Evaluation of the Maximum Potential HDS Activity
and the Active Site Structure of Co-Mo/Al$_2$O$_3$ Catalysts

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ABSTRACT
Better characterization and understanding of the nature of HDS catalysts on the molecular scale are of great importance for the rational design of highly active HDS catalysts. Our approaches for this purpose involve selective preparation of the active sites of Co-Mo HDS catalysts using metal carbonyls to overcome the difficulties caused by the heterogeneity of practical catalysts. Selective preparation method of the active phase of Co-Mo sulfide catalysts, the CoMoS phase, supported on refractory oxides was established to understand the nature of practical HDS catalysts. The CoMoS phase supported on Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ showed identical TOF (no effects of the support), whereas the CoMoS phase supported on SiO$_2$ exhibited a higher TOF. It is proposed for the first time that the maximum potential HDS activity of Co-Mo/Al$_2$O$_3$ catalysts can be evaluated by applying the CVD-technique. The number of the vacant edge sites and the extent of edge blocking by inactive Co sulfide clusters can be determined by comparing the HDS activity of CVD-Co/MoS$_2$/Al$_2$O$_3$ and CVD-Co/Co-MoS$_2$/Al$_2$O$_3$. The fraction of the CoMoS phase accessible for NO adsorption was elucidated, based on the amount of the CoMoS phase in the catalysts, leading to a new model of the CoMoS structure. The structure of the CoMoS phase was suggested to be Co sulfide dimer species on the edge of MoS$_2$ particles. This was supported by the magnetic property of the CoMoS phase.

1. INTRODUCTION
Hydrotreatment of petroleum feedstocks has recently become more and more important to protect the environment and to achieve efficient utilization of limited natural resources. Development of highly active and selective hydrotreatment catalysts, in particular hydro-de-sulfurization (HDS) catalysts, is one of the most urgent problems in the petroleum industry. Sulfided Co-Mo or Ni-Mo(W) based catalysts have previously been used for industrial HDS reactions$^{1-5)}$. Numerous attempts have already been made to develop more active HDS catalysts. However, the present catalyst performance cannot meet the more severe requirements of legislative restriction of sulfur content in petroleum products.

Supported Co(Ni)-Mo sulfide catalysts have been extensively studied$^2$ to understand the structure and reactivity of the catalytically active sites, the microscopic reaction mechanisms of HDS and hydrogenation, the effects of the support and additives, and so on. The so-called CoMoS phase was originally proposed by Topsøe et al. as a catalytically active sites$^2$, in which Co is located on the edges of highly dispersed MoS$_2$ clusters, and can explain many aspects of catalytic and spectroscopic properties. Two types of the CoMoS phase, Type I and Type II, can be differentiated depending on their
intrinsic HDS activity. It is accordingly expected that highly active HDS catalysts are composed of a highly dispersed CoMoS type II phase. It is also very effective in increasing the coverage of Co on the edge of MoS₂ particles. For this purpose, chelating agents play an important role by forming complexes with increased thermal stability of promoter atoms.

The structure of the CoMoS phase was investigated mainly by XAFS techniques. However, the heterogeneity inherent to practical Co(Ni)-Mo sulfides supported on Al₂O₃ or SiO₂-Al₂O₃ results in little knowledge of the detailed structures of the active sites and particularly HDS reaction mechanisms. Better characterizations and understandings of the nature of Co(Ni)-Mo sulfide catalyst systems on the molecular scale are of great importance to the rational design of highly active HDS catalysts. Selective preparation of the CoMoS phase supported on refractory oxides would be a promising approach to understand the nature of practical HDS catalysts.

2. EXPERIMENTS

Sulfided MoS₂/Al₂O₃ was exposed to Co(CO)₃NO vapor at room temperature for 5 min (CVD technique), followed by evacuation at room temperature. Co(CO)₃NO/MoS₂/Al₂O₃ was subse-quently sulfided again at 673 K to prepare the Co-Mo/Al₂O₃ catalyst. The resulting catalyst was designated CVD-Co/MoS₂/Al₂O₃. Supports other than Al₂O₃ were also examined. Figure 1 shows the Co/Mo ratio of the CVD-Co/MoS₂/support catalyst (support; Al₂O₃, SiO₂, ZrO₂, and TiO₂) as a function of the NO/Mo ratio of the MoS₂/support samples. The Co/Mo ratio was proportional to the NO/Mo ratio, showing that the Co sulfide species were located on the edge sites of MoS₂ particles, since it is well established that NO molecules preferentially adsorb on the edge sites of MoS₂ particles.

![Figure 1. Correlation between the Co/Mo atomic ratio and the NO/Mo ratio for supported CVD-Co/MoS₂ catalysts.](image)

3. RESULTS and DISCUSSION

3.1. Selective Preparation of CoMoS phase supported on refractory oxides
Figure 2 presents the Co 2p XPS spectra of CVD-Co/Al_2O_3 and CVD-Co/MoS_2/Al_2O_3 (8.7 wt.% Mo)^11,12. The Co 2p_{3/2} binding energy for CVD-Co/Al_2O_3 was close to that of CoS_8, indicating that Co sulfide clusters are formed as expected. However, in the presence of MoS_2 particles, the Co 2p_{3/2} binding energy increased by 0.9 eV, clearly demonstrating that the Co species chemically interact with the edges of MoS_2 particles. We conclude that the Co sulfide species prepared in this way is characteristic of the CoMoS phase^2) and that the CoMoS phase is preferentially formed by the CVD technique, irrespective of the support. The selective formation of the CoMoS phase by the CVD technique was also confirmed by Co K-edge XANES spectra^13) and magnetic property.\(^14,15\)

Repeated exposure of CVD-Co/MoS_2/Al_2O_3 to Co(CO)_3NO vapor and resulfidation caused little change to the HDS activity of CVD-Co/MoS_2/Al_2O_3 in spite of the increase of the Co content by a factor of 1.7^16,17). Therefore, applying CVD once fills the edge sites of MoS_2 particles with Co atoms, constituting the CoMoS phase, and Co(CO)_3NO molecules adsorbed on the edge sites of Co-MoS_2 particles are transformed into separate Co sulfide clusters. In agreement with this, the Co 2p_{3/2} binding energy of CVD-Co/MoS_2/Al_2O_3 was reduced by 0.4 eV after the second addition of Co (Figure 2)^11). This was also supported by the FTIR spectra^16) of NO adsorption on CVD-Co/MoS_2/Al_2O_3, CVD-Co/Al_2O_3, MoS_2/Al_2O_3 and a conventional Co-Mo/Al_2O_3 impregnation catalyst, showing that essentially all the edge sites of MoS_2 particles accessible to NO adsorption are covered by Co atoms, forming the CoMoS phase. Figure 3 schematically illustrates the surface structure of CVD-Co/MoS_2 catalysts.\(^12\)

### 3.2. Real effects of the support on Co-Mo sulfide catalysts

The effect of the support on Co-Mo sulfide catalysts was examined by preparing CVD-Co/MoS_2/support catalysts (SiO_2, ZrO_2, TiO_2, and Al_2O_3)^11). The turnover frequency (TOF) of the
thiophene HDS for MoS$_2$/support depended strongly on the support, if TOF was calculated on the basis of the adsorption capacity of NO$^{11}$. The TOF value for MoS$_2$/SiO$_2$ was 1.6 times higher than that for MoS$_2$/TiO$_2$ or MoS$_2$/ZrO$_2$. The TOF of the latter catalysts was twice as high as the TOF for MoS$_2$/Al$_2$O$_3$ in agreement with other studies$^2$. The TOF probably reflects the morphology of the MoS$_2$ particles and/or their interactions with the support.

Figure 3 shows the catalytic activity of CVD-Co/MoS$_2$/support for the HDS of thiophene as a function of Co loading$^{11}$. A good proportional correlation was obtained for Al$_2$O$_3$-, TiO$_2$- and ZrO$_2$-supported Co-Mo catalysts, regardless of the support and the pretreatment (pre-reduced before exposure to Co(CO)$_3$NO or thermally decomposed after exposure). Since the straight line in Figure 3 passes through the origin, the activity is ascribed to the Co species interacting with MoS$_2$ or the CoMoS phase. The TOF values of the CoMoS phase (the slope of the line) of the Al$_2$O$_3$-, TiO$_2$- and ZrO$_2$-supported catalysts are identical. Therefore, the support had no significant effects on these catalyst systems. Figure 3 shows that the TOF of the Co species supported on SiO$_2$ is 1.7 times higher than the TOF on the other supports. Taking into account the difference in activity between CoMoS Type I and Type II$^2$, CoMoS Type I probably forms on the Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ supports under the present sulfidation conditions (673 K, atmospheric H$_2$S/H$_2$), whereas CoMoS Type II is formed on SiO$_2$. The difference is attributed to the difference in the stacking number of MoS$_2$ particles and/or the electronic interactions between the support and MoS$_2$ particles.$^{18}$

### 3.3. Evaluation of the maximum potential HDS activity

The effect of the CVD-cycle and the FTIR of NO adsorption indicate that the CVD technique fully covers the edge of MoS$_2$ particles by Co atoms as the CoMoS phase but that the pre-existing CoMoS phase is not blocked by the Co sulfide clusters added afterward using Co(CO)$_3$NO. Therefore, the maximum potential HDS activity of the MoS$_2$/Al$_2$O$_3$ and Co-MoS$_2$/Al$_2$O$_3$ catalysts under study can be predicted by using Co(CO)$_3$NO as a “probe” molecule.
Figure 4. HDS activity of CVD-Co/MoS$_2$/support as a function of the Co content. See the caption to Figure 1 for the symbols.

Figure 5. HDS activity of CVD-Co/Co-Mo/Al$_2$O$_3$ (□) and Co-MoS$_2$/Al$_2$O$_3$ impregnation catalysts (△) as a function of the Co content in the impregnation catalyst.

Figure 5 shows the HDS activity of CVD-Co/Co-Mo/Al$_2$O$_3$, which was prepared by exposing sulfided Co-Mo/Al$_2$O$_3$ to Co(CO)$_3$NO vapor and subsequent sulfidation, as a function of the Co content in Co-MoS$_2$/Al$_2$O$_3$ impregnation catalysts. The HDS activity of Co-MoS$_2$/Al$_2$O$_3$ was increased, over the whole range of Co content, by the addition of Co by means of the CVD technique. CVD-Co/Co-Mo/Al$_2$O$_3$ had identical activity with CVD-Co/MoS$_2$/Al$_2$O$_3$, if the Co content was lower than 2 wt.% and the activity of CVD-Co/Co-Mo/Al$_2$O$_3$ gradually decreased with increasing Co content at > 2 wt.%. Based on the results in Figure 3 and the FTIR of NO adsorption, the activity increase in Figure 5 results from the increased amount of the CoMoS phase caused by the addition of Co(CO)$_3$NO.
The HDS activity of CVD-Co/MoS$_2$/Al$_2$O$_3$ provides the maximum potential HDS activity for a series of Co-Mo/Al$_2$O$_3$ catalysts, if the dispersion of MoS$_2$ particles is not modified by the impregnation of Co.

In conjunction with NO adsorption$^{13}$, the decrease in the activity of CVD-Co/Co-MoS$_2$/Al$_2$O$_3$ ($>2$ wt.% Co) was ascribed to the increasing blocking of the edge of MoS$_2$ particles by Co sulfide particles formed during the sulfidation of the Co-MoS$_2$/Al$_2$O$_3$ impregnation catalysts. The maximum HDS activity of Co-Mo/Al$_2$O$_3$ attained at 3 wt.% Co was lower than the activity of CVD-Co/MoS$_2$/Al$_2$O$_3$ or CVD-Co/Co-MoS$_2$/Al$_2$O$_3$ ($<2$ wt.% Co). This is obviously caused by the blocking of the edges of MoS$_2$ particles by Co sulfide particles before the completion of full coverage of the edges of the MoS$_2$ particles by Co. The surface structure of Co-MoS$_2$/Al$_2$O$_3$ as elucidated by the CVD-technique is schematically illustrated in Figure 6.$^{13}$

The CVD technique can also be applied to Ni-MoS$_2$ catalysts to evaluate the maximum potential HDS activity.$^{13}$ The evaluation of the maximum potential HDS activity is a promising method for providing guidelines for improving catalyst performances. The maximum potential activity depends on the dispersion and stacking properties of MoS$_2$ particles.

Figure 6. A schematic illustration of the surface structure of Co-MoS$_2$/Al$_2$O$_3$ impregnation catalysts as estimated by the CVD-technique using Co(CO)$_3$NO
3.4. NO adsorption and the structure of the CoMoS phase

The chemisorption of NO, O₂ or CO has been frequently and widely used to evaluate the dispersion of active phases in HDS catalysts². In particular, NO chemisorption is very informative, when combined with IR techniques, to distinguish coordinatively unsaturated (cus) Mo and Co(Ni) sites on supported Co(Ni)-Mo sulfide catalysts². However, in spite of frequent use of NO as a probe molecule and its practical importance, unresolved crucial problems remain with NO adsorption on HDS catalysts involving the oxidation and/or reconstruction of active sites and the fraction of the Co(Ni)MoS phase accessible to NO adsorption, the latter of which is closely connected to measuring the number of active sites from the amount of NO adsorption. The CVD-catalysts in the present study provide a promising approach to these problems.

The amount of NO adsorption on CVD-Co/MoS₂/support catalyst was measured at room temperature using a pulse technique after cooling from 673 K in a H₂S/H₂ stream or after treating in a H₂-stream at 623 or 673 K after sulfidation.¹⁵,¹⁹ Figure 7 compares the Co K-edge XANES spectra for CVD-Co/MoS₂/Al₂O₃, Co₉S₈ and Co-Mo/Al₂O₃ impregnation catalyst¹⁵,¹⁹. Full adsorption of NO caused small but significant changes in CVD-Co/MoS₂/Al₂O₃: an increase in the edge energy by 0.5 eV and fine spectral changes, indicating modification of the electronic state and geometry of Co species. No white line peak appeared around 7725 eV due to oxidized Co species, clearly demonstrating that the effect of oxidation of Co species by NO adsorption was negligibly small on the adsorption of NO at room temperature by the pulse technique, in contrast to volumetric NO adsorption on Ni-Mo/Al₂O₃, in which considerable oxidation of Ni was observed by XANES.²⁰

Figure 7. Co K-edge XANES spectra for CVD-Co/MoS₂/Al₂O₃ (8.7 wt.% Mo) before and after NO adsorption at room temperature by the pulse technique. The XANES spectra are also shown for bulk Co₉S₈ and sulfided Co-Mo/Al₂O₃ prepared by an impregnation method.
The amounts of NO adsorption on supported CVD-Co/MoS\(_2\) catalysts are shown in Figure 8 as a function of Co content\(^{13,15}\). A single proportional line was obtained for the Co-Mo model sulfide catalysts, irrespective of Type I (Al\(_2\)O\(_3\), TiO\(_2\) and ZrO\(_2\)) and Type II (SiO\(_2\)) CoMoS phases. FTIR spectra of NO adsorption on CVD-Co/MoS\(_2\)/Al\(_2\)O\(_3\) showed exclusively doublet bands at 1845 and 1785 cm\(^{-1}\) characteristic of NO adsorbed on Co sites. Hence, the slope of the line corresponds to the NO/Co molar ratio of 0.67 ± 0.03 for the model catalysts. The impregnation catalyst showed considerably less NO adsorption capacity than the model catalysts. Taking into consideration the formation of dinitrosyl species, \((\text{NO})_2/\text{Co}\), the NO molecules are adsorbed on only 34% of the Co atoms in the CoMoS phase.

![Figure 8. Amount of NO adsorption and Co content for CVD-Co/MoS\(_2\)/support model catalysts. Supports are \(\square\): Al\(_2\)O\(_3\), \(\bigcirc\): SiO\(_2\), \(\square\): TiO\(_2\) and \(\triangle\): ZrO\(_2\). The amount of NO adsorption on a Co-Mo/Al\(_2\)O\(_3\) impregnation catalyst (\(\square\)) is also shown.](image)

To estimate the maximum amount of Co accessible to NO molecules under usual HDS conditions (reaction temperature: 623-673 K in a H\(_2\) stream), CVD-Co/MoS\(_2\)/Al\(_2\)O\(_3\) was treated in a stream of H\(_2\) at 623 or 673 K after sulfidation at 673 K before NO adsorption. The NO/Co ratio increased and leveled off at 1.05. This ratio \((\text{NO})_2/\text{Co} = 0.53\) strongly suggests that only a half of the Co atoms in the CoMoS phase is susceptible to NO chemisorption at the highest coordinative unsaturation attainable under usual HDS reaction conditions.

These findings can be interpreted by assuming a novel model for CoMoS phase, i.e. paired sites of Co atoms on MoS\(_2\) edge sites, \(\text{(S}_\text{Mo})_4\text{Co-S}_4\text{(S}_\text{Mo})_4\), where \(\text{S}_\text{Mo}\) represents a sulfur atom bonding to Mo atoms. When two NO molecules adsorb on the pair site, one of Co-S bonds is cleaved to form an isolated Co species:

\[
\text{(S}_\text{Mo})_4\text{Co-S}_4\text{(S}_\text{Mo})_4 + 2\text{NO} \rightarrow \text{(S}_\text{Mo})_4\text{Co-S}_4 + \text{(NO)}_2\text{Co(S}_\text{Mo})_4
\]

Very recently, DFT calculations have suggested the possibility of the formation of energetically stable \(\text{(S}_\text{Mo})_4\text{Co-S}_4\text{(S}_\text{Mo})_4\) structures on the edges of MoS\(_2\) particles promoted by Co, in conformity with the present NO adsorption results.

The magnetic property of CVD-Co/MoS\(_2\)/Al\(_2\)O\(_3\) is shown in Figure 9. The temperature dependency
of the magnetic susceptibility of Co definitely shows the presence of antiferromagnetic interactions between two Co atoms constituting dimers,\(^ {14,15}\) in agreement with the structural model of the CoMoS phase estimated from the NO adsorption behavior. Figure 10 shows a schematic structural model of the CoMoS phase and NO adsorption mechanism.

Figure 9. Magnetic susceptibility \(\chi\) and effective magnetic moment (\(\mu_B\)) of Co for CVD-Co/MoS\(_2\)/Al\(_2\)O\(_3\) as a function of temperature. The best fitting curve, assuming a dinuclear cluster, for the observed magnetic susceptibility is also shown.

![Figure 9](image1)

Figure 10. A proposed structural model of the CoMoS phase and NO adsorption mechanism.

4. CONCLUSIONS

Selective preparation of the CoMoS phase supported on refractory oxides provides a promising approach to understand the nature of practical HDS catalysts. The real effects of the support were evaluated in terms of the turnover frequency on the CoMoS phase. With Co-MoS\(_2\)/Al\(_2\)O\(_3\) impregnation catalysts, part of the edge sites of MoS\(_2\) particles remain unoccupied by Co atoms in a wide range of Co content. In contrast, with the Ni\(^+\) counterpart, the edge of MoS\(_2\) particles are completely occupied by Ni.
atoms above 2 wt% Ni. Blocking of the active sites by overlayers of Co(Ni) sulfide clusters decreases the HDS activity to a considerable extent. The potential maximum HDS activity of Co-MoS$_2$/Al$_2$O$_3$ catalysts can be evaluated by applying the CVD-technique using Co(CO)$_3$NO as a probe molecule. The fraction of the CoMoS phase accessible to NO adsorption was, for the first time, elucidated based on the number of the CoMoS phase in the CVD-catalysts, leading to a new empirical model for the CoMoS structure. The model was supported by the magnetic study of CVD-Co/MoS$_2$/Al$_2$O$_3$. Furthermore, our recent study$^{14}$ has shown that the unique information on the maximum potential HDS activity of Co(Ni)-Mo(W) catalysts can be obtained, which is very helpful for the design of highly active HDS catalysts.

5. REFERENCES