

Molybdena on Titania

II. Thiophene Hydrodesulfurization Activity and Selectivity

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I. INTRODUCTION

Hydrodesulfurization (HDS) catalysis is one of the heavily studied branches of catalysis. The most common catalysts employed in these studies are molybdena-alumina catalysts (*i.e.*, alumina-supported molybdenum oxide). Molybdena catalysts used in industry are usually promoted with cobalt or nickel to improve their activity. Molybdena-alumina HDS catalysts are extensively reviewed by Schuit and Gates (1), Massoth (2), Delmon (3), Grange (4), and many others. Despite the very large number of research papers in the area, there is still disagreement about the structure and nature of active sites of the molybdena catalysts. One good example concerns the role of support in determining the HDS activity. de Beer *et al.* (5, 6), in a review on the role of support for the molybdena system, suggested the support interaction is not the most important factor in determining HDS activity, and that less reactive, high-surface-area support materials such as silica and carbon can also be used as support for HDS catalysts and still have high activity. In another study by Topsøe *et al.* (7), it was found that the support material (alumina, silica, and carbon) has significant influence on the final structure of catalysts due to their different strengths of interaction (alumina > silica > carbon). More controversy can be found in the recent literature. Duchet *et al.* (8) studied a series of supported sulfided catalysts and they found that the

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thiophene HDS activity per mole of Mo increased in the order $\text{Mo}/\gamma\text{-Al}_2\text{O}_3 < \text{Mo}/\text{SiO}_2 < \text{Mo}/\text{C}$. They explained the difference in activity as being due to different degrees of interaction, and apparently the stronger the interaction, the lower the activity. Muralidhar *et al.* (9) found the opposite trend in their studies of a series of alumina- and silica-supported catalysts. They attribute the high HDS activity of alumina-supported catalyst to a stronger interaction with the alumina, thus better dispersion in oxidic and sulfided state. Previous studies (10, 11) report similar findings.

Instead of going to relatively inert supports such as silica and carbon, we started an investigation of the other extreme by using a strongly interacting support, titania. In a previous study (12) we characterized a series of molybdena-titania catalysts by Raman and IR spectroscopy as a function of preparative variables. We found that, with some important exceptions, the structure of molybdena on the titania surface is quite similar to that on the alumina surface. Our results indicated that the adsorption of molybdates was very uniform on the titania surface and the strength of interaction between the support and the surface molybdenum species was very strong. However, unlike the alumina case, the interaction between molybdena and the promoter, cobalt, did not depend on the order of impregnation. In this communication we report our results for the HDS activity and selectivity of these titania-supported molybdena catalysts.

If stronger interaction between molyb-

dena and the support has an important role in determining the dispersion of catalysts as described in the monolayer model by Massoth (2), one would expect to see an increase in HDS activity for the titania-supported catalysts. In the only other investigation of HDS activity of molybdena-titania catalysts MuraliDhar *et al.* (9) found that compared to the standard alumina-supported catalysts titania decreases the HDS and hydrogenation (HYD) activities while increasing the hydrocracking (HCG) activity both as a support and as a promoter.

II. EXPERIMENTAL

Catalysts. All the molybdena-titania catalysts were prepared from ammonium heptamolybdate (Fisher Scientific ACS certified) solutions and Degussa P-25 nonporous titania with a BET area of 50 ± 5 m²/g. A large number of catalysts were used in order to elucidate the effects of Mo loading, impregnating solution pH, cobalt addition, and method of preparation. Details of the preparations and Raman and IR characterization of the catalysts can be found elsewhere (12). In order to compare with previous investigations charcoal and alumina supports were also used. Finally, an industrial Co-Mo HDS catalyst (Harshaw CoMo-0603T) with a composition of 12% MoO₃ and 3% CoO on an alumina support was also used as a standard to compare our catalysts with.

HDS activity measurement. HDS activities were measured in an all-Pyrex differential microreactor at atmospheric pressure. A catalyst charge of 50 mg was used throughout the study. The catalysts were first reduced under hydrogen at 350°C for 12 h with a flow rate of 40 cm³/min. Hydrogen flow rate was controlled to $\pm 1\%$ by a Matheson mass flow control system. Reduced catalysts were then exposed to a reactant mixture of thiophene and hydrogen also at 350°C. Thiophene was introduced into the feed stream by bubbling hydrogen through a bubbler containing liquid thio-

phene at room temperature. Thiophene-saturated hydrogen was passed through a trap at 0°C to regulate the thiophene concentration. Gas-phase sampling was taken at 15-min intervals and product analysis was performed using a Hewlett-Packard 5710 gas chromatograph equipped with dual thermal conductivity detectors. Separation of the products was achieved with a 5-foot-long, $\frac{1}{8}$ -in.-diameter Teflon column packed with *n*-octane-Porasil C. Typical reaction products were hydrogen sulfide, *n*-butane, *n*-butene, *trans*- and *cis*-butene. These C₄ products were used to calculate the thiophene conversion. A trace amount of butadiene could also be observed for some catalysts. The reproducibility of a typical catalyst was found to be within 5% in duplicate runs and different catalyst charges. The ratio of $k_{\text{HYG}}/k_{\text{HDS}}$ was also calculated according to the method used by Okamoto *et al.* (13).

III. RESULTS AND DISCUSSION

It is well known that preparative variables can affect the final structure of molybdena catalysts. Massoth (2) pointed out that most of the discrepancy in literature can be attributed to the lack of attention in catalyst preparation. Therefore, our first effort on the molybdena-titania system was focused on the preparative variables. Among the variables we wanted to test were the effect of Mo loading, effect of pH, method of loading, and the effect of Co promotion on the selectivity and activity of molybdena-titania catalysts.

The physical parameters and the thiophene HDS activity of the molybdena catalysts tested in this study are summarized in Table 1. All the catalysts tested showed high initial activity. The conversion data shown in Table 1 were all taken after 5 h of operation when steady-state activity was apparent. Usually the steady-state value was found to be approximately half of the value of $t = 15$ min. A blank run using pure titania support was also made under the same pretreatment and experimental condi-

TABLE 1

Hydrodesulfurization of Thiophene at 350°C and Atmospheric Pressure over Molybdena Catalysts

Wt.%		Support material	pH	Method of prep.	BET surface area (m ² /g)	Raw conv. (%)	Intrinsic activity (%/mg Mo)	$k_{\text{HYD}}/k_{\text{HDS}}$
Mo	Co							
0	0	Titania	—	Imp.	45.3	0.0	—	—
1	0	Titania	5	Imp.	43.0	4.2	8.40	1.82
3	0	Titania	5	Imp.	43.2	5.9	3.94	1.38
5	0	Titania	5	Imp.	43.8	7.5	3.00	1.07
10	0	Titania	5	Imp.	40.9	6.6	1.32	1.26
15	0	Titania	5	Imp.	39.3	6.6	0.88	1.64
0	3	Titania	—	Imp.	42.1	0.2	—	—
1	3	Titania	5	Imp.	41.2	6.5	13.00	1.25
3	1	Titania	5	Imp.	40.9	10.2	6.79	0.61
3	3	Titania	5	Imp.	39.6	10.0	6.66	0.70
5	3	Titania	5	Imp.	36.7	9.8	3.92	0.67
10	3	Titania	5	Imp.	38.5	8.3	1.66	0.44
15	3	Titania	5	Imp.	37.0	9.4	1.26	0.36
3	0	Titania	1	Imp.	45.4	7.1	4.74	1.62
3	0	Titania	2	Imp.	44.6	6.4	4.26	1.62
3	0	Titania	9	Imp.	50.2	6.5	4.34	1.32
1	0	Titania	10	E.A.	50.5	5.9	11.80	1.70
3	0	Titania	5	E.A.	52.3	6.6	4.40	1.57
4	0	Titania	1	E.A.	49.5	7.0	3.50	1.36
9	2.4	Alumina ^a	—	—	166	10.3	2.28	0.75
6	0	Alumina	5	Imp.	69.4	4.9	1.64	1.82
6	0	Carbon	5	Imp.	—	3.1	1.03	1.00

^a Harshaw CoMo-0603T.

tions. No thiophene HDS activity could be detected.

Loading Effect

Since the amount of catalyst used was constant (50 mg) for each run, it is quite surprising to find that the increase in raw conversion as a result of increase in metal loading was much less than expected. Figure 1 further illustrates this point by plotting the intrinsic activity as a function of loading. The intrinsic activity is calculated by dividing the activity per gram of the sample by the percentage of Mo loading. Perhaps the most striking point about Fig. 1 is the high activities of our low-loading catalysts compared to the alumina-supported catalyst, especially if one considers the fact that they contain no cobalt promoter. We also see that the intrinsic activity decreases

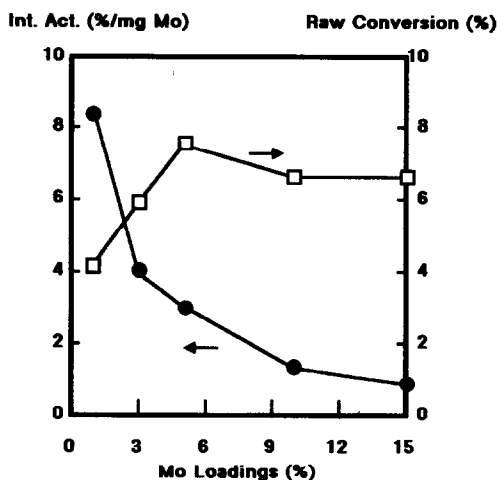


FIG. 1. The raw conversion and intrinsic activities of Mo/TiO₂ catalysts in HDS as a function of Mo loading. The trend of intrinsic activity as a function of Mo loading for titania-supported catalysts is very different from those of alumina-, silica-, and carbon-supported catalysts.

as the metal loading increases. This is very different from the studies of Mo loading effect for other supports. For the alumina support it was found that catalysts with low Mo loading (<3%) have low specific HDS activities (13), which was attributed to the difficulty of reducing molybdenum oxide on alumina surface at low concentrations (14). Thus, the intrinsic activity for the molybdena-alumina system increases as Mo loading increases (13, 15). Bachelier *et al.* (15) further suggested the marked difference in the HDS activity between dilute and concentrated Mo catalysts was due to a change in the distribution of two kinds of active sites on the surface. For silica and carbon support systems, Duchet *et al.* (8) observed the general trend is that the intrinsic activity also increases with metal loading, but unlike alumina support, there is an "efficiency maximum" for these less reactive supports.

In our previous work (12) it was shown that up to 3% Mo there was a significant amount of tetrahedrally coordinated oxide species on the support. Bulk like MoO_3 was seen after 5% Mo loading. Assuming that the final dispersion and activity of the sulfided catalysts are strongly correlated with the dispersion of the oxidic precursor, we can explain the differences in activity as a function of surface species on the titania surface. Along this line, the total activity should be constant after monolayer coverage (which is calculated to be around 4.5%) since the BET surface area of these catalysts are more or less the same (Table 1). If we look at the total activity curve in Fig. 1 for catalysts prepared by the impregnation method we see that this is approximately correct. In going from 5% to 15% Mo loading our previous work (12) shows that the amount of surface molybdate does not change, but rather, the amount of bulk-like MoO_3 increases. Thus this finding seems to indicate that once the monolayer coverage is reached the activity of the sulfided catalyst does not depend on the amount of oxidic precursor on titania support. This also

explains why the specific activity reported by Massoth (9) for 8% Mo/TiO_2 was low compared to the same loading on alumina. A loading of 8% corresponds to approximately twice the monolayer coverage on their titania support (the same as ours) and less than a monolayer coverage on alumina. As seen in Fig. 1, if the loading is less than a monolayer, titania-supported catalysts are more active than the corresponding alumina-supported catalysts. In the region of 1 to 5% Mo loading the relative activity decreases almost by a factor of 3 while the surface area (Table 1) essentially remains constant. If we follow the assumption that the activity of the catalyst depends on the oxide precursor then we can explain the decrease as being due to increased amounts of octahedrally coordinated Mo species (12) leading to the conclusion that the tetrahedrally coordinated oxide precursors have more active sites for the HDS reaction. The other possibility is that the higher dispersion catalysts are formed at low loading, yielding higher specific activities. Even though previous studies (17, 18) also suggest that a large amount of tetrahedral species is present on the alumina support at low loadings, the activity reported for this species is not high. As mentioned earlier, this may be due to the difficulty in reducing tetrahedral molybdenum species on alumina, and HDS activity has a strong correlation with the degree of reduction of the surface molybdates (14). On the other hand, Tanaka *et al.* (19) found that MoO_3 loaded on the TiO_2 with 10 wt% or less could be reduced to nearly the zero-valent state of molybdenum with hydrogen at 500°C in 1 h, which is in contrast to the findings on alumina. Moreover, Nakamura *et al.* (20) reported that the reduction of titania-supported MoO_3 was much faster than those of MoO_3 supported on SiO_2 , MgO , ThO_2 , etc. Therefore, it is entirely possible that the high HDS activity of these low-loading molybdena-titania catalysts compared to alumina support results from the ease of reduction. As suggested by Du-

chet *et al.* (8), carbon-supported Mo catalysts should be most readily reduced because of the inertness of the support. However, our only data point using a carbon support does not give a high intrinsic activity. Since the titania support used has a maximum of 0.3 wt% of HCl, another possible explanation for the high activity of these low-loading catalysts is due to the presence of chloride ion. It has been shown that F- and Cl-containing additives (0.5 wt%) increases the HDS activity slightly (around 20%) because of a possible inductive, electron-withdrawing effect which increases the electron-accepting capacity of the Mo anion vacancies (9). However, we do not think the chlorine effect alone can sufficiently explain the large increase in activity of these low-loading catalysts.

pH Effect

Figure 2 shows the effect of impregnation pH on the HDS activity at a constant catalyst loading of 3% Mo. Relative intrinsic activity decreases from 1.85 at pH 1 down to 1.55 at pH 5 and then increases to 1.7 at pH 9, showing a maximum variation of 20%. This is not surprising because the starting solution's pH is not the pH on the support surface due to the small amounts of

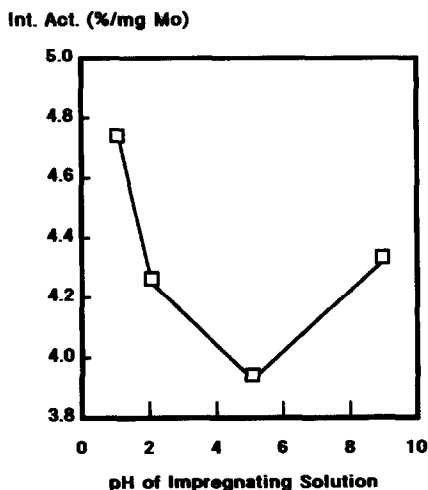


FIG. 2. The effect of impregnation pH on HDS activity of 3% Mo/TiO₂ catalysts.

solution used and the high buffer capacity of titania support. However, the activity trend correlates well with our previous spectroscopic data (12) which indicate that a larger amount of tetrahedral species exists in the pH 9 sample when compared to the acidic one. Following the same argument as in the previous section, this explains the higher activity of the pH 9 sample as compared to the pH 5 sample. However, this does not explain the higher activities of the acidic preparations. It has been shown that acidic impregnation will provide better dispersion (21); therefore, even though we do not observe much difference in the structure of the acidic spectra (12), higher HDS activities were obtained for a better-dispersed, low-pH preparation as shown here. Houalla *et al.* (22) also found a pH effect in the alumina-support system. They observed an increase in HDS activity from pH 11 to pH 5.4; however, further decreasing the pH to 4.0 decreased their activity. They explained the decrease by suggesting that the presence of the nitrate ion causes a repartition of Mo phase over the alumina support. We think the more probable reason is, as they reported in the paper, due to the slight precipitation of their pH 4 sample. We do not have the same problem because of our lower concentration preparation.

Equilibrium Adsorption Catalysts

Figure 3 shows the effect of loading (and pH) for equilibrium adsorption catalysts. It has been shown that by equilibrium adsorption technique, more dispersed and more homogeneous catalysts can be prepared on the alumina support (23). Our studies on titania support show essentially the same result (12). Unfortunately, in equilibrium adsorption the solution pH determines the amount of loading, and as a result, the effect of pH and the effect of loading cannot be studied independently. Nevertheless, the equilibrium adsorption catalysts show reproducible higher activity when compared to impregnation catalysts at the same

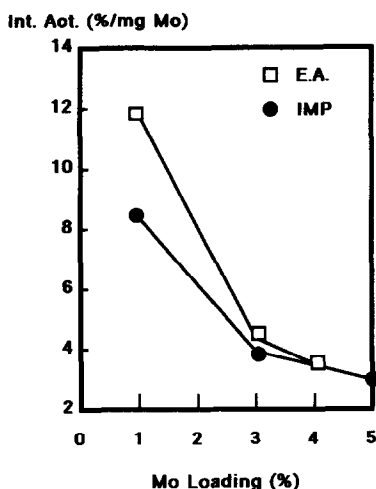


FIG. 3. The HDS activities of Mo/TiO₂ catalysts prepared by equilibrium adsorption technique. Impregnation catalysts with the same loading range are also shown for comparison purposes.

loading, which indicates a better dispersion. The most active catalyst is the one prepared by bringing the support into equilibrium with the pH 10 solution and it contains almost only tetrahedral species (12). At low pH the loading approaches complete monolayer coverage and, as seen in Fig. 3, the activity curves become independent of the method of preparation above 4% loading.

Cobalt Promotion

The role cobalt plays in molybdena catalysts has been extensively investigated. Many theories have been put forth to explain the promotion effect of cobalt in HDS reaction. However, the primary function of cobalt is still subject to disagreement (2). Perhaps the most significant finding in our study on cobalt promotion is the extremely low HDS activity of the 3% Co/titania catalyst (Table 1). When supported on alumina, cobalt has more or less the same activity as molybdenum, while on the carbon support, cobalt has demonstrated an almost fourfold increase in activity when compared to carbon-supported molybdenum catalysts. These results indicate that there is a strong support effect for cobalt in the HDS reac-

tion. Thus, the support inevitably influences the promotional function of cobalt in the Co-Mo catalysts. Figure 4 shows the effect of cobalt promotion on HDS activity in comparison to the unpromoted catalyst containing the same amount of molybdenum and 3% cobalt. The activities of all the promoted catalysts are higher by 25 to 70%. This improvement is low by about a factor of 2 when compared to the results of a similar study on the alumina support (5). Co-Mo/carbon system, on the other hand, shows a three- to fourfold activity enhancement (8). It should be noted that since Co/carbon are active HDS catalysts, the higher activity of Co-Mo/carbon catalyst may result from the Co itself as an active phase (8). Our catalysts do not have this problem since cobalt alone is a very poor catalyst. Our previous work (12) showed that just as in the case of alumina support, on titania a uniform surface Co-Mo oxidic species are formed at a Co-to-Mo ratio of 3 to 10% by weight (or atomic ratio of 1 to 2). Unlike the alumina case, however, we do not observe a sharp increase in activity in our 10% Mo, 3% Co catalysts. This is probably because

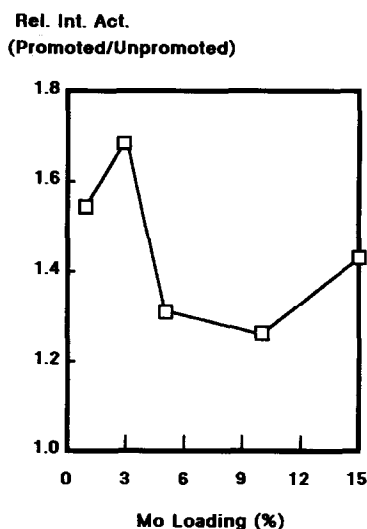


FIG. 4. The effect of addition of 3% Co to a loading series of Mo/TiO₂ catalysts. The activity is promoted by 25 to 70%, which is much less for those observed in alumina or carbon-supported promoted catalysts.

the surface of the support is covered by multilayers of Co-Mo species. We also prepared and tested a 3% Mo, 1% Co catalyst to ensure below monolayer coverage while keeping a 2:1 Mo-to-Co atomic ratio. The HDS activity (Table 1) of this catalyst was found to be the same as a 3% Mo, 3% Co catalyst, which implies that the excess cobalt as shown in the Raman spectra (12) is useless in the HDS reaction.

Selectivity

There is a general belief that butane is produced from hydrogenation of butenes in the HDS reaction. Recent research has suggested that the sites for hydrogenation are different from the sites for hydrogenolysis (16), the distribution of which may affect the selectivity of the catalyst. For our catalysts the $k_{\text{HYD}}/k_{\text{HDS}}$ ratio of our unpromoted Mo/TiO₂ catalysts exhibit a local minimum at a loading of 5% (Table 1), which implies the distribution of hydrogenation and hydrogenolysis sites depends on the type of molybdate species on the titania surface. As for cobalt-promoted catalysts, the ratio $k_{\text{HYD}}/k_{\text{HDS}}$ decreases monotonically as the loading increases for the cobalt-promoted catalysts. These ratios are also lower when compared to the unpromoted catalysts. This is quite surprising because one would expect a higher rate of hydrogenation since cobalt is a good hydrogenation catalyst. The formation of three-dimensional bulk MoO₃ is greatly suppressed for the high-loading catalysts when cobalt is added; instead, layers of two-dimensional "cobalt molybdate" species results (12), which may explain the low $k_{\text{HYD}}/k_{\text{HDS}}$ ratios of these promoted catalysts.

Conclusions

The effect of preparative variables on HDS activities of molybdena-titania catalysts were studied. It was found that for the reaction conditions used in this study, low-loading titania-supported catalysts are

more active in HDS reaction compared to alumina-supported catalysts. Unlike alumina- and carbon-supported catalysts, promotion with cobalt increases the activity only modestly.

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