

**Catalyst
Characterization
Science**

Catalyst Characterization Science

Surface and Solid State Chemistry

Marvin L. Deviney, EDITOR

Ashland Chemical Company

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FOREWORD

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PREFACE

AS THE GROWTH OF INDUSTRIAL heterogeneous catalysis continues to accelerate, the role and contributions of surface scientists and mechanism specialists become increasingly vital. Scientists in these fields are making major efforts to keep pace by developing the fundamental techniques to provide the basic knowledge needed to sustain rapid progress in basic and applied catalysis. Many recent developments in our ability to characterize catalytic materials and reaction mechanisms have resulted in important advances in our understanding of catalytic phenomena. This book highlights a large number of these major new developments in catalyst characterization science, involving both surface and solid state chemistry.

We would like to thank the Colloid and Surface Chemistry Division and the Petroleum Chemistry Division of the American Chemical Society for their support and encouragement. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this activity. The encouragement of Ashland Chemical Company, Exxon Research and Engineering Company, and General Motors Research Laboratory is gratefully acknowledged, and special thanks is expressed to James D. Idol, Andrew Kaldor, and John Larson. The excellent cooperation of the many authors and coauthors of the chapters included in this book is sincerely appreciated. Finally, we would like to thank our families, particularly our wives, Marie Deviney and Wanda Gland, for their patience and continuous support.

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MULTIPLE SURFACE TECHNIQUES ON COMPLEX CATALYST SYSTEMS

Arsenic Poisoning of Hydrodesulfurization Catalysts

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X-ray photoelectron spectroscopy (XPS), Mössbauer emission spectroscopy (MES), and activity tests show that arsenic poisons hydrodesulfurization (HDS) catalysts by affecting the chemical nature of the sulfided catalyst. Activity tests show that Co-Mo/ Al_2O_3 and Mo/ Al_2O_3 catalysts are deactivated when arsenic is added to the catalyst, either as a contaminant from the reactor feed or as As_2O_5 by laboratory impregnation. XPS shows one form of arsenic, As^{+5} , on the calcined catalyst and two forms, probably As^{+3} and As^0 , on the sulfided catalyst. XPS also shows sintering of the molybdenum on the sulfided catalyst. We have used MES to study the effect of arsenic on the Co-Mo-S phase (believed to be active for HDS). Arsenic does not destroy this structure, but alters its electronic state. The arsenic appears to be interacting strongly with the cobalt, possibly filling the anion vacancies with atoms or clusters.

Arsenic poisoning of catalysts, particularly reforming and hydrotreating catalysts, is a long standing problem. Interest in shale oil refining emphasized this problem, as shale oils often contain 20-40 ppm arsenic. In this study we have used several methods to clarify the nature of arsenic poisoning on hydrodesulfurization (HDS) catalysts. HDS activity tests were used to determine the extent of poisoning. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Mössbauer emission spectroscopy (MES) have been used to study metals on the catalyst and to identify specific compounds where possible.

Co-Mo/ Al_2O_3 catalysts have been studied extensively, both for their structure and reaction mechanisms, and many studies have been reported in the literature (1-14). However, the HDS activity is not completely understood and many conflicting views have been reported. No attempt is made here to explain the HDS mechanism,

but only to describe the state of arsenic on these catalysts and its effect on activity.

Experimental

Catalyst Preparation. Most samples were prepared using a Ketjen alumina (1/16 inch extrudate with 280 m²/g surface area and 0.71 ml/g pore volume) and the incipient wetness technique for impregnation. Catalysts were stirred on a hot plate until visibly dry, dried overnight in a 100°C oven, and calcined in air at 500°C for three hours. Ammonium paramolybdate, cobalt nitrate, and arsenic pentoxide solutions were used, with drying and calcining after each addition. Molybdenum was always added first, followed by cobalt where applicable, then the arsenic. On catalysts with high loadings of arsenic, some arsenic was lost during calcination and sulfiding. Catalyst compositions as determined by X-ray fluorescence are given in Table I. Another sample, a Catapal N alumina, was coimpregnated with 9.9% Co and 8.5 % As for use as a reference material.

Table I. Catalyst Composition by X-Ray Fluorescence (Wt. %)

Catalyst	Mo	Co	As
Mo/Al ₂ O ₃	8.9		
Mo/Al ₂ O ₃ + As	7.9		3.6
Co-Mo/Al ₂ O ₃	9.6	2.4	
Co-Mo/Al ₂ O ₃ + As	8.6	2.2	3.9
Co-Mo/Al ₂ O ₃ + As (Used Catalyst)	8.4	1.9	3.6

Arsenic was added to an American Cyanamid HDS-2 catalyst for comparison with a used catalyst containing 3.6% As. This used catalyst was also an American Cyanamid HDS-2 catalyst which had been in service in a refinery distillate HDS unit for about six years. Again, X-ray fluorescence determined compositions are in Table I.

The same Ketjen alumina described earlier was used for the Mössbauer experiments. The samples were prepared identically, with the following exceptions. The extrudate was ground to 20-40 mesh before impregnation, and 0.5 gram samples were prepared using 2 mCi of Co⁵⁷. The samples were prepared to give 8.9% Mo and 1.2% Co (Co/Mo = 0.21). These samples were not analyzed, but the arsenic compositions based on the preparation are given in Table IV.

Catalyst Sulfiding. The calcined samples were sulfided prior to XPS examination by purging the sample at room temperature with nitrogen, heating to 149°C, then switching to 10% H₂S in hydrogen and raising the temperature gradually over a four hour period to 316°C. After cooling in H₂S/H₂, the sample was flushed in nitrogen and placed in a glove box. There it was loaded onto the XPS sample holder and transported to the spectrometer in an air-tight carrier.

Sulfiding for the Mössbauer experiments was similar. All conditions were identical except an 8% H₂S/H₂ blend was used. Figure

1 shows the reactor used for calcining and sulfiding the radioactive samples. The sample was transferred to the Mössbauer cell without exposure to air and transported to the spectrometer.

Presulfiding for the activity tests was accomplished by first heating the catalyst in nitrogen at 204°C. 10% H₂S/H₂ was introduced at this temperature and allowed to flow over the catalyst for five hours. The temperature was then raised gradually to 371°C and held for an additional five hours. The catalyst was cooled in nitrogen.

XPS Measurements. XPS measurements were performed using a Physical Electronics Model 548 electron spectrometer with Al K α radiation (1486.6 eV). The spectrometer was interfaced to a Hewlett-Packard 21MX computer for data acquisition and manipulation. The instrument was operated at about 2×10^{-9} torr, with the samples being introduced into the ultrahigh vacuum from a prechamber evacuated to about 1×10^{-6} torr. Binding energies were referenced to Au 4f(7/2) at 84.0 eV. A thin film of gold was evaporated onto the sample after a complete set of spectra had been obtained, and another set of spectra was then taken. On the supported samples, binding energies were referenced to the Al 2s peak at 119.6 eV, as determined by gold referencing. The surface concentrations given in Table III are determined relative to the Al 2s peak as 100 using Scofield's cross sections (15) and the method of calculation described by Carter et al. (16).

Pretreatment of the samples was performed in the prechamber of the spectrometer, except for the sulfiding described previously. Catalysts were calcined in air at 500°C for one hour, or reduced in hydrogen at 310°C or 350°C for up to four hours. The prechamber was then evacuated and the sample introduced into the spectrometer without exposure to the atmosphere.

For the XPS work, reference materials were examined to establish binding energies for the various arsenic oxidation states. Arsenic metal, As₂O₃, As₂S₂, As₂S₃, all from Ventron, and As₂O₅ from J. T. Baker Chemicals were used. The arsenic metal powder was imbedded in indium foil for examination. An arsenic mirror formed on a reaction flask was also examined.

HDS Activity Measurements. HDS activity measurements were made isothermally in a 3/4 inch i.d. high pressure trickle bed reactor. Catalysts were ground to 20-40 mesh and diluted with alundum (37.5cc alundum to 12.5cc catalyst). After presulfiding, light cycle oil (a cracking product boiling between 177°C and 343°C and containing 1.7 wt % sulfur) was introduced along with hydrogen (7 moles H₂/mole feed). Most of the sulfur in the oil was present as benzothiophenes and dibenzothiophenes. The reaction was run at 600 psig and 4.0 LHSV. A temperature survey was made from 257°C to 357°C at 14°C intervals over a sixty hour period.

Mössbauer. The Mössbauer emission spectroscopy measurements were made using the Co⁵⁷ doped catalyst as a stationary source. The moving absorber was Fe⁵⁷ enriched K₄Fe(CN)₆·3H₂O. Both the Co⁵⁷ and the absorber were obtained from New England Nuclear. The con-

stant acceleration mode Mössbauer spectrometer was calibrated using a source of Co^{57} in palladium and an adsorber of enriched Fe^{57} iron foil. The catalyst samples were loaded into a glass cell with a one inch diameter beryllium window. Spectra were accumulated for at least 24 hours and fit by computer for Lorentzian curves using a least squares fit.

Results and Discussions

Activity Tests. Figure 2 shows results of activity tests for a commercial American Cyanamid HDS-2 catalyst which had been in use for about six years. The catalyst was sampled at various depths and results for three samples containing 0.01% As, 0.6% As, and 3.6% As show a decrease in activity with increasing arsenic content. A similar catalyst to which 3.9% arsenic had been added in the laboratory was tested and its activity (Figure 3) compared to the activity of a fresh catalyst and also to that of the used catalyst. The activity loss of the used catalyst containing 3.6% As corresponds closely with that for the prepared sample, indicating that arsenic added by impregnation acts like that deposited under actual operating conditions. When the used catalysts were regenerated in air at 482°C , the arsenic was not removed.

The molybdenum on alumina catalyst was also tested for activity with and without arsenic. Although this catalyst has a much lower intrinsic activity for HDS, the results in Figure 4 show that 3.6% arsenic almost completely deactivates the catalyst. The small amount of activity remaining is that expected for Al_2O_3 alone. Thus arsenic also deactivates catalysts without cobalt promoters.

XPS. Several bulk materials and one supported sample were examined by XPS to establish binding energies for the arsenic. These values, given in Table II, correspond closely to those reported in the literature (17-19). The binding energy found for As_2O_5 on alumina is comparable to that found on the bulk As_2O_5 , indicating that the values for supported arsenic should be similar to those for the bulk materials.

Table II. XPS Binding Energies for Arsenic Reference Materials

	As 3d Be(eV)		As 3d Be(eV)
As metal	41.9	$\text{As}_2\text{S}_2(\text{As}_4\text{S}_4)$	42.4
As mirrored on flask	41.7		
As_2O_3	45.2	As_2S_3	42.8
As_2O_5	45.6	$\text{As}_2\text{O}_5/\text{Al}_2\text{O}_3$	45.5

XPS spectra were obtained for the catalysts in the calcined, sulfided, and sometimes in the reduced state, as described before. Table III gives the binding energies and relative surface concentrations for the $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts, with and without arsenic. Data for the used catalysts, which are not listed in the table, are similar to those for the catalysts prepared in the laboratory.

Table III. XPS Results on Prepared Samples

	As 3d		Mo3P		Co 2P		S 2P		As Auger	
	BE(eV)	RSC ^a	BE(eV)	RSC ^a	BE(eV)	RSC ^a	BE(eV)	RSC ^a	KE(eV)	RSC ^a
<u>Mo/Al₂O₃</u>										
Calcined			399.1	9.93						
Presulfided			399.0	1.92			162.2	11.9		
			395.2	4.71						
<u>Mo/Al₂O₃ + As</u>										
Calcined	45.9	4.94	399.3	6.99					1217	
Presulfided	44.8	1.24	398.1	1.45					1218	
	41.9	2.16	395.3	3.22			162.2	8.7	1224	
<u>Co-Mo/Al₂O₃</u>										
Calcined			398.9	7.15	782.5	2.29				
Presulfided			399.3	1.72	782.2	{2.21	162.2	12.5		
			395.2	4.00	779.1					
<u>Co-Mo/Al₂O₃ + As</u>										
Calcined	45.1	5.44	398.8	6.04	782.3	1.96			1218	
Presulfided	44.4	1.50	398.7	1.70	782.1	{1.98			1218	
	42.0	2.55	394.9	3.15	779.1		162.1	10.1	1225	
<u>Co-As/Al₂O₃ (Coprecipitated)</u>										
Dried	45.6	15.4			782.3	17.1			1218	
Presulfided	41.2	15.9			777.9	16.2	161.9	12.1	1226	
Reduced	44.8	4.7			781.7	{23.2			1218	
	40.9	18.9			777.6				1226	

a. Relative Surface Concentration, ratioed to Al 2S as 100.

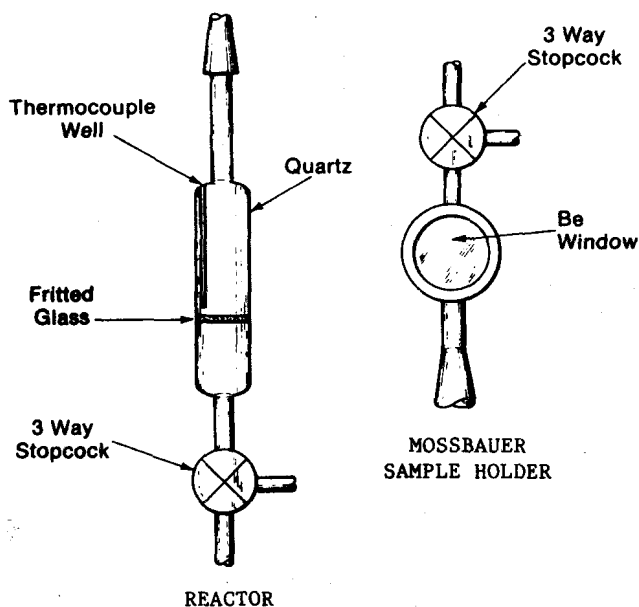


Figure 1. Sample reactor and Mössbauer cell.

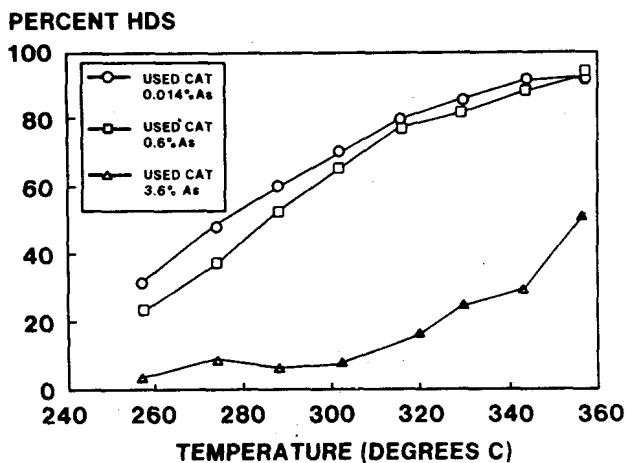


Figure 2. HDS activity of poisoned plant catalysts.