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OIL SAND BITUMEN AND ON COAL HYDROGENOLYSIS

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The Effect of Tin Catalysts on Hydrorefining
of Athabasca Oil Sand Bitumen and on Coal Hydrogenolysis

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INTRODUCTION

The development of catalysts for up-grading of Canadian oil-sand bitumen and for conversion of coal into liquid products has been of considerable interest at the Energy Research Laboratories. The study reported below was part of an investigation of the suitability of different catalyst systems for hydrocracking heavy oils, and involved the use of tin compounds with bitumen and heavy oil feeds.

Tin compounds have generally been found to be particularly effective in coal hydrogenation processes (1-4). Recent studies have included the use of tin catalysts in hydrorefining of coal-derived feeds such as asphaltenes (3) and solvent refined coal (4). Although much attention has been given to the activity of supported and unsupported tin catalysts, little effort has been made to examine the fate of the tin during the liquefaction process.

Guided by the outcome of previously published work, a series of tin-containing catalysts was tested for bitumen and coal up-grading. Emphasis was placed on studying the changes occurring within the catalysts during these processes. Results obtained in preliminary tests stimulated further development such as the use of different methods of catalyst preparation.

EXPERIMENTAL

Feedstocks and Equipment

Athabasca bitumen was obtained from Great Canadian Oil Sands, Fort McMurray, Alberta, Canada, and some of its properties are given in Table I. Asphaltene feedstock from bitumen was obtained by precipitating the asphaltenes by addition of pentane to bitumen according to the ASTM method (7). High volatile Devco 26 coal was obtained from Cape Breton Development Corporation, Nova Scotia, Canada. The properties of this coal are given in Table II.

TABLE I

Properties of Athabasca Bitumen

Specific gravity	1.009 (15/15°C)	Benzene insolubles	0.72	wt%
Sulphur	4.48	Carbon	86.36	wt%
Ash	0.59	Hydrogen	10.52	wt%
Conradson carbon residue	13.3	Nitrogen	0.45	wt%
Pentane insolubles	15.5	Pitch (524°C+)	51.5	wt%

TABLE II

Properties of Devco 26 Coal
(High Volatile Bituminous A)

Proximate Analysis wt%		Ultimate Analysis wt%		Petrographic Analysis vol%	
Moisture	1.13	Carbon	83.97	Vitrinite	77.8
Ash	2.18	Hydrogen	5.36	Exinite	6.6
Volatile matter	31.35	Sulphur	0.62	Micrinite	3.6
Fixed carbon	65.34	Nitrogen	1.80	Semi-fusinite	8.8
		Oxygen (by dif)	4.94	Fusinite	2.6
				Pyrite	0.6

Bitumen tests were carried out in a bench-scale fixed bed reactor having a volume of 155 cm³, a length to diameter ratio of 12 and a continuous up-flow arrangement (5). Experiments were performed at a pressure of 13.9 MPa, a liquid volumetric space velocity of 0.278 ks⁻¹ (1.0 h⁻¹) based on the reactor volume and a hydrogen (electrolytic) flow rate of 37.5 cm³s⁻¹ at STP (5000 cu ft/bbl). The temperature range was 420^o-460^oC.

A batch shaker autoclave, into which about 25 g of coal was charged, was used for experiments involving coal hydrogenolysis. The runs were carried out without a vehicle oil, at an initial (cold) hydrogen pressure of 6.5 MPa and a temperature of 350^oC for 2 hours.

Optical microscopic examinations of the catalysts were made before and after use and were complemented by electron microprobe analysis.

Catalyst Description and Preparation

The catalysts tested with bitumen were alumina-supported and were prepared as described below.

Catalyst A:

Alpha alumina monohydrate (obtained from the Continental Oil Company, Peterboro, New Jersey) was gelled with slightly acidified water and made into 3.2 mm (1/8 in) extrudates. These were then dried at 110^oC for 6 hours and calcined at 500^oC for 6 hours. The calcined extrudates were impregnated with a solution of SnCl₂ in methanol, the volume of which was about one-half that of the extrudates. Methanol was subsequently purged out of the extrudates in a nitrogen flow at 150^oC. The final concentration of Sn was ca. 7 wt%.

Catalyst B:

Extrudates of Catalyst A were sulfided in a flow of a mixture of H₂S and H₂ (1:3 by vol.) at 150^oC for 5 hours at atmospheric pressure.

Catalyst C:

An aqueous solution of SnCl₂ was added to the alpha alumina monohydrate and milled in a mix-muller. The resulting paste was extruded, dried and calcined as in the case of Catalyst A. The final concentration of Sn was ca. 7 wt%.

Catalyst D:

A solution of aluminum isopropoxide and SnCl_2 in isopropanol was co-precipitated by hydrolysis using diluted ammonium hydroxide. The precipitate was extruded, dried and calcined as in the case of Catalyst A. The final concentration of Sn was ca. 15 wt%.

Separate experiments with bitumen involved testing alumina extrudates used for preparation of Catalyst A and B, and also testing a series of catalysts containing both Mo and Sn in different concentrations. The latter series was prepared by adding, successively, an aqueous solution of ammonium paramolybdate $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$ and an aqueous solution of stannic chloride $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ to alumina monohydrate in the mix-muller. Atomic ratios of molybdenum and tin added were, respectively, either 1:1 or 1:0. The resulting paste was extruded, dried and calcined as described above.

For experiments involving hydrogenolysis of coal and bitumen-derived asphaltenes, an aqueous slurry of pulverized feed and tin catalyst was prepared and subsequently dried under vacuum at 80°C . The catalysts tested included stannous chloride, stannous oxalate and stannous sulfide. The concentration of tin in the feed was approximately 5 wt%.

RESULTS AND DISCUSSION

Compared with pure alumina, tin compounds supported on alumina were generally found to exhibit only marginal improvements in liquid product quality in bitumen hydrorefining. The usual properties of the liquid product, such as specific gravity, sulfur and nitrogen content and percent pitch conversion, were not significantly changed when, for instance, in one series of tests the tin concentration was varied. The results are shown in Figure 1, which compares Mo/ Al_2O_3 -type catalysts both with and without a tin additive. It was found that the extent of decrease in the specific gravity of the liquid product caused by an increasing molybdenum concentration was not significantly affected by a simultaneous increase in tin loading.

The influence of the conversion of bitumen-derived asphaltenes into pentane-soluble products was also investigated. The influence of SnS on asphaltene conversion was much less apparent than on coal. The conversion of bitumen-derived asphaltenes increased from 69% with no catalyst to about 75% in the presence of SnS.

The conversion of coal into benzene-soluble products was found to increase substantially in the presence of the various tin catalysts tested. The conversion increased from 12.4% with no catalyst to an average of approximately 51% for all three tin catalysts investigated. The effectiveness of tin compared favourably with other catalysts tested, as shown in Table III.

TABLE III

Effect of Catalysts on Conversion of Coal
into Benzene-Soluble Products (350°C)

Catalyst	None	SnCl_2	SnS	$\text{Sn}(\text{COO})_2$	FeSO_4	FeCl_2	ZnCl_2
Conversion (% daf)	12.4	53.2	52.0	47.5	23.2	19.3	51.5

These results agree well with those obtained previously by Kawa *et al* (2,3) showing high activity of tin compounds for coal hydrogenolysis. Asphaltene production is probably the first step in coal liquefaction and more severe conditions are needed to increase the yield of pentane-soluble products. The conversion of asphaltenes produced from coal was not determined in the present work. However, the effect of stannous chloride on bitumen-derived asphaltenes appeared smaller than would be expected if asphaltenes produced from coal were used (2). In this respect the work with asphaltenes from solvent refined coal (4) produced more comparable results. The reason for the differences in reactivity between asphaltenes from coal and asphaltenes from bitumen feedstocks are not known and one can only speculate that they result from variations in chemical structures. A detailed analysis of bitumen-derived asphaltenes was presented by Strausz (6), and the sulfur content (about 8 wt%) is higher and oxygen content (about 1 wt%) is lower than those in asphaltenes produced from coal (2,3,4). The high sulfur content suggests that Mo/Al₂O₃ based catalysts may be the most efficient catalysts for hydrogenolysis since they seem to be the best hydrodesulfurizing agents.

Notable changes resulting from different catalyst preparation methods were observed. Table IV presents some results of analyses of liquid products from bitumen experiments for different tin-containing catalysts.

TABLE IV

Effect of Catalysts on Liquid Products from Bitumen***

Catalyst	Specific Gravity	%S Removed	%N Removed	% Pitch Converted
Al ₂ O ₃	0.951	33.3	26	62
A	0.932*	41.1*	52*	77*
	0.952**	31.0**	32**	66**
B	0.947	30.1	28	67
C	0.928	34.2	-	87
D	0.903	41.6	40.0	97

* Initial run
 ** Second run
 *** Run at 440°C

It is noteworthy that there was a drop in the activity of Catalyst A from the initial run to the second. Presumably, the impregnated SnCl₂ initially present was not completely transferred into SnS before the first run commenced and exhibited a greater activity at that stage. Two separate batches of SnCl₂ impregnated on alumina showed such deactivation. The deactivation was not observed when pre-sulfided batches were used (Catalyst B). Liquid products of improved quality, namely lower specific gravity, were obtained when Catalysts C and D were used. A different procedure was applied to prepare these catalysts and their properties are discussed below.

The supported tin catalysts of the type A and B tested with bitumen were found to exhibit little increased activity when compared with alumina alone. Microscopic examinations of the used extrudates revealed extensive sintering of the tin component within the cracks in the alumina, (Figure 2). Identical results were obtained regardless of whether the starting material was SnCl₂ (Catalyst A) or SnS (Catalyst B). These observations suggested that very little of the tin catalyst was actually exposed to the bitumen during the process. The optical reflectance of the streaks seen in Figure 2 compared well with that of pure SnS.

In addition, electron microprobe analysis of the spent catalyst confirmed that the high reflectance streaks were composed of tin and sulfur in atomic ratios of approximately 1:1. No streaks were observed in the unused extrudates, indicating even dispersion of the tin compounds on the surface of alumina. This was confirmed by electron microprobe analysis. Microscopic examination of the benzene-insoluble residue from coal liquefaction experiments revealed a sintering effect similar to that noted with bitumen runs, irrespective of whether SnCl_2 , $\text{Sn}(\text{COO})_2$ or SnS was used as the catalyst, (Figure 3). The high reflectance streaks were again found to be composed of tin and sulfur in atomic ratios of about 1:1.

The formation of SnS from SnCl_2 is feasible under typical hydrogenation or hydrorefining conditions provided sufficient sulfur is present in the feed material. It has been suggested (1) that SnS becomes the most stable form of tin and would be formed from SnCl_2 , for example, according to:



At reaction temperatures, SnCl_2 could conceivably flow into pores and cracks of the support or coal, and subsequently be converted to the sulfide form. On the other hand, SnS melts at 880°C , which is considerably higher than the reaction temperature used. Nonetheless, sintering had occurred to the same extent when SnS was used. The migration mechanism may therefore involve an intermediate species having a low melting point, such as elemental tin. This species could then migrate into void areas of the support before being converted back to SnS . In a separate experiment the fresh SnS - and SnCl_2 -containing catalysts were subjected to reaction conditions in the absence of the feed. Spots of high reflectance indicated the possible formation of metallic tin in extrudates subjected to this type of reducing condition.

In view of the extensive sintering effect the original dispersion of the tin compound was reduced considerably and consequently the effectiveness of both high- and low-surface area supports was expected to be comparable, as reported by Kawa *et al* (3). Figures 4 and 5 show sintering of SnS in the extrudates of Catalysts C and D (Table IV). Comparison with Figure 2 indicates that a more even dispersion of tin sulfide was established in the extrudates of Catalysts C and D. The sintering still occurred but the SnS appeared to assume a larger surface area. The higher dispersion correlated well with the activity observed with bitumen tests using these catalysts. One additional observation relates to Catalyst D in Figure 5. It appears that concentration of the tin component is greater in the regions between the particles of alumina than inside the particles. One could speculate that these regions may have been more accessible to the reactant fluids than the regions within the alumina particles. This would be in agreement with the enhanced activity of Catalyst D.

In conclusion, the present findings may be summarized as follows:

Tin compounds were found relatively less effective for bitumen hydrorefining than for hydrogenolysis of high volatile bituminous coals, possibly because of the different structure of bitumen-derived asphaltenes. The original dispersion of the catalyst on the support was significantly reduced. The extent of sintering of tin catalysts under reaction conditions correlated with their activity. It may be that an improved catalytic system would require a stronger bond between the tin compound and the support to hinder surface migration.

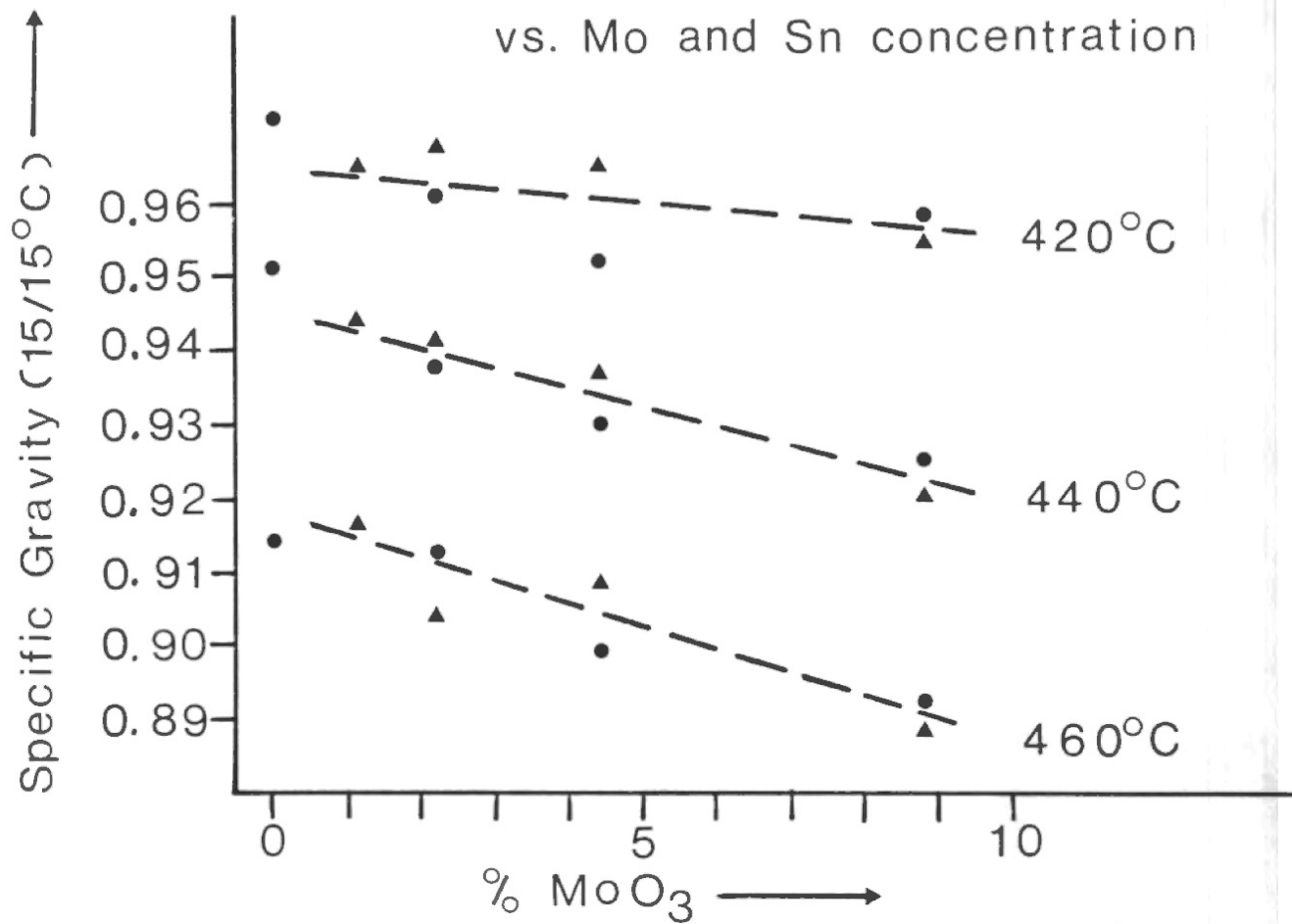
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Figure 1: Specific Gravity of Liquid Product vs. Mo and Sn concentration



- ▲ Mo : Sn = 1 : 1
- Mo : Sn = 1 : 0

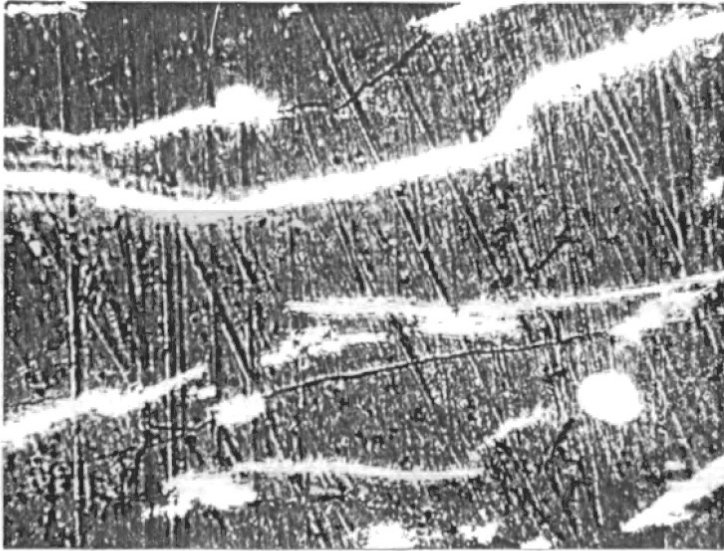


FIGURE 2: OPTICAL MICROGRAPH OF USED CATALYST A SHOWING HIGH REFLECTANCE STREAKS OF SINTERED TIN COMPONENT

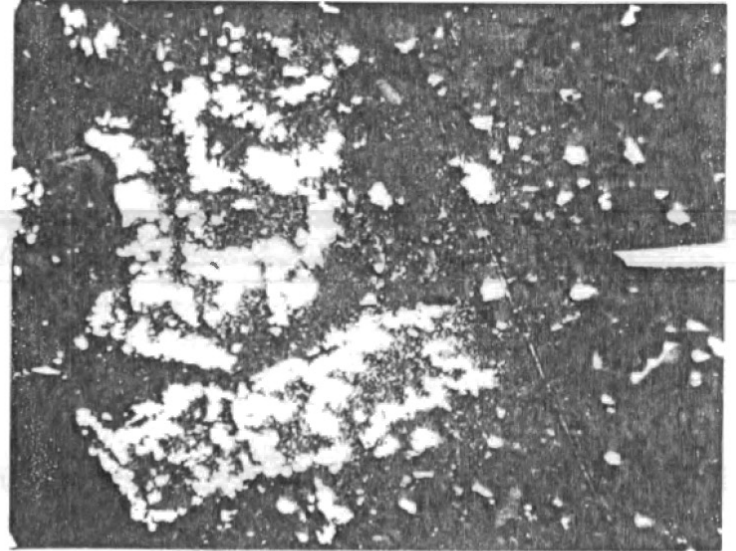


FIGURE 3: MICROGRAPH OF THE BENZENE-INSOLUBLE RESIDUE FROM COAL LIQUEFACTION EXPERIMENTS WITH STANNOUS OXALATE

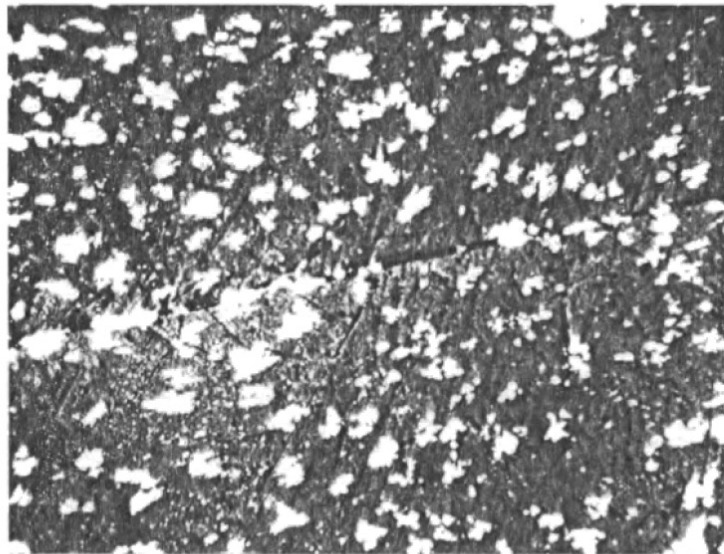


FIGURE 4: OPTICAL MICROGRAPH OF USED CATALYST C

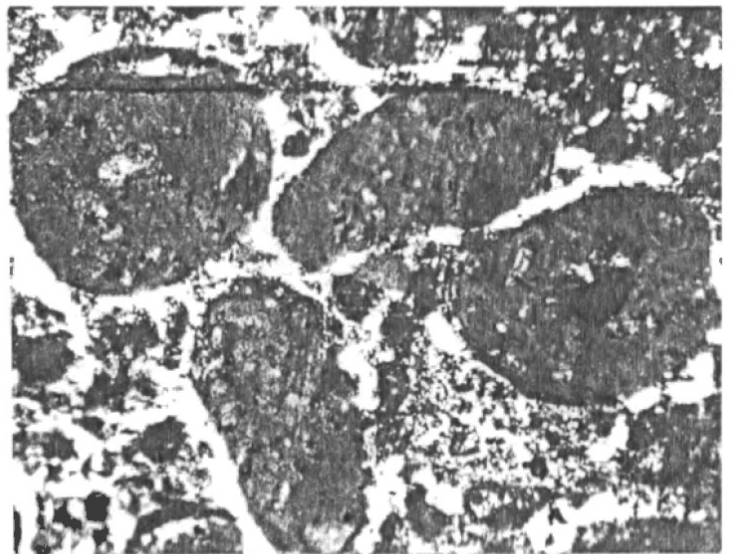


FIGURE 5: OPTICAL MICROGRAPH OF USED CATALYST D

50 μ m