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Synthesis of Transition Metal Arsenides and Arsenic Metal Sulfides and Their Role in the Dearsenation of Shale Oils

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One of the chief problems in upgrading shale oil is the presence of inherent arsenic, which is known to poison downstream catalysts. Highly dispersed transition metal sulfides formed *in situ* from the decomposition of dithiocarbamate (DTC) complexes of transition metals show excellent potential as dearsenation agents. We have studied the reaction of these sulfides with various arsenic compositions, and characterized the metal arsenides and arsenic metal sulfides formed as well as the ease of their formation. Thus, the reaction of bis(butyldithiocarbamato)Ni, (NiBuDTC), with model compounds was very facile and gave NiAs, NiAsS, and $NiAs_{2-x}S_x$. In general the effectiveness of the sulfides for dearsenation followed the sequence Ni > Mo ≫ Co, while iron sulfides were totally ineffective. Based upon these results, tests where run in autoclaves (as well as a fixed-bed flow-through unit) with Ni BuDTC and shale oil having 73 ppm inherent As. Under optimum conditions, dearsenation down to less than 1 ppm was obtained.

INTRODUCTION

Upgrading of oil derived from oil shale is a very demanding and challenging task. In contrast to similar oils from petroleum feeds, shale oil as well as other synthetic liquids contains a high concentration of nitrogen relative to sulfur. In the synthetic fuels category, shale oil is beset with additional problems. Thus, shale oil obtained from retorting oil shale contains a significant amount of fines, which can be as high as 10% or more of the heavy oil. In addition, depending upon the source, shale oil contains 10–100 ppm of arsenic both as oxides and as organic complexes. Since arsenic is an acute poison for downstream upgrading catalysts, its concentration must be reduced to less than 1 ppm. Metal oxides and sulfides on supports such as Al_2O_3 are used as adsorbents and reactants (1) for arsenic compounds. Irreversible plugging problems associated with fixed beds (2) in the presence of significant amounts of fines are obvious. Therefore, for a viable process the material used for dearsenation should not be affected by the presence of large amounts of fines. Similarly, the disposal of spent guard beds which cannot be easily regenerated poses significant toxicological and environmental problems (3, 4).

As a prelude to studying the dearsenation of shale oils we have studied the reactions involved in the synthesis of As–Metal and As–Metal–S compounds by the interaction of dithiolato complexes, primarily dithiocarbamates (DTCs) of Ni, Co, Fe, and Mo. In another paper, the decomposition of DTCs of Ni, Co, Fe, and Mo to give the corresponding metal sulfides is described (5). This paper presents the synthesis of As–Metal and As–Metal–S compounds by the reaction of *in situ* formed metal sulfides with arsenic compounds as well as its application to the dearsenation of shale oil.

EXPERIMENTAL

Kerosene was obtained from Exxon Baton Rouge refinery. For most of the work a shale oil obtained by retorting Colorado shale by the Paraho process (designated here as Paraho shale oil) was used; it contained 73 ppm As. In some cases shale oil obtained by the Exxon shale retort process was also used, which contained 14 ppm of arsenic. Arsenic(III) oxide and phenylarsonic acid were obtained from Alfa Products. Arsenic metal powder was purchased from Cerac, and tributylarsine was obtained from Pfaltz & Bauer.

Dioxobis(dibutyldithiocarbamato)molybdenum ($MoO_2DiBuDTC$) was prepared according to the method of Singhal (6). Metal DTCs other than Mo were prepared by one of the general methods given in the review by Coucouvanis (7) or as described by Singhal *et al.* (8). All the complexes were crystallized from suitable solvents to give compounds with sharp melting/decomposition points. All the compounds gave acceptable elemental analyses, and their physical characterization by IR spectroscopy or H^1 NMR was consistent with the structure.

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Abbreviations Used for Dithiolato Complexes

Compound name	Abbreviation	Compound name	Abbreviation
Bis(*N*-butyldithiocarbamato)Ni	NiBuDTC	Bis(*N*, *N*-dibutyldithiocarbamato)Ni	NiDiBuDTC
Bis(butylxanthato)Ni	NiBuX	Tris(*N*, *N*-dibutyldithiocarbamato)Fe	FeDiBuDTC
Dioxobis(dibutyldithiocarbamato)Mo	MoO_2DiBuDTC	Tris(*N*, *N*-dibutyldithiocarbamato)Co	CoDiBuDTC

Procedure

Reactions aimed at studying the synthesis of metal arsenides and arsenic metal sulfides were carried out in a 300-ml stirred autoclave. Mixtures of transition metal DTC, arsenic model compound, and solvent were allowed to react under different conditions. Details of the experimental conditions are given in Tables 1 and 2. After the experiment, the residue was collected by filtration, washed with a suitable solvent, dried, and analyzed by X-ray diffraction. Experiments aimed at dearsenation of shale oil were carried out either in a 300-ml stirred autoclave or in a small continuous flow-through unit. As given in Table 3, a few experiments to ascertain the effect of actual shale fines on dearsenation were also carried out. In dearsenation experiments, arsenic in solution was analyzed by X-ray fluorescence.

RESULTS AND DISCUSSION

Dithiolato complexes of Ni, such as DTCs or xanthates, are very effective in reacting with arsenic model compounds as well as with the arsenic compounds present in shale oil. During initial heatup, decomposition of NiBuDTC produces the active catalyst NiS. This sulfide effectively scavenges a variety of arsenic compounds to give gersdorffite, NiAsS. This reaction takes place both in N_2 and in H_2 environment. In H_2 atmosphere, gersdorffite reacts further to give niccolite. NiAs, and H_2S. However, if excess arsenic is present, an arsenic-rich form of gersdorffite ($NiAs_{2-x}S_X$) is formed. These transformations are given in Fig. 1 as well as in Table 1. As shown in Fig. 2, the effective utilization of nickel depends on the Ni/As ratio. A system with excessive Ni present will form $Ni_{11}As_8$ (maucherite) and Ni_7S_6 (godlevskite), whereas a system deficient in nickel can yield $NiAs_2$ (rammelsbergite).

The complexes of other metals, Mo, Co, and Fe also decompose in a similar way to give molybdenite (MoS_2), CoS_X, and pyrrhotite ($Fe_{1-x}S$), respectively. These results are presented in Table 2. The molybdenite formed from MoO_2DiBuDTC is very effective in removing many forms of arsenic. However, the molybdenum arsenides are formed as amorphous compounds and thus could not be characterized by X-ray diffraction. Elemental analysis of the product showed it to be composed primarily (>95%) of Mo and As. Several molybdenum arsenides, including $MoAs_2$ and Mo_5As_4 have been reported (9).

In the case of CoS_X from CoDiBuDTC, CoAsS was formed in the presence of arsenic compounds under autoclave conditions. No evidence for its reduction in hydrogen to form cobalt arsenide was found.

As shown in Table 2, the pyrrhotite formed from FeDi BuDTC did not react with arsenic compounds under autoclave conditions. It should be pointed out that in the absence of sulfur compounds both iron and iron oxalate react with arsenic compounds to give iron arsenides:

TABLE 1

Reaction Products from NiBuDTC with Arsenic Compounds[a]

Run no.	NiBuDTC (g)	As compound	Amount (g)	T(°F)	Gas used	Pressure (psig)	Time (Hr)	Products obtained
1	3.552	As_2O_3	1.001	550	N_2	500	2	NiAsS
2	8.901	As_2O_3	1.000	550	N_2	500	2	NiAsS, NiS
3	8.913	As_2O_3	1.002	550	H_2	1000	2	NiAsS, NiS, NiAs
4	2.660	As_2O_3	0.730	650	H_2	500	1	NiAsS, NiAs
5	1.320	As_2O_3	0.370	650	H_2	1000	1	NiAs
6	5.610	Bu_3As	3.694	650	H_2	500	3	NiAsS
7	1.320	As	0.280	650	H_2	500	1	NiAsS
8	2.110	As_2O_3	0.200	650	H_2	1000	2	$Ni_{11}As_8$
9	2.213	$PhAsO_3H$	1.005	600	H_2	500	2	NiAs

[a] In all the runs 60 g of kerosene was used.

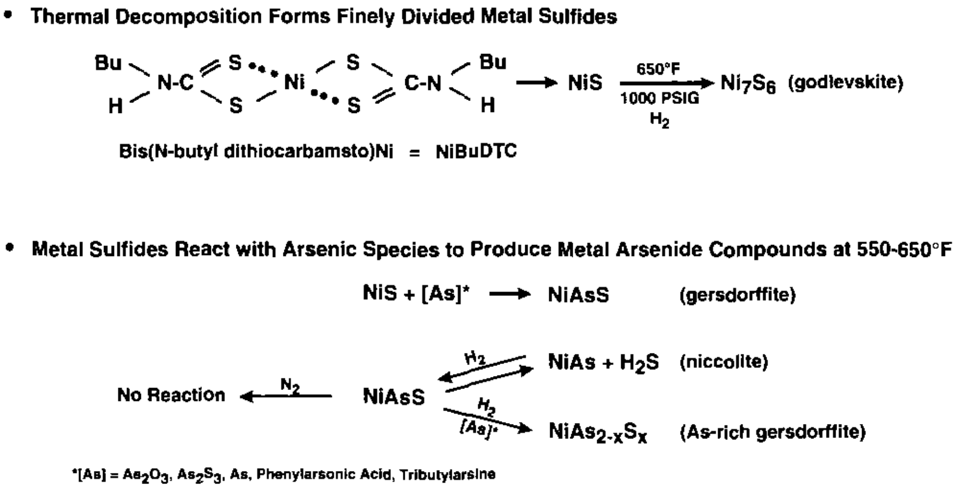

FIG. 1. Reaction of *in situ* formed NiS with arsenic compounds.

$$2\text{Fe} + \text{As}_2\text{O}_3 \xrightarrow[\text{2 hr, 650°F}]{\text{1000 psi H}_2} 2\ \text{FeAs (westerveldite)}$$

$$\text{FeC}_2\text{O}_4 + \text{As}_2\text{O}_3 \xrightarrow[\text{2 hr, 650°F}]{\text{1000 psi H}_2} \text{FeAs}_2\ \text{(loellingite).}$$

However, as is well known, shale oil contains significant amounts of sulfur compounds. Similarly, in the absence of sulfur compounds, cobalt acetonylacetonate reacts with arsenic to form CoAs.

$$\text{Co(II) (acac)}_2 + 1/2\ \text{As}_2\text{O}_3 \xrightarrow[\text{2 hr, 650°F}]{\text{H}_2} \text{CoAs (modderite).}$$

Using NiBuDTC as the catalyst, the effect of temperature and time on arsenic removal from Paraho shale oil was measured. These results are presented in Fig. 3. It is clear that dearsenation is temperature dependent between 550 and 675°F. The effectiveness of NiBuDTC in removing arsenic is not impaired by the presence of large quantities (~10%) of mineral fines in the shale oil. Since shale oil produced by retorting contains significant amounts of fines, this property is critical for any effective material. As shown in Table 3, NiBuDTC shows similar dearsenation of shale oil in the presence or absence of high fines loading from two different oil shales.

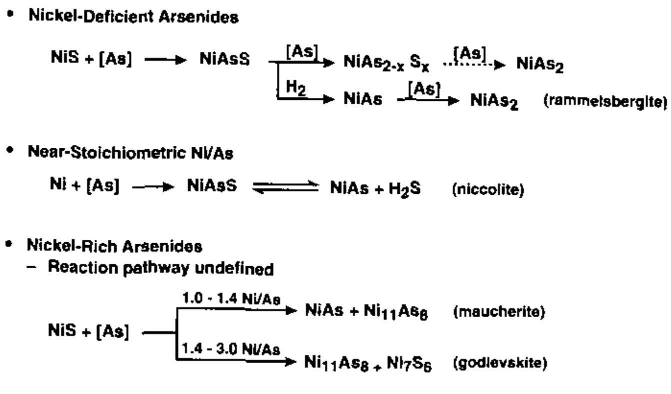

FIG. 2. Dependence of Ni utilization upon Ni/As ratio.

CONCLUSIONS

Dithiolato metal organic complexes offer a unique method for dearsenation of shale oils. Competitive experiments show that the order of activity for the metals is NiS > $\text{MoS}_2 \gg \text{CoS}_x \gg \text{Fe}_{1-x}\text{S}$ (ineffective). From experiments using Fe complexes, no iron arsenides or iron arsenic sulfides were observed, indicating low reactivity of iron sulfides for scavenging arsenic compounds from shale oil. The inactivity of iron sulfides is surprising in view of the suggestions made for the association of arsenic and iron sulfide minerals (10, 11). Experiments with

TABLE 2

Reaction of Other Metal Organic Complexes with As_2O_3[a]

Run no.	Metal organic complex	As compound	Products formed
10	MoO_2DiBuDTC	As_2O_3	MoAs_2 or Mo_5As_4
11	CoDiBuDTC	As_2O_3	CoAsS
12	NiBuX	As_2O_3	NiAsS
13	NiDiBuDTC	As_2O_3	NiAsS
14	FeDiBuDTC	As_2O_3	Fe_{1-x}S, As^0

[a] All the runs were carried out in a 300-ml stirred autoclave at 650°F under 1000 psig H_2 for 2 hr in 60 g of kerosene.

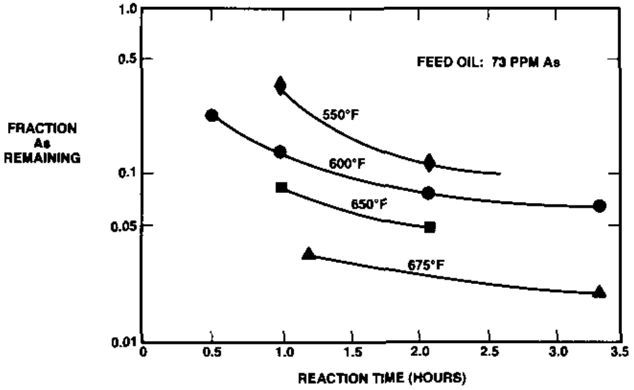

FIG. 3. Effect of temperature and time on arsenic removal. Feed, Paraho shale oil; catalyst, NiBuDTC; pressure-1000 psig H_2.

TABLE 3

Dearsenation of Paraho Shale Oil with NiBuDTC in the Presence or Absence of Fines[a]

Run no.	Description of shale fines	Weight of fines (g)	ppm As in product	% Dearsenation
15	None		1.6	97.8
16	Kerosene Creek shale fines	10	1.1	98.4
17	Colorado shale fines	10	2.55	96.5

[a] All the runs were carried out with 100 g of Paraho shale oil, 1 g of NiBuDTC, and 0.5 g of CS_2, at 600°F for 2 hr under H_2 pressure of 500 psig.

NiBuDTC clearly demonstrate that the reactions of the dithiocarbamate with arsenic compounds present in shale oil are not hindered by the presence of solids such as shale oil fines; even at 600°F the arsenic levels in shale oil were reduced from 73 ppm to 1–2 ppm. Flow-through dearsenation results were almost identical to the results given for autoclaves. In view of this observation, this process should be considered as a viable approach for shale oil dearsenation.

REFERENCES

1. D. J. Curtin, U. S. Patent No. 3,954,603 (1976).
2. G. H. Singhal and D. F. Ryan, U. S. Patent No. 4,853,110 (1989).
3. T. D. Nevens, W. J. Culbertson, Jr., J. R. Wallace, G. C. Taylor, A. P. Javanovich, and C. H. Prien, U. S. DOE Report COO-5107-1, July 1979.
4. L. B. Gurley, R. A. Tobey, J. G. Valdez, M. S. Halleck, and S. Bahrman, *Sci. Total Environ* **28,** 415 (1983).
5. G. H. Singhal, R. I. Botto, L. D. Brown, and K. S. Colle, *J. Solid State Chem.*, in press.
6. G. H. Singhal, U. S. Patent No. 4,683, 316 (1987).
7. D. Coucouvanis, *Prog. Inorg. Chem.* **11,** 233 (1977).
8. G. H. Singhal, B. L. Wilson, E. H. Edelson, and M. A. Mikita, U. S. Patent No. 5,064,527 (1991).
9. F. A. Shunk, "Constitution of Binary Alloys, Second Supplement," p. 56. McGraw–Hill, New York, 1969.
10. J. Jaganathan, M. S. Mohan, and R. A. Zingaro, *Fuel* **65,** 266 (1986).
11. G. A. Desborough, J. K. Pitman, and C. Huffman, Jr., *Chem. Geol.* **17,** 13 (1976).