Ceramic Catalyst Materials

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ABSTRACT

This project focuses on the modification of silica and alumina surfaces by titania and hydrous titanium oxide ion-exchange films, and the use of these modified materials as supports for MoS₂ catalysts. Fourier transform infrared spectroscopy (FTIR) studies of molybdena interaction with γ-Al₂O₃ demonstrate that at low loadings molybdenum interacts with the most basic hydroxyl groups, and that these hydroxyls are associated with tetrahedrally coordinated aluminum. Furthermore, hydrodesulfurization (HDS) activity as a function of Mo loading shows a maximum in specific activity with loading. The Mo species bound to tetrahedrally coordinated Al sites are therefore believed to be inactive for the HDS reaction. Only after the tetrahedral Al sites have completely consumed does molybdena adsorb on the alumina in a manner that leads to an active catalyst. According to this scheme, the activity of alumina supported MoS₂ catalysts could be greatly improved by either titrating the tetrahedral Al sites with a modifier, or by using α-Al₂O₃ which contains no tetrahedrally coordinated Al. HDS tests over MoS₂ supported on both α-Al₂O₃ and γ-Al₂O₃ modified by a titania film confirm this hypothesis. Neither support material gives rise to a maximum in activity with Mo loading, but rather exhibits a smooth decrease in activity with loading. Furthermore, for equivalent Mo loadings the activity of both of these support materials exceeds that of unmodified γ-Al₂O₃ due to the fact that no Mo is tied up in the inactive form. FTIR, X-ray photoelectron spectroscopy, and transmission electron microscopy are currently being used to determine whether our model can indeed account for the observed activity trends. Although the surface area of α-Al₂O₃ is too low (∼10 m²/g) for use as a commercial catalyst, the titania coated γ-
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Al₂O₃ represents an important, practical improvement in support materials for hydrotreating catalysts.

INTRODUCTION

In previous years, this project has focused on the deposition and characterization of titania films on high surface area substrates, such as silica and alumina. In order to determine the effects that these films have on catalyst activity, we have focused efforts in the current fiscal year on depositing MoS₂ onto modified and unmodified alumina substrates, and measuring the resulting activity for hydrodesulfurization (HDS) of dibenzothiophene (DBT). On unmodified γ-alumina or silica supports it is known that the specific activity of MoS₂ goes through a maximum with molybdenum loading, while on titania or zirconia the activity appears to decrease monotonically with coverage¹. Unfortunately, due to the low surface area of the titania and zirconia supports, and to the fact that a flow reactor was employed for the activity measurements, the data reported on these two supports did not extend to low enough Mo loadings to confirm the absence of a maximum in activity. Assuming, however, that no maximum occurs for titania and zirconia, the different behavior of γ-alumina and silica relative to titania and zirconia has been attributed to differing morphology of the MoS₂ active phase. For supports that exhibit no maximum with loading, MoS₂ is proposed to lie flat with the basal plane parallel to the support surface, while for supports that exhibit a maximum the MoS₂ is proposed to bond perpendicular to the surface in a so-called “bookend” morphology. The evidence for the bookend morphology is indirect, relying on transmission electron microscopy (TEM) images that show MoS₂ platelets lying parallel to the direction of viewing and perpendicular to the γ-alumina crystallites which preferentially align with the TEM grid. These MoS₂ platelets could easily be located on the sides of γ-alumina particles, however, and therefore appear to be bound in a bookend morphology even though bonding is primarily through interaction of the basal plane with the sides of the particles. Recent TEM images of MoS₂ bound to low surface area silica and γ-alumina particles, where the uncertainty introduced by the possibility of bonding at crystallite edges is eliminated, show no evidence
for a bookend morphology, but show ample evidence for basal plane bonding of MoS\textsubscript{2} (ref. 2).

Given the difficulties arising from a morphological explanation of the activity trends, it seems prudent to explore possible chemical differences between the supports that could explain the data. It is known that at very low loadings molybdena binds to the \(\gamma\)-alumina surface as isolated monomeric species that are very difficult to reduce and convert to the sulfide\textsuperscript{3,4}. As coverage increases, polymeric molybdena species begin to form ultimately resulting in bulk MoO\textsubscript{3} particles. Since at low loadings (<1 Mo/nm\textsuperscript{2}) most of the molybdenum is tightly bound in the inactive form, specific activity for HDS is expected to be very low. As more easily reduced polymeric species form at higher loadings, the specific activity rises, ultimately reaching a maximum at the point at which MoS\textsubscript{2} platelet growth begins to compensate for the increase in the fraction of the molybdenum that is reducible to MoS\textsubscript{2}. In order to explain why a similar phenomenon does not operate on titania and zirconia, one must explore the specific interactions that give rise to the inactive Mo species on \(\gamma\)-alumina.

Fourier transform infrared (FTIR) studies of molybdena adsorption on \(\gamma\)-alumina demonstrate that the initial mode of interaction is through the most basic (highest frequency) hydroxyl groups\textsuperscript{5}. These hydroxyl groups are associated with tetrahedrally coordinated aluminum cations in the \(\gamma\)-alumina support\textsuperscript{6}. It is therefore postulated that the presence of tetrahedrally coordinated cations in the support material can give rise to strongly bound, inactive molybdena species. Comparing silica and \(\gamma\)-alumina with titania and zirconia in this context reveals that supports that give rise to a maximum in activity with coverage do indeed possess tetrahedrally coordinated cations, while supports that show only a monotonic decrease in activity with coverage contain only octahedrally coordinated cations.

Given this excellent correlation, activity studies and spectroscopic and TEM characterization of supported molybdena as a function of loading were performed to verify this explanation of activity trends. Accordingly, we report here the results of activity studies that confirm the published activity trends over a wider range of Mo coverages, and also
explore the potential of titania films to modify γ-alumina substrates such that the unfavorable, highly basic OH groups are consumed prior to molybdena loading.

RESULTS AND DISCUSSION

Based on the information and suppositions presented above, it is informative to compare the HDS activity of MoS$_2$ measured on several different supports. Mo was loaded onto various supports by aqueous incipient wetness impregnation of ammonium heptamolybdate followed by calcining at 500°C to disperse the molybdenum. Sulfiding was performed \textit{ex situ} at 400°C in a flowing mixture of 10% H$_2$S in hydrogen. Kinetic measurements were made using a batch reactor rather than the flow reactor employed in earlier studies. This arrangement allows activity measurements to be made with low Mo loadings on very low surface area supports by simply extending the reaction time until measurable conversions are achieved. The advantage of being able to measure activity on such catalysts is offset to a certain degree by the need to account for poisoning of the reaction by competitive adsorption of product H$_2$S, and for a finite heat up time at the start of the reaction. A method for accounting for these factors is presented elsewhere$^7$. The result of the analysis is a psuedo-first order rate constant that provides a measure of the specific activity (per g Mo) for a wide range of Mo loadings.

Results of this analysis are presented in figure 1, which shows the first order rate
constant as a function of Mo coverage. First, note the maximum in activity for MoS$_2$/γ-alumina at ~1.0 Mo/nm$^2$, in excellent agreement with previous measurements of thiophene HDS$^1$. Second, when the data for titania supports is extended below 1.0 Mo/nm$^2$ the monotonic trend of decreasing activity with loading is maintained, unambiguously confirming a fundamental difference between the activity trends on γ-alumina and titania. Finally, and most significantly, α-alumina exhibits an activity trend closely resembling that of titania, with no apparent maximum. This result is entirely consistent the hypothesis that isolated molybdate species, formed by reaction with basic hydroxyl groups bound to tetrahedrally coordinated aluminum cations, give rise to the low activity of MoS$_2$/γ-alumina at coverages below 1.0 Mo/nm$^2$. Since no tetrahedrally coordinated aluminum cations are present in α-alumina$^8$, the possibility of forming the inactive species is precluded and a normal activity trend is observed. While this result alone does not confirm the validity of the proposed explanation for the maximum observed with γ-alumina, it does demonstrate that the effect is related to the structure of the support and not to the specific chemical identity of the support cations.

In order to verify the nature of the chemical interactions leading to the different activity trends for α- and γ-alumina, spectroscopic evidence for the presence or absence of certain molybdena species on each support is required. This evidence is presented in figures 2 and 3. Figure 2 shows FTIR spectra of both α- and γ-alumina in the hydroxyl stretching regions. The spectrum of γ-alumina agrees well with literature spectra$^5,9$, showing multiple bands corresponding to various binding sites and coordinations$^6$. The spectrum of

![Image of FTIR spectra showing hydroxyl stretching region on α- and γ-alumina.](image)
α-alumina is of much poorer quality due to the very low surface area, but it is nevertheless apparent that little intensity is present at the high frequencies characteristic of the most basic hydroxyl groups on γ-alumina. Further evidence for a difference in chemical behavior of Mo loaded on the two supports comes from X-ray photoelectron spectroscopy (XPS) measurements of the percent reduction of Mo on α- and γ-alumina after treatment in pure H₂ at 500°C for 12h (figure 3). γ-alumina shows an increase in reducibility with loading as reported elsewhere⁴⁸, consistent with formation of an unreducible, and therefore inactive Mo species at low loadings. α-alumina, on the other hand, shows no variation of reducibility with loading, consistent with the absence of any changes in the bonding mode of molybdena with loading. The constant reducibility therefore gives rise to a monotonic decrease in activity with loading due to the growth of MoS₂ islands and consequent loss of edge sites.

![Graph showing Mo reduction at 500°C in hydrogen for 12h, measured by XPS.](image)

While the results for α-alumina are encouraging, and demonstrate the potential of supports without tetrahedrally coordinated cations for improving supported MoS₂ catalysts, the low surface area of α-alumina renders it unsuitable for practical use. In other words, although the activity per gram of Mo is quite high on α-alumina, the activity per gram or unit volume of catalyst is very low. In order to apply the knowledge gained so far to the development of an improved practical catalyst, a method must be found to block the adsorption of Mo species at the most basic hydroxyls on γ-alumina. As alluded to earlier, one possible method for accomplishing this result is preadsorption of an additive to consume these basic hydroxyls prior to Mo adsorption. Since a major focus of this program has been the formation of titania films on various supports,
Titanium oxide was chosen as the additive. Measurements were made of the activity of MoS2 supported on titania coated γ-alumina, and figure 4 shows the results for a support coated with 16 wt% titania, an amount sufficient to cover approximately two thirds of the γ-alumina surface. Clearly, the presence of the titania alters the specific activity trends associated with γ-alumina and results in behavior closely resembling that of bulk titania or α-alumina. FTIR spectra show that the titania film indeed preferentially consumes the most basic, high frequency hydroxyls, thereby preventing the formation of inactive Mo species.

A final important result arises from analysis of TEM images of MoS2 supported on coated and uncoated γ-alumina samples. Figure 5 shows that the two samples are indistinguishable based on MoS2 morphology alone. Even the presence of titania cannot be detected indicating excellent dispersion of this additive. Thus, even if one concedes that the presence of MoS2 platelets perpendicular to the viewing direction, as observed in figure 5, is evidence for a bookend morphology, one cannot use this morphology as an explanation for the different activity trends observed on uncoated and titania coated γ-alumina. Instead, a chemical explanation must be sought. Based on the evidence presented here, the formation of an inactive Mo species on γ-alumina associated with tetrahedrally coordinated aluminum cations, and the absence of this species on supports that do not contain tetrahedrally
coordinated cations, must be considered a strong candidate for explaining the observed activity trends.

Fig. 5a. TEM image of MoS$_2$/γ-alumina.  
Fig. 5b. TEM image of MoS$_2$/titania/γ-alumina

CONCLUSIONS

The widely diverging activity trends observed for MoS$_2$/γ-alumina vs. MoS$_2$/TiO$_2$/γ-alumina, coupled with the extreme similarity in MoS$_2$ morphologies, clearly rules out a morphological explanation for the behavior of different supports. Furthermore, the differences observed between α- and γ-alumina indicate that the activity trends are related to the specific structure of the support surface and not to the chemical identity of the oxide support cations. These conclusions, coupled with spectroscopic data on the nature of hydroxyl groups and Mo reducibility lend strong support to an explanation of activity trends involving the formation of inactive Mo species at low loadings on γ-alumina. These species
result from interaction of molybdena with highly basic hydroxyls associated with tetrahedrally coordinated aluminum cations. As coverage increases, a greater fraction of the molybdenum atoms becomes associated with other sites and the extent of Mo reducibility increases, causing a concomitant increase in activity. Ultimately, growth of MoS₂ platelets with coverage decreases the fraction of Mo atoms located at the active edges of the platelets and activity begins to fall. For supports which lack tetrahedrally coordinated cations, formation of unreducible Mo species does not occur and activity trends are dominated by MoS₂ platelet growth over the entire range of coverages studied. A monotonic decrease of activity with coverage results. By using a titania overlayer to consume the basic hydroxyls that lead to unreducible molybdate species, the activity of γ-alumina can be increased significantly at all Mo loadings, and the activity trends can be made similar to those of α-alumina and titania. This result provides a simple, practical method for increasing the overall activity of supported MoS₂ catalysts.

REFERENCES


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