

INFRARED SPECTROSCOPIC CHARACTERIZATION OF SULFIDE CLUSTER-DERIVED ENSEMBLES

JAMES R. BRENNER* AND LEVI T. THOMPSON**

* Argonne National Laboratory, Department of Chemistry, 9700 S. Cass Ave., Bldg. 200, Room C-113, Argonne, IL 60439

** The University of Michigan, Department of Chemical Engineering, 2300 Hayward Ave., 3230 H.H. Dow Bldg., Ann Arbor, MI 48109-2136

ABSTRACT

The transition metal sulfide clusters $(\text{MeCp})_2\text{Mo}_2(\mu\text{-SH})_2(\mu\text{-S})_2$, $(\text{MeCp})_2\text{Mo}_2\text{Co}_2(\mu_3\text{-S})_2(\mu_4\text{-S})(\text{CO})_4$ [MoCoS], and $(\text{MeCp})_2\text{Mo}_2\text{Fe}_2(\mu_3\text{-S})_2(\text{CO})_8$, (MeCp = methylcyclopentadienyl) were used to prepare $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts. For comparison, a series of supported materials was also prepared using conventional incipient wetness impregnation.

Infrared spectroscopy of adsorbed species was used to characterize the sites in the cluster-derived and conventionally prepared catalysts. Nitric oxide chemisorbed onto the MoCoS/A catalyst was associated initially only with Co sites and then upon gentle heating shifted to the Mo sites, indicating that Co and Mo were in close proximity. In contrast, NO adsorbed onto both Co and Mo sites in the conventionally prepared materials and desorbed independently from these two types of sites. Infrared spectra of adsorbed thiophene and pyridine were similar for the cluster-derived and conventionally prepared catalysts. Thiophene reacted at 100 °C to produce both olefinic species. The most abundant products from thiophene HDS were 1-butene, cis-2-butene, and trans-2-butene. Displacement studies showed that thiophene, pyridine, and NO adsorbed to the same site. The most active sites for HDS and HDN contained both Mo and a late transition metal. The HDN product distributions suggested that Mo was selective for C=N bond cleavage while the late transition metals were more active for C=C hydrogenolysis.

I. EXPERIMENTAL

Synthesis. The clusters $(\text{MeCp})_2\text{Mo}_2(\mu\text{-SH})_2(\mu\text{-S})_2$ [MoS], $(\text{MeCp})_2\text{Mo}_2\text{Fe}_2(\mu_3\text{-S})_2(\text{CO})_8$ [MoFeS], $(\text{MeCp})_2\text{Mo}_2\text{Co}_2(\mu_3\text{-S})_2(\mu_4\text{-S})(\text{CO})_4$ [MoCoS], $\text{Fe}(\mu\text{-S})_2(\text{CO})_6$ [FeS], and $\text{Cp}_4\text{Co}_4(\mu_3\text{-S})_2(\mu_3\text{-S}_2)_2$ [CoS] were synthesized according to procedures described in the literature (MeCp = methylcyclopentadienyl) [1-5]. Gamma-alumina (Catapal, 150 m²/g) was calcined at 500 °C in dry air for 5 hours. A solution of the desired sulfide cluster was added to a slurry of the support using standard Schlenk techniques to produce a total metal loading of 1.0 wt. %. The resulting slurry was stirred under N₂ for one hour before the solvent was evaporated off under vacuum and the materials stored under N₂. The cluster-derived catalysts have been coded K/A, where K denotes the type of cluster and A denotes $\gamma\text{-Al}_2\text{O}_3$. Transmission electron microscopy has shown the cluster-derived materials to be molecularly dispersed [6].

A second series of catalysts was prepared using conventional synthesis methods to provide a basis for comparison with the cluster-derived materials. Ammonium heptamolybdate and Co, Ni, or Fe nitrate salts were impregnated onto $\gamma\text{-Al}_2\text{O}_3$ to the point of incipient wetness (IW) sequentially with Mo first to produce nominal loadings of 1.0 wt. % total metal and a 1:1 atomic ratio of Mo to promoter. After each impregnation step, the resulting material was calcined in dry air at 500 °C for 5 hours. A series of 1 wt. % Fe, Co, and Ni oxides supported on $\gamma\text{-Al}_2\text{O}_3$ were also prepared via the incipient wetness impregnation of the metal nitrates. The calcined $\gamma\text{-Al}_2\text{O}_3$ -supported oxides were sulfided in flowing 2% H₂S/H₂ at 400 °C for at least 4 hours.

Infrared Spectroscopy. Thin wafers of the materials were pressed and infrared spectroscopy was performed inside a N₂-filled drybox. Details concerning the system are given elsewhere [6]. Because the cluster derived materials were air sensitive and the press could not be placed in the drybox, preparation of these materials involved pipetting a solution of the cluster in CH₂Cl₂ onto pressed wafers of calcined $\gamma\text{-Al}_2\text{O}_3$. Treatments were carried out by flowing gas

through a treatment cell at 100 ccm and 10 psig. Following a purge with flowing He at 100 ccm for one hour, the wafers were transferred under N₂ to the spectroscopy cell. The temperatures used for the adsorption of NO, thiophene, and pyridine were 25, 100 and 60 °C, respectively.

II. RESULTS AND DISCUSSION

Catalytic Properties. The hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities and product distributions of the sulfide cluster-derived catalysts have previously been shown to be similar to those of conventionally prepared, sulfided Mo-Co/A, Mo-Fe/A and Mo/A catalysts [6-9]. The HDS and HDN activities which are summarized in Table 1 suggest that the sulfide cluster-derived ensembles are adequate models of the active sites in commercial hydrotreatment catalysts.

Table 1 - Thiophene HDS and Pyridine HDN Activities

Catalyst	HDS Activity* (10 ³ mol/mol O ₂ /s)	ΔE _{act} (kJ/mole)	HDN Activity* (10 ⁶ mol/mol O ₂ /s)	ΔE _{act} (kJ/mole)
MoS/A	1.9	92	1.2	92
Mo/A IW	2.7	84	8.2	75
FeS/A	0.06	‡	1.3	142
MoFeS/A	4.3	79	5.2	79
Mo-Fe/A IW	3.8	71	13	172
CoS/A	0.07	‡	2.7	67
MoCoS/A	9.6	59	23	84
Mo-Co/A IW	7.3	92	48	105

*HDS and HDN activities at 365 °C and 1 atm

‡Too low to accurately measure

NO Adsorption. Evidence for NO adsorption on the γ-Al₂O₃ support was observed in the 1500-1700 cm⁻¹ range when the NO dose was greater than 15 minutes. The "NO-on-γ-Al₂O₃" features were much more significant for the cluster-derived materials than for the conventionally prepared sulfide catalysts. This observation may be a consequence of the reaction of aluminum carbonates produced during the decarbonylation of the clusters with NO. Nitric oxide saturated the Mo or promoter sites after 2 minutes of exposure; therefore, the NO dose was restricted to 2 minutes in all cases.

The infrared spectra of NO adsorbed on the MoS/A and conventionally prepared Mo/A IW catalysts were remarkably similar (Fig. 1). The band positions suggested that NO adsorbed onto Mo as a dinitrosyl [10]. The infrared spectra of NO adsorbed onto the cluster-derived MoFeS/A have been compared with those for conventionally prepared Mo-Fe/A IW, Mo/A IW, and Fe/A IW sulfide catalysts in Fig. 2. There was a significant degree of overlap between the peaks corresponding to the symmetric stretches of NO on Fe and Mo (~1800-1810 cm⁻¹). The assignment of the asymmetric NO stretches (1745 cm⁻¹ for Fe and 1700 cm⁻¹ for Mo) was clear, however. Spectra for the conventionally prepared Mo-Fe/A catalysts indicated that NO adsorbed onto both Fe and Mo. In contrast, character of the MoFeS/A catalyst appeared to be dominated by Fe. In fact, the spectrum for MoFeS/A was similar to that for the Fe/A IW catalyst.

Nitric oxide adsorption on Co/A gave rise to two peaks, one at ≈1865 cm⁻¹ and the other which overlapped the 1805 cm⁻¹ peak for Mo (Fig. 3). Nitric oxide adsorbed onto the conventionally prepared Mo-Co/A catalysts produced three peaks that were approximately but not exactly the weighted sum of the spectra of NO adsorbed onto the Co and Mo sulfides. The strong similarities of the spectra for the MoCoS/A and Co/A IW catalysts suggested that NO adsorption sites on the MoCoS/A catalyst were predominantly Co. Nitric oxide desorbed from the Mo and Co sites independently for the conventionally prepared Mo-Co/A IW materials.

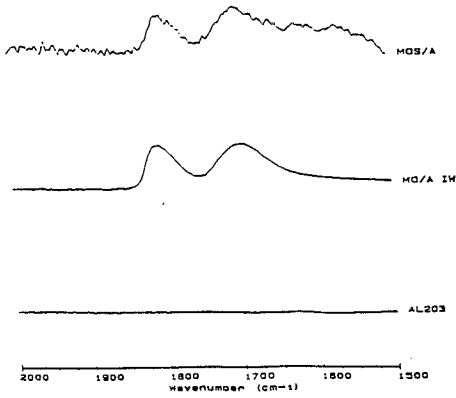


Fig. 1 - NO adsorption on Mo-containing catalysts and γ -Al₂O₃.

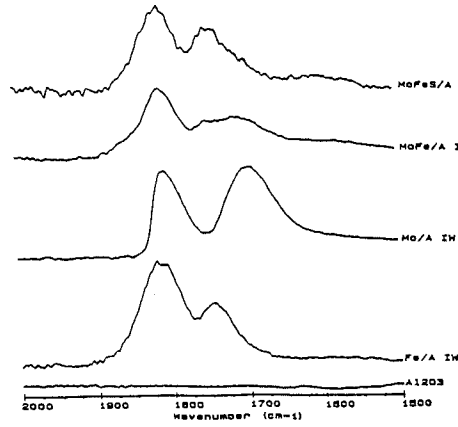


Fig. 2 - NO adsorption on Mo and Fe containing catalysts and γ -Al₂O₃.

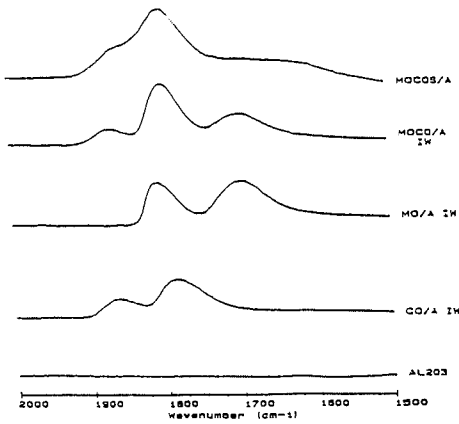


Fig. 3 - NO adsorption onto Mo- and/or Co-containing catalysts and γ -Al₂O₃.

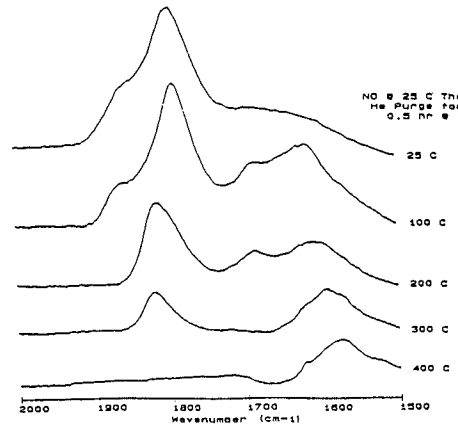


Fig. 4 - Desorption of NO from MoCoS/A catalyst.

For both the cluster-derived and conventionally prepared catalysts, NO desorbed from Co by 200 °C and from Mo between 200 and 300 °C. A series of spectra detailing the consequences of heating the MoCoS/A catalyst following NO adsorption is given in Fig. 4. Upon heating to 100 °C, the peak at 1865 cm⁻¹ (NO on Co) decreased with respect to the peak at 1805 cm⁻¹. Concomitantly, the intensity of the peak at 1692 cm⁻¹, consistent with NO associated with unpromoted sites, increased. This result was reproduced several times. The ratio of the areas of the symmetric (shifted from 1805 cm⁻¹ to 1820 cm⁻¹) and asymmetric (1692 cm⁻¹) NO-Mo stretches remained very high. After desorption at 300 °C, only the symmetric NO-Mo stretch was present. These results indicated that desorption of NO from Co had an effect on the bonding of NO to Mo and can be explained if either NO adsorption onto Co blocked NO adsorption onto Mo or if NO migrated from Co to Mo. Regardless of which explanation is correct, both imply that Mo and Co were in close enough proximity in MoCoS/A in that desorption of NO from Co had an effect on the bonding of NO to Mo.

Thiophene Adsorption. There were no C-H stretch features (3200-2800 cm⁻¹) attributable to thiophene on metal sulfides. The failure to detect these C-H stretch features was due both to the relatively low loadings (1 wt. % metal) employed and to the strong infrared absorption of γ -Al₂O₃ in this region. Spectra after thiophene adsorption for the cluster-derived catalysts are shown in Fig. 5. The strong similarities between the spectra of thiophene adsorbed onto cluster-derived and conventionally prepared catalysts again suggested that the sulfide cluster-derived ensembles modeled sites in conventionally prepared sulfide catalysts.

A sharp peak at 1253 cm⁻¹ was observed only for the Mo-containing catalysts suggesting that thiophene adsorbed onto Mo. This feature is expected for the in-plane C-H bending of liquid and vapor-phase thiophene [11]. The C=C stretching frequencies at 1680 and 1470 cm⁻¹ were absent in spectra of the cluster-derived catalysts. This observation is consistent with π -bound thiophene as opposed to S-bound thiophene. Features in the 1700-1850 cm⁻¹ range were observed for all the catalysts. This range is too high to be attributable to aromatic C=C stretches and is more consistent with olefinic C=C stretches, suggesting that opening of the thiophene ring had occurred by 100 °C. The band at 1850 cm⁻¹ indicated the presence of a terminal olefin; there are no C-H, C-S, S-H or other C=C vibrational modes between 1800 and 2000 cm⁻¹.

Much of the thiophene desorbed between 100 and 200 °C. The olefin desorption temperature was approximately 300 °C for the MoCoS/A catalyst. The temperature for olefin desorption from the MoS/A and MoFeS/A catalysts was between 300 and 400 °C. Reduction at 400 °C was sufficient to regenerate all the catalysts.

Pyridine Adsorption. The adsorption of pyridine onto the cluster-derived materials and blank γ -Al₂O₃ is shown in Fig. 6. The spectra for the Mo-containing materials contained a band at 1595 cm⁻¹. This band was not observed for the Co/A, Fe/A, and Ni/A materials. Pyridine populated the γ -Al₂O₃ first and then filled the Mo sites. This suggested that the Mo sites were less acidic than those on γ -Al₂O₃. Pyridine desorbed upon He purging at 100 °C.

Adsorbate Displacement Studies. Exposures to thiophene of up to 5 hours did not significantly influence the spectrum of an MoS/A catalyst that had been dosed with NO (Fig. 7). The NO; however, was completely removed upon H₂ reduction at 400 °C. A subsequent one-hour thiophene exposure at 100 °C produced both the thiophene-on-Mo vibration at 1253 cm⁻¹ and the C=C stretch at 1800 cm⁻¹. The vibrational frequencies for NO and C=C bonds overlap, so it was not entirely clear whether or not NO displaced the olefinic species. Nonetheless, it was clear that NO displaced the thiophene that had adsorbed to Mo. Nitric oxide also completely displaced thiophene from Mo sites in the MoFeS/A and MoCoS/A catalysts. The NO and C=C stretching frequencies also overlapped for the MoFeS/A and MoCoS/A catalysts. Recall that most of the olefin adsorbed to the bimetallic catalysts was adsorbed to the late transition metal. Therefore, it was not clear whether NO displaced olefin from either Mo or the late transition metal sites.

For both the cluster-derived and conventionally prepared catalysts, pyridine adsorbed at 60 °C displaced all of the NO adsorbed at 25 °C (Fig. 8 for MoS/A). Much of this pyridine was displaced upon NO readsorption.

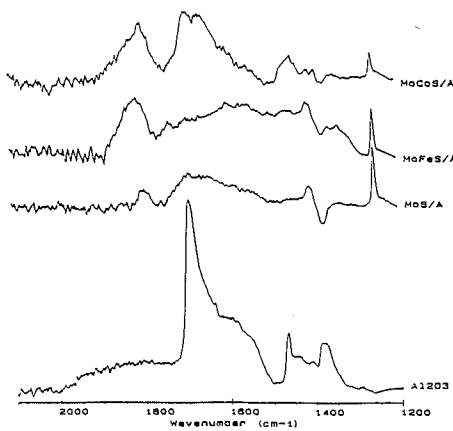


Fig. 5 - Thiophene adsorption onto cluster-derived catalysts and γ -Al₂O₃.

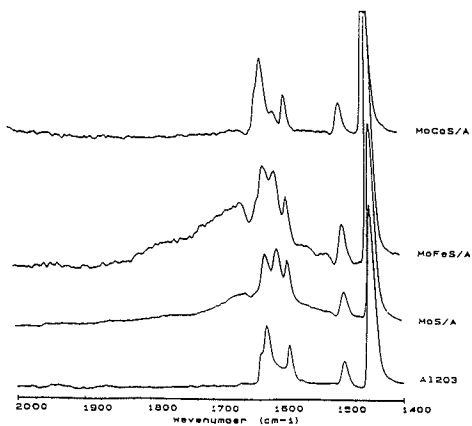


Fig. 6 - Pyridine adsorption onto cluster-derived catalysts and γ -Al₂O₃.

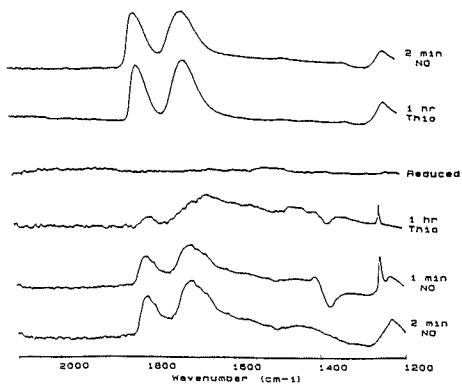


Fig. 7 - NO displacement by thiophene for MoS/A catalyst.

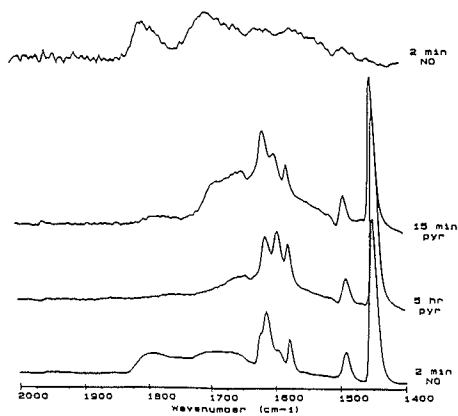


Fig. 8 - Pyridine displacement by NO and vice versa for MoS/A catalyst.

III. CONCLUSIONS

Infrared spectroscopic results indicated that the character of active sites derived from the sulfide clusters closely resembled that of sites present on the surfaces of conventionally prepared unpromoted and promoted Mo sulfide hydrotreatment catalysts. In particular, the positions and relative intensities of bands for NO adsorbed on the sulfide cluster derived ensembles were similar to those for the conventionally prepared HDS/HDN catalysts. This conclusion is consistent with our earlier findings that the catalytic properties of the cluster derived and conventionally prepared catalysts were similar. Evidence was also presented which suggested that Mo and the promoter element (Co or Fe) were in close proximity to each other. It is plausible, but not verified, that Mo and the promoter were bonded together forming highly dispersed cluster derived ensembles. Finally, our results indicated that the hydrogenolysis of C-S bonds in thiophene is facile while the hydrogenation of surface-bound sulfur is the rate limiting step during HDS over the cluster derived catalysts.

IV. REFERENCES

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