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CHANGES WITHIN TIN-CONTAINING CATALYSTS UNDER HYDROREFINING CONDITIONS

J.F. KRIZ, K. BELINKO, B.N. NANDI AND D.S. MONTGOMERY

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Changes Within Tin-Containing Catalysts Under Hydrorefining Conditions

Tin compounds have generally been found particularly effective in liquid phase 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 hydrorefining process.

The development of catalysts for upgrading of Canadian oil-sand bitumen and for conversion of coal into liquid products has been of considerable interest at the Energy Research Laboratories. Guided by the outcome of previously published work, a series of tin-containing catalysts was tested for bitumen upgrading. Emphasis was placed on studying the changes occurring within the catalysts during this process. Results obtained in preliminary tests stimulated further development such as the use of different methods of catalyst preparation.

Athabasca bitumen was obtained from Great Canadian Oil Sands Ltd., Fort McMurray, Alberta, Canada, and some of its properties are given in Table 1. Tests were carried out in a bench-scale fixed bed reactor having a volume of 155 cm^3, 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 $cm^3\ s^{-1}$ at STP. The product leaving the top of the reactor flowed into receiver vessels where the liquid and vapour were separated. The reaction system was maintained at steady state conditions for 1 hour prior to, and 2 hours during, the period in which the liquid sample was collected.

The catalysts tested 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°C for 6 hours and calcined at 500°C for 6 hours. The calcined extrudates were impregnated with a solution of $SnCl_2$ 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°C. The final concentration of Sn was ca. 7 wt%.

Catalyst B:

Extrudates of Catalyst A were sulfided in a flow of a mixture of H_2S and H_2 (1:3 by vol.) at 150°C for 5 hours at atmospheric pressure.

Catalyst C:

An aqueous solution of $SnCl_2$ was added to the alpha alumina monohydrate and mulled 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%.

Compared with pure alumina, tin compounds supported on alumina were frequently found to exhibit only marginal improvements in liquid product quality in bitumen hydrorefining. However, notable changes resulting from different catalyst preparation methods were observed. Table 2 presents some results of analyses of liquid products from bitumen experiments for different

tin-containing catalysts. It is noteworthy that there was a drop in the activity of Catalyst A from the initial run to the second. Presumably, the impregnated $SnCl_2$ initially present was not completely transformed into SnS before the first run commenced and exhibited a greater activity at that stage. Two separate batches of $SnCl_2$ 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. These catalysts were prepared differently from Catalysts A and B and their properties are discussed below.

The supported tin catalysts of 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 into the cracks of the alumina (Figure 1). Identical results were obtained regardless of whether the starting material was $SnCl_2$ (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 1 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.

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:

$$SnCl_2 + H_2S \rightarrow SnS + 2HCl$$

At reaction temperatures, $SnCl_2$ could conceivably flow into pores and cracks of the support, 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. Consequently, the effectiveness of both high- and low-surface area supports would be expected to be comparable to the case of coal liquefaction, as reported by Kawa et al *(3)*. Figures 2 and 3 show sintering of SnS in the extrudates of Catalysts C and D (Table 2). Comparison with Figure 1 indicates that a more even dispersion of SnS 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 with the activity observed in the tests using these catalysts. It is not known, however, whether the sintering in Figures 1, 2 and 3 reached the final (or a steady) state under conditions of the present study, since the findings relate to comparatively short periods of operation amounting to about 8 hours in each case.

These findings show that the original dispersion of tin compounds on the supports was significantly decreased within a short period of time. Changes in the dispersion were observed when different methods of preparation were applied. 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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J.F. Kriz, K. Belinko, B.N. Nandi and D.S. Montgomery

Energy Research Laboratories,

Canada Centre for Mineral and Energy Technology

Department of Energy, Mines and Resources, Ottawa, Canada

TABLE 1

Properties of Athabasca Bitumen

Specific gravity	1.009 (15/15°C)	Benzene insolubles	0.72 wt%
Sulphur	4.48 wt%	Carbon	86.36 wt%
Ash	0.59 wt%	Hydrogen	10.52 wt%
Conradson carbon residue	13.3 wt%	Nitrogen	0.38 wt%
Pentane insolubles	15.5 wt%	Pitch (524°C+)	51.5 wt%

TABLE 2

Effect of Catalysts on Liquid Products from Bitumen[c]

Catalyst	Specific Gravity	wt% S in liquid	wt% N in liquid
Al_2O_3	0.951	2.97	0.33
A	0.932[a]	2.62[a]	0.20[a]
	0.952[b]	2.80[b]	0.28[b]
B	0.947	3.11	0.31
C	0.928	2.77	0.31
D	0.903	2.60	0.25

a Initial run

b Second run

c Run at 440°C

Figure 1

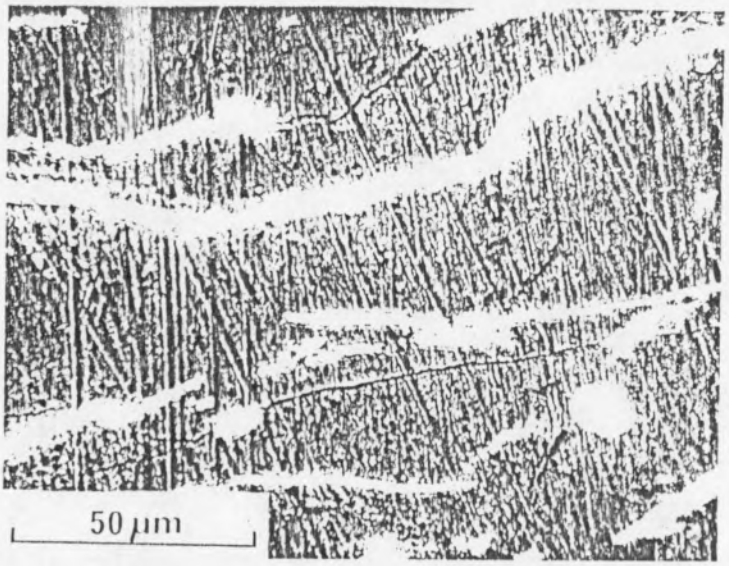

Figure 2

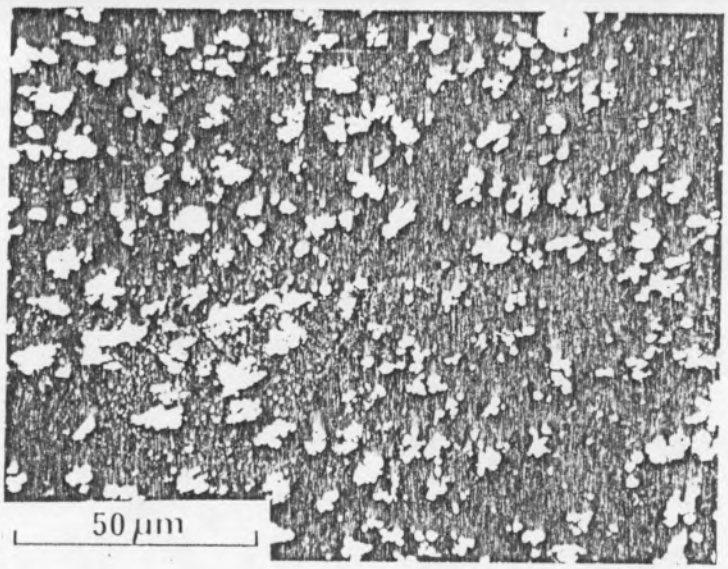
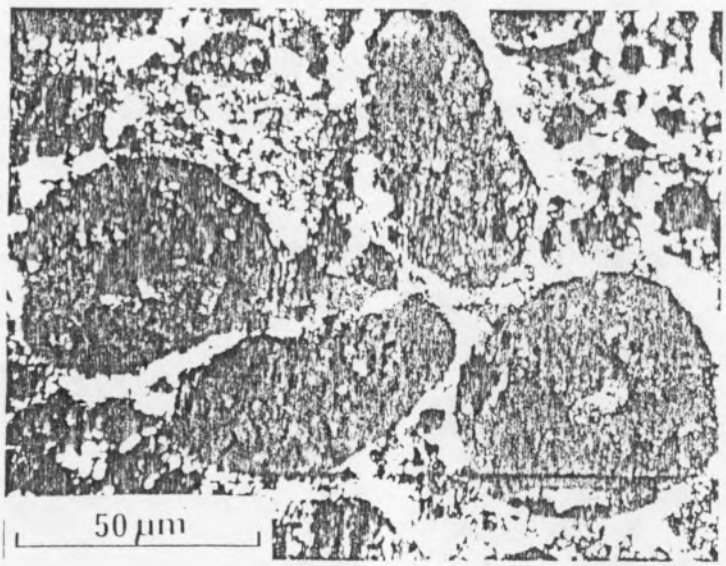
Figure 3