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Effect of sintering on the catalytic functionalities of MoS_2/Al_2O_3 catalysts

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Effect of sintering on physico-chemical and catalytic properties of Mo, Co–Mo, Ni–Mo supported on γ-Al_2O_3 is reported. Such effects on hydrodesulfurization (HDS), hydrogenation (HYD) and hydrodeoxygenation (HDO) are investigated as a function of sintering temperature. The results indicated that HDS and HYD have different optimum calcination temperatures and these functionalities originate from different sites. The results are discussed in the light of molybdenum sulfide dispersion, promotional effects and phase transformations of active component, promoters and support.

Keywords: Sintering; hydrotreating catalysts; HDS; HYD; HDO

1. Introduction

Sulfided Mo catalysts supported on γ-Al_2O_3 and promoted by Co and Ni are well established in hydrotreating of petroleum fractions [1–3]. These catalysts are used in industrial reactors for hydrotreating of various petroleum fractions. They are regenerated in oxygen atmosphere at temperatures higher than the reaction temperatures. During operation as well as regenerations the catalysts are likely to be exposed to higher temperature than the usual calcination temperatures. These conditions may result in sintering of the catalysts and irreversible phase transformations. In order to understand the effect of such thermal shocks and also to find out the optimum conditions of preparation for various functionalities, it is necessary to expose the catalysts to such conditions and find out the effect of those treatments on catalytic functionalities. In addition such studies will give information about the origin of these catalytic functionalities.

There have been a number of reports in literature on sintering of supported and promoted molybdenum catalysts [4–9]. Among these catalysts Co–Mo/Al_2O_3 received much attention [4–6,9], while Ni–Mo/Al_2O_3 and Mo/Al_2O_3 figured in a few investigations [6,8]. These studies contributed towards a better understanding of the phase transformations, molybdenum loss, etc. However, only a few investigations considered evaluation of catalytic activity along with sintering and characterization [6]. In most of these studies, commercial catalysts [5,6] were used and activities were evaluated for HDS using real feed stocks [6,10]. The difficulty with the commercial catalysts is that information about their preparation is proprietary in nature and they may contain unspecified components, such as stabilizers and/ or binders, which make the interpretation of the results uncertain. In addition, activity variation while testing with real feed stocks could be due to processes other than sintering, such as metal deposition, carbon formation, etc. It is also not easy in these studies to distinguish the effect of sintering on individual functionalities. In most of the studies only HDS functionality is considered whereas a complete understanding of these catalysts needs information about the hydrogenation function also. Considering these points, a systematic study of Mo/Al_2O_3, Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts, prepared, sintered and sulfided under identical conditions is considered in this investigation. In this communication the emphasis is on catalytic functionalities although relevant characterization results are also reported. The reactions with representative model compounds like thiophene, cyclohexene and furan, conducted under similar conditions as a function of sintering temperatures, form the main aspect of this work.

2. Experimental

The catalysts were prepared by incipient wetting of commercial γ-Al_2O_3 (Harshaw A_1-111-61E) support with a solution of appropriate concentration of ammonium heptamolybdate. The impregnated samples were dried at 120°C for 16 h. The Co and Ni promoted catalysts were prepared from oven dried 8% Mo catalyst using nitrate solutions following an identical procedure to the one used for Mo/Al_2O_3. The catalysts after impregnation, were dried in an oven at 120°C for 16 h and calcined in air at 550°C for 5 h. The catalysts were sintered at 650, 750, 850 and 1050°C, each time taking a fresh sample and heating at that temperature for 5 h. The oxygen chemisorption and catalytic activities were evaluated following procedures reported by us earlier [11,12]. X-ray diffractograms were recorded with a Philips P.W. 1051 diffractometer using Ni filtered Cu K_α radiation.

3. Results and discussion

3.1. SURFACE AREAS

The surface areas of the fresh and sulfided catalysts as a function of the sintering temperature are given in table 1. It can be seen that surface areas, in all the three cases, viz. Mo, Co–Mo, Ni–Mo catalysts supported on γ-Al_2O_3 decrease with an increase in the sintering temperature. It can also be seen that the decrease in surface area is only marginal for Co–Mo and Ni–Mo catalysts upto 650°C within the lim-

Table 1
Effect of calcination temperature on BET SA and oxygen chemisorption on sulfided Mo, Co(Ni)Mo catalysts supported on alumina

Catalyst	Calcination temperature	BET SA ($m^2\ g^{-1}$)		Decrease of surface area (%)	O_2-uptake (mol/g)	O/Mo	EM SA ($m^2\ g^{-1}$)	Crystallite size (Å)
		fresh	sulfided					
8% Mo/ Al_2O_3	550	133	136	–	22.8	0.053	12.5	66.7
	650	113	115	15	33.29	0.079	18.67	44.6
	750	97	99	27	28.99	0.069	16.4	50.7
	850	44	47	66	15.0	0.036	8.49	98.1
	1050	25	26	80	7.0	0.017	3.96	210.4
3 : 8 Co–Mo/ Al_2O_3	550	163	166	–	29.66	0.071	16.80	49.0
	650	158	162	3.3	39.7	0.095	22.47	37.0
	750	128	132	22	30.0	0.072	16.98	49.0
	850	42	45	74	18.86	0.045	10.67	78.1
	1050	28	30	83	10.52	0.025	5.95	140.0
3 : 8 Ni–Mo/ Al_2O_3	550	144	146	–	24.5	0.058	13.7	60.0
	650	137	140	5	29.13	0.07	16.49	50.5
	750	102	104	29	26.06	0.062	14.75	56.5
	850	37	39	74	16.33	0.039	9.24	90.2
	1050	27	26	81	7.99	0.019	4.52	184.4

its of experimental error. At 750°C, the surface area decrease is comparable in the case of Ni–Mo and Mo catalysts. However, at this temperature also, the decrease of surface areas is less in the case of Co–Mo catalysts indicating that the presence of Co helps in preserving the surface areas better than Mo and Ni–Mo catalysts. At higher temperatures there is drastic decrease in surface area suggesting collapse of the γ-Al_2O_3 structure. The surface areas after sulfidation follow trends similar to those of the oxidized catalysts, in the three systems studied, indicating that sulfiding at 400°C for 2 h did not cause any further changes in these catalysts.

3.2. X-RAY DIFFRACTION

X-ray diffraction studies were conducted on Mo, Co–Mo and Ni–Mo catalysts supported on γ-Al_2O_3 in the oxidized as well as the sulfided states. The results indicated that upto 650°C the only phase that could be observed was γ-Al_2O_3 both in the case of oxidized as well as the sulfided catalysts. This result is also in agreement with surface area measurements which indicated only minor changes in surface area. The X-ray diffractograms get increasingly complicated with further increase in sintering temperature. In the case of pure support as well as supported catalysts, the X-ray data indicated minor amounts of δ, θ and α-phases even at 750°C. With an increase in temperature the concentration of these phases was found to increase. In addition to structural changes of γ-Al_2O_3, the active component also undergoes significant changes. At 750°C, there is evidence for formation of $NiAl_2O_4$ and $CoAl_2O_4$ phases in Ni–Mo and Co–Mo catalysts respectively. There were also indications for the presence of $CoMoO_4$ and $NiMoO_4$ phases at this temperature in the above mentioned catalysts. In the case of Mo and Ni–Mo catalysts formation of $Al_2(MoO_4)_3$ is also noted. It is interesting to note that there is no $Al_2(MoO_4)_3$ formation in the case of Co–Mo/Al_2O_3 catalyst. The extent of these phases increased with the increase in temperature of sintering.

3.3. OXYGEN CHEMISORPTION

Oxygen uptakes on sulfided Mo, Co–Mo and Ni–Mo catalysts as a function of sintering temperature are shown in table 1 and also in fig. 1. O/Mo, crystallite size, equivalent molybdenum sulfide areas derived from oxygen chemisorption are also presented in table 1. It can be seen that oxygen uptakes on all these systems increase uptot 650°C and then start decreasing. The oxygen uptakes on Co–Mo catalysts are higher compared to Mo, Ni–Mo catalysts throughout the temperature range studied. In the case of Ni–Mo catalysts at a sintering temperature of 550°C the oxygen uptake is marginally higher compared to Mo catalysts but at 650 and 750°C Mo catalysts exhibit higher oxygen uptakes while Ni–Mo catalysts show marginally higher uptakes at higher temperatures. The O/Mo, which is a measure

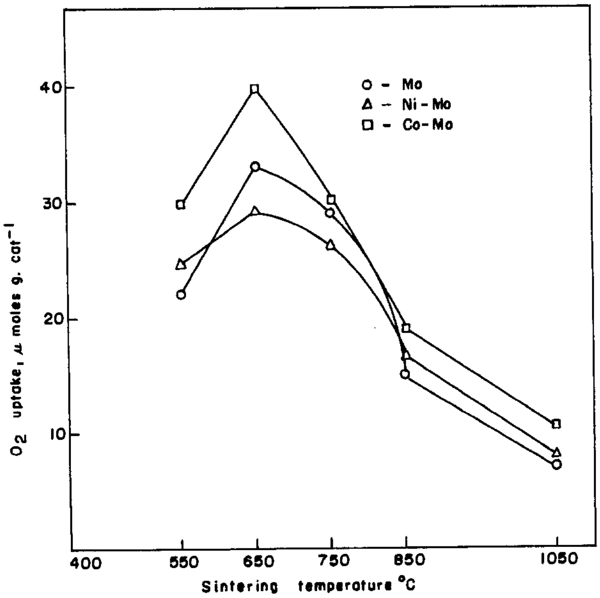

Fig. 1. Variation of O_2 uptake as a function of sintering temperature.

of dispersion, the crystallite size which is inversely related to dispersion indicates that the dispersion of molybdenum sulfide passes through a maximum around 650°C. It is well documented that oxygen uptakes measure general state of dispersion of the molybdenum sulfide phase and, therefore, the oxygen uptake variation can be attributed to the changes in dispersion of MoS_2 phase [13]. The crystallite size and O / Mo data support this conclusion.

3.4. CATALYTIC FUNCTIONALITIES

HDS, HYD and HDO rates as a function of sintering temperature are shown in fig. 2. It can be noticed that HDS activity increases with the increase of sintering temperature upto 650°C on all the three systems considered. However, the increase is highest in the case of Co–Mo catalysts followed by Mo and Ni–Mo catalysts. The increase in the case of Ni–Mo catalysts was only marginal. The activity of Co–Mo catalysts was high and stays so throughout the temperature range studied. The Ni–Mo catalysts showed lower activity than Mo catalysts at 650°C and comparable activity in the temperature range of 750–850°C and higher activity at 1050°C. These trends are in general in agreement with oxygen uptake variation. It is also informative to consider the changes in promotional effect as a function of

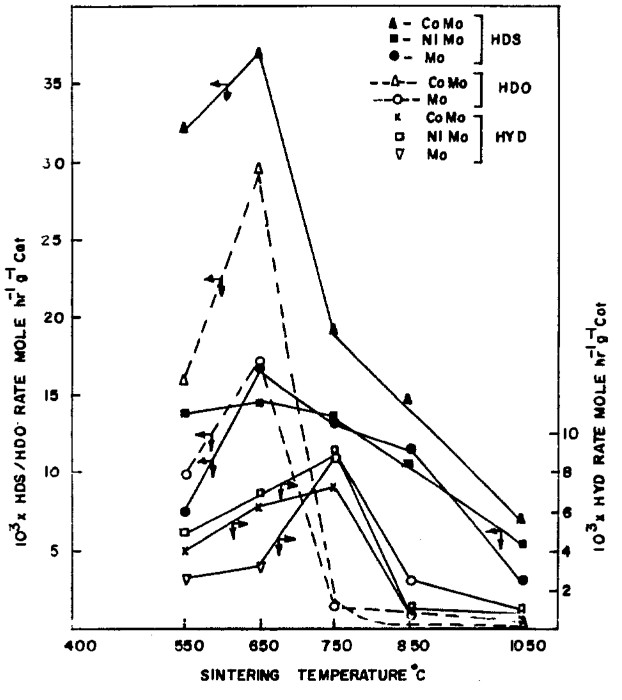

Fig. 2. Variation of catalytic functionalities with sintering temperature.

sintering temperature. In the Co–Mo catalysts the HDS is promoted 4.2 times at 550°C. At 650°C, the promotional effect is only 2.2 times. These results indicate two things, firstly the activity increase is not only due to increase in surface area of MoS_2 phase but also due to considerable promotional effect due to redistribution of Co^{2+} ions. Mobility of Co^{2+}, Ni^{2+} ions in this temperature range was inferred from IR spectra of adsorbed NO molecules by Laine et al. [7]. In the case of Ni–Mo catalysts the promotional effect is about 1.8 times at 550°C. At 650°C the HDS activity is lower than even Mo catalysts. This indicates that there is loss of promotional effect as well as molybdenum sulfide area. This can be due to migration of Ni^{2+} ions and also formation of $Al_2(MoO_4)_3$. It has been reported by several authors [6,14] that Ni^{2+} ions migrate into γ-Al_2O_3 at lower temperatures than Co^{2+} ions. There is also evidence from X-ray data for $NiAl_2O_4$ and $Al_2(MoO_4)_3$ formation at 750°C. These phases may be present at lower temperature also but as small crystallites that are outside the X-ray detection limits. Therefore, Co as promoter is clearly superior in HDS compared to Ni in the range of sintering temperatures considered. The reasons for variation of the catalytic activity and the difference in behaviour of the two promoters will be further considered later.

The HDO activity (fig. 2) increases sharply upto 650°C on both Co–Mo and Mo systems. Co–Mo catalysts show higher activity than Mo catalysts. However, a sharp drop in activity is observed beyond 650°C in the case of HDO as compared to HDS. Beyond 650°C there is no significant difference in HDO activities. The general behaviour is similar to HDS activities and the oxygen uptake variation. The similarity between HDS and HDO variation suggests that the two functionalities may originate from similar sets of sites. The promotional effect of Co on HDO is 1.20 times at 550°C and 1.46 at 650°C. Such an observation suggests that in addition to increase in dispersion of MoS_2, alteration of the Co ion distribution is taking place and this is also an important factor in determining the catalytic activity.

The variation of cyclohexene hydrogenation rates as a function of sintering temperature is shown in fig. 2. It can be observed that in all the three catalyst systems the hydrogenation increases with the increase of temperature upto 750°C and then decreases upto the highest temperature studied. The hydrogenation activity is highest for Ni–Mo catalyst and continues to be so at all the sintering temperatures investigated. The activity of the Co–Mo catalysts is considerably lower than that of the Ni–Mo catalysts. A comparison of Co–Mo and Mo catalysts indicates that the hydrogenation activity of Co–Mo is higher than that of the Mo catalysts upto 650°C and at 750°C Mo catalysts display higher activity. Beyond this temperature, however, there is not much difference between Mo and Co–Mo catalysts. One important point to be noted is that the sintering temperature at which the maximum activity is observed is different for HDS and HYD. For HDS the maximum is at 650°C whereas for hydrogenation it is at 750°C. The difference in behaviour suggests that HDS and HYD take place on different sets of sites. It is also interesting to note that the dispersion is higher for Co–Mo catalysts at all sintering temperatures. However, the activity for hydrogenation is more in the case of Ni–Mo catalysts. These differences in behaviour can be explained considering variation in intrinsic activities.

The measured activities are determined by the number of sites and also by the activity of each site, i.e., intrinsic activity. The intrinsic activities were evaluated using oxygen uptakes and such data as a function of sintering temperature are shown in fig. 3. It can be seen that Ni–Mo catalysts have higher intrinsic activity for hydrogenation compared to Co–Mo catalysts. The intrinsic activity for HDS is higher in the case of Co–Mo catalysts compared to that of Ni–Mo catalysts. The observed activity is due to the combined effect of these two factors. In the case of NiMo catalyst the increase of intrinsic activity of the sites more than compensated the decrease in number of sites for hydrogenation. In the case of HDS on Co–Mo catalysts both the number of sites as well as intrinsic activity are higher resulting in higher activities for HDS. It may also be noted that trends in variation of intrinsic activity are entirely different for HDS and HYD. The differences in behaviour also support our earlier suggestion that HDS and HYD originate from different sets of sites.

At this juncture it is instructive to visualize what are the possible modifications that can occur in these catalysts as a function of sintering temperature and the implications of such changes on activities for hydrogenolysis and hydrogenation. These following are the possible modifications that can occur as the temperature of

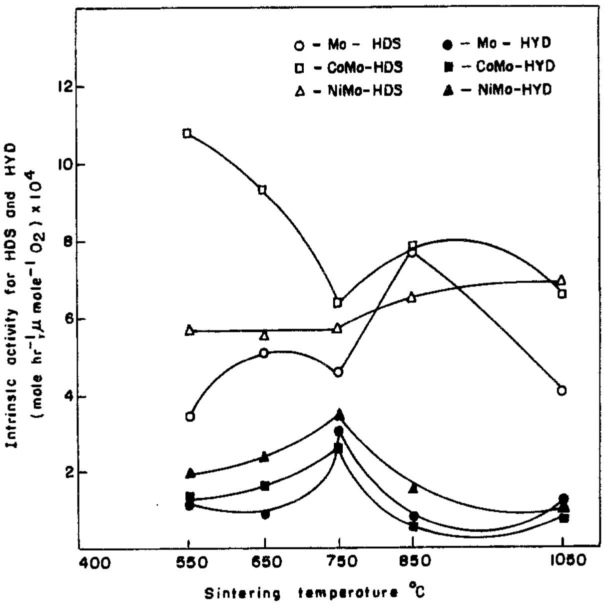

Fig. 3. Variation of intrinsic activity for HDS and HYD as a function of sintering temperature.

sintering increases. (i) Redistribution and spreading of molybdena, (ii) volatalization of molybdena, (iii) reaction between molybdena and support, (iv) mobility of promoter ions, (v) reaction of the promoters with γ-Al_2O_3, (vi) reaction of the active component and promoters, (vii) structural breakdown of the support.

Molybdenum oxide whose melting point (795°C) and Tammann temperatures (270°C) are low, is expected to be mobile considerably at all sintering temperatures studied. Due to the low melting point molybdenum volatalizes considerably at higher temperatures. The spreading of molybdenum oxide is evidenced by increase in oxygen chemisorption and molybdenum volatalization by chemical analysis. Similar observations about molybdenum loss also are reported in literature [4,6,8]. The mobility of molybdena is expected to increase with the temperature and so does molybdenum volatalization. Of these two forces, molybdena spreading is dominant at low temperatures while at high temperatures molybdena volatalization takes over. The occurrence of a maximum in oxygen uptake supports this view.

Among other factors $Al_2(MoO_4)_3$ formation is important in Mo/NiMo catalysts. Since $Al_2(MoO_4)_3$ is not sulfided and is reported to have no HDS activity [1], the formation wherever it is there decreases the activity for HDS. The mobility of promoter ions in low temperature region on spreading of molybdena can cause increase in activity which is in fact observed. However, as the temperature increases the same mobility can decrease the activity due to formation of $CoAl_2O_4$ and $NiAl_2O_4$. The presence of these phases is noticed in the XRD patterns. It is well known that these phases are not active for the functionalities studied here. Therefore formation of these phases will decrease the catalytic activity. The reaction between MoO_3 and promoters results in formation of $CoMoO_4$ and $NiMoO_4$ phases as can be inferred from XRD results. However, these phases get sulfided and can contribute catalytic activity. Crystallite size of these phases and the resulting MoS_2 has a bearing on catalytic activity but it is difficult to comment on such effects with the data presented in this investigation. As can be inferred from XRD and surface area data significant structural changes occur beyond 750°C. These structural changes in the support are expected to decrease the catalytic activity of all the functionalities, as the loss of surface area of the support decreases molybdenum sulfide area, decreases the promotional effect, increases molybdenum volatalization etc. This in fact was observed experimentally (fig. 2).

For convenience of interpretation the sintering temperatures may be grouped as upto 650°C, and 750°C and beyond. In the former range spreading of molybdena and redistribution of promoter ions are the dominant factors in controlling the activity. Over this the effect of formation of phases like $NiAl_2O_4$, $CoAl_2O_4$, $Al_2(MoO_4)_3$ is superimposed, altering the activity. The lower activity of Ni–Mo catalysts for HDS can be ascribed to such phenomena. Beyond 750°C the forces that decrease activity like structural break down, molybdenum volatalization, compound formation all contribute in decreasing active centres and consequent decrease in all the functionalities.

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