

1. Massoth, F. E., *Adv. Catal.* **27,** 265 (1978).
2. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," Chap. 5, McGraw–Hill, New York, 1979.
3. Nag, N. K., *J. Phys. Chem.* **91,** 2324 (1987).
4. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Morup, S., *J. Catal.* **68,** 433 (1981).
5. Massoth, F. E., and Chung, K. S., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 629. Elsevier, New York, 1981.
6. Hargreaves, A. E., and Ross, J. R. H., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.) Vol. 2, p. 937. The Chem. Soc., London, 1977.
7. Sivaraj, Ch., Prabhakara Reddy, B., Rama Rao, B., and Kanta Rao, P., *Appl. Catal.* **24,** 25 (1986).
8. Sivaraj, Ch., and Kanta Rao, P., *Appl. Catal.* **45,** 103 (1988).
9. Sivaraj, Ch., Mahipal Reddy, B., and Kanta Rao, P., *Appl. Catal.* **45,** L 11 (1988).
10. Schaper, H., Doesburg, E. B. M., Quartel, J. M. C., and Van Reijen, L. L., *in* "Preparation of Catalysts" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), Vol. 3, p. 301. Elsevier, Amsterdam, 1983.
11. van Dillen, J. A., Geus, J. W., Hermans, L. A. M., vander Meijden, J., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 2, p. 677. The Chemical Society, London, 1977.
12. Prasad Vemulapalli., Chary Komondur., Somasekhara Rao Kaza., and Kanta Rao Panja., *J. Chem. Soc. Chem. Commun.,* 1746 (1989).
13. Chary, K. V. R., Kanta Rao, P., Prasad, V. V. D. N., and Somasekhara Rao, K., *J. Mol. Catal.* **63,** L 21 (1990).
14. Somasekhara Rao, K., Prasad, V. V. D. N., Chary, K. V. R., and Kanta Rao, P., *Stud. Surf. Sci. Catal.* **63,** 611 (1991).
15. Parekh, B. S., and Weller, S. W., *J. Catal.* **47,** 100 (1977).
16. Froment, G. F., and Bischoff, K. B., "Chemical Reactor Analysis and Design," Wiley, New York, 1979.
17. Derouane, E. G., Pedersen, E., Clausen, B. S., Gabelica, Z., Candia, R., and Topsøe, H., *J. Catal.* **99,** 253 (1986).
18. Konings, A. J. A., van Dooren, A. M., Koningsberger, D. C., deBeer, V. H. J., Farragher, A. L., and Schuit, G. C. A., *J. Catal.* **54,** 1 (1978).
19. Thakur, Deepak, S., and Delmon, B., *J. Catal.* **91,** 308 (1985).
20. Kim, Seo Il., and Seong, Ihl Woo., *Appl. Catal.* **74,** 109 (1991).
21. Johnston, D. C., Jacobson, A. J., Silbernagel, B. G., Frysinger, S. P., Rich, S. M., and Gebhard, L. A., *J. Catal.* **89,** 244 (1984).
22. Bhaduri, M., Hernandez, J., and Thomas, W. J., *Appl. Catal.* **8,** 85 (1983).
23. Nag, N. K., Rao, K. S. P., Chary, K. V. R., Rama Rao, B., and Subrahmanyam, V. S., *Appl. Catal.* **41,** 165 (1988).
24. Zmierczak, W., Murali Dhar, G., and Massoth, F. E., *J. Catal.* **77,** 432 (1982).
25. Reddy, B. M., Chary, K. V. R., Subrahmanyam, V. S., and Nag, N. K., *J. Chem. Soc. Faraday Trans. 1* **81,** 1655 (1985).
26. Nag, N. K., *J. Catal.* **92,** 432 (1985).

27. Okamoto, Y., Tomioka, H., Katoh, Y., Imanaka, T., and Teranishi, S., *J. Phys. Chem.* **84,** 1833 (1980).
28. Okamoto, Y., Katoh, Y., Mori, Y., Imanaka, T., and Teranishi, S., *J. Catal.* **70,** 445 (1981).
29. Fierro, J. L. G., Tejuca, L. G., Agudo, A. L., and Weller, S. W., *J. Catal.* **89,** 111 (1984).
30. Tauster, S. J., Picararo, T. A., and Chianelli, R. R., *J. Catal.* **63,** 515 (1980).
31. Bodrero, T. A., and Bartholomew, C. H., *J. Catal.* **84,** 145 (1983).
32. Topsøe, H., *in* "Surface Properties and Catalysis by Non-metals" (J. P. Bonnelle, B. Delmon, and E. Derouane, Eds.), p. 329. Reidel, Dordrecht, Amsterdam, 1983.
33. Yermakov Yu, I., Startsev, A. N., Burmistrov, V. A., Shumilo, O. N., and Bulgakov., N. N., *Appl. Catal.* **18,** 33 (1985).
34. Reddy, B. M., Ph.D. Thesis, Osmania University, Hyderabad, India, 1986.
35. Chianelli, R. R., *Catal. Rev. Sci. Eng.* **26,** 361 (1984).
36. Topsøe, H., and Clausen, B. S., *Catal. Rev. Sci. Eng.* **26,** 395 (1984).
37. Delmon, B. *Surf Interface Anal.* **9,** 195 (1986).
38. Wivel, C., Candia, R., Clausen, B. S., Morup, S., and Topsøe, H., *J. Catal.* **68,** 453 (1981).
39. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Morup, S., *Bull. Soc. Chim. Belg.* **90,** 1189 (1981).
40. Candia, R., Clausen, B. S., and Topsøe, H., *J. Catal.* **77,** 564 (1982).
41. Topsøe, N. Y., *J. Catal.* **64,** 235 (1980).
42. Candia, R., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **90,** 1225 (1981).
43. Niemann, W., Clausen, B. S., and Topsøe, H., *Catal. Lett.* **4,** 355 (1990).
44. Candia, R., Topsøe, H., and Clausen, B. S., *in* "Proceedings 9th Iberoamerican Symposium on Catalysis, Lisbon, 16–21 July, 1984," p. 211.
45. Candia, R., Sorensen, O., Villadsen, J., Topsøe, N. Y., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93,** 763 (1984).