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TREATMENT OF SYNTHETIC CRUDES WITH METAL CHLORIDES AND METAL CARBONYLS

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ABSTRACT

The removal of problematic synthetic crude compounds with limited amounts of transition metal chlorides, carbonyls and hydrido carbonyls was investigated. A middle distillate fraction containing pure compounds of nitrogen and sulphur that are typical of this fraction was used. Chlorides of copper, iron, tin and zinc showed significant potential for removal of the nitrogen compounds and ethyl and phenyl mercuric chlorides reacted with these compounds at 200°C. These chlorides reacted with mercaptans and alkyl sulphides to varying degrees and with the exception of ethyl mercuric chloride had little effect on benzo and dibenzothiophene. However, the carbonyls of cobalt and manganese were quite promising for these thiophenes. Hydrido carbonyls of these metals were more favourable for the nitrogen compounds. There is evidence of competition for sites on the solid metal salts.

INTRODUCTION

In general, synthetic crude fractions have high levels of nitrogen and sulphur compounds which require costly hydrotreating. The possibility of their elimination by separation processes through complexation with metal chlorides is being considered.

Complexation of nitrogen compounds in petroleum and shale oil with some transition metal chlorides has been studied by other workers. Recently, Choi and Dines (1) studied the complexation of these compounds with hydrated copper chlorides. Rayner-Canham and

Table 1. Composition of Synthetic Crude Test Blend

Nitrogen Compounds	Sulphur Compounds
0.2985 g (50 ppm N) Carbazole	0.2093 g (100 ppm) Benzothiophene
0.4685 g (100 ppm N) 2 Methyl indole	0.2873 g (100 ppm) Dibenzothiophene
0.3200 g (50 ppm N) 7,8 Benzoquinole	0.7893 g (250 ppm) Dodecylmercaptan
0.6975 g (100 ppm N) N Ethyl carbazole	1.1155 g (250 ppm) Dinonyl sulphide

Dissolved in 500 g of Syncrude light distillate

(Total nitrogen and sulphur - 1000 ppm)

Dickerson (2) carried out a detailed study of ferric chloride-clay for their removal. The ferric chloride-clay system had been developed and used for analytical purposes by Jewell and co-workers (3,4,5,6). Other workers have reported the complexation of petroleum sulphur compounds with mercury (7,8,9), zinc (10) and copper (11) salts.

The work described here concerns the complexation of selected typical synthetic crude organo-nitrogen (12) and sulphur (13) species dissolved in synthetic crude distillate with a series of metal chlorides and transition metal carbonyls. The chlorides were those of copper, iron, tin and zinc, as well as two organomercuric chlorides. The transition metal carbonyls included those of iron (iron pentacarbonyl and diiron nonacarbonyl), cobalt (dicobalt octacarbonyl) and manganese (dimanganese decacarbonyl) as well as cobalt hydridocarbonyl and manganese hydridocarbonyl.

EXPERIMENTAL

Test Solution

A solution of the selected model compounds in hydrotreated "Syncrude" light distillate was prepared as shown in Table 1. The light distillate had a boiling range of 191-328°C, and contained 79% saturated, 19.3% monocyclic aromatic, 0.29% dicyclic aromatic, 1.32% tricyclic aromatic and 0.079%, tetracyclic aromatic hydrocarbons. Nitrogen and sulphur contents were 1.3 and 11 ppm respectively.

Procedure

The treatment with metal chlorides at 25°C used 50 mL of the model compound solution in a 200 mL Erlenmeyer flask containing a 10% stoichiometric excess of solid metal chlorides based on the total nitrogen and sulphur contents and assuming that 1/1 adducts formed with these elements. The mixture was stirred for 1 h and filtered. The filtrate was analyzed by gas chromatography to determine the amounts of model compounds that had been removed.

For treatment with metal chlorides at 200°C, the mixture of metal chlorides and model compound solution was heated for 2 h in a 200 mL round bottom flask equipped with a condenser. The mixture was allowed to cool overnight and then treated by the same procedure as the mixtures from the room temperature experiments.

The treatments with metal carbonyls were similarly conducted at room temperature in a 100 mL Erlenmeyer flask. The mixture was stirred for 30 minutes at 25°C and 1 mL of the supernatent liquid was removed for analysis. The remaining mixture was transferred to a 200 mL round bottom flask fitted with a condenser and then heated to 100°C for 10 min. Upon cooling the mixture was filtered and the filtrate analyzed.

The hydridocarbonyls of manganese and cobalt were formed in situ by reaction of the metal carbonyl with sodium hydroxide and acidification of the mix to form hydridocarbonyl. These systems are quite complex and no attempt was made to isolate the active species, which are quite labile.

Analyses

The quantities of model compounds remaining in the filtrates were determined by gas chromatography using a Varian thermionic specific detector for nitrogen compounds and a Perkin Elmer photometric detector for sulphur compounds. Detector responses were determined for each compound. Determination of the mercaptans was problematic and done by difference using the other sulphur analyses and imposing a mass balance.

DISCUSSION

Contrary to most other studies investigating the removal of nitrogen and sulphur compounds from petroleum or oil shale fractions with metal chlorides, this study involved dilute solutions of these compounds. Also, only slight (10%) stoichiometric excesses of metal chlorides and carbonyls were used assuming 1:1 ratios of these compounds with the metal ions. Of course this assumption is probably unrealistic considering the complexity of the systems, especially since most of the metal chlorides are solids. In the case of the carbonyls, complexation could lead to further reactions involving cleavage of carbon-nitrogen and carbon-sulphur bonds (15,16).

The nitrogen compounds for this study were selected because they were considered to be representatives of those least reactive in synthetic crudes. Thus, they would complex less readily and also would be more difficult to remove by hydrotreating than other nitrogen compounds. Carbazole, 2-methyl-indole and N-ethyl carbazole all contain acidic or pyrrolic type nitrogen. Carbazole would be the most acidic compound by vitrue of its three aromatic rings. 2-methylindole would be less acidic and the nitrogen is partially shielded by the methyl group. The N-ethylcarbazole would be least reactive because of the complete substitution on the nitrogen atom. The 7,8 benzoquinoline, a basic nitrogen compound was also thought to be difficult to remove because the nitrogen atom is partially shielded by the third aromatic ring.

The sulphur compounds were selected because they represent major types of compounds in synthetic crudes (13). The mercaptans are fairly reactive and dialklsulphides are known to coordinate with metal ions, but the thiophenes are difficult to separate from corresponding polycyclic aromatic hydrocarbons that are found in petroleum and synthetic crudes.

The results of treatment with metal chlorides are shown in Table 2. With the exception of methyl indole reactions with copper and tin, all nitrogen compounds are removed in significant amounts at 25°C. Also the mercaptan was removed in significant amounts by these base metals. Zinc chloride also removed some benzo- and dibenzothiophenes. Ethyl mercuric chloride removed no nitrogen compounds but did remove small amounts of dibenzothiophene and the dinonyl sulphide. Phenyl mercuric chloride removed some of the methyl indole and small amounts of carbazole and benzoquinoline.

At 200°C the results were considerably different. The amounts of ethyl carbazole removed by the base metals decreased markedly for all chlorides. Quantitative removal of the benzoquinoline and methyl indole by the copper and iron was achieved while tin and zinc removed major portions of these compounds. Also the methyl indole was quantitatively removed by the phenyl mercuric chloride. All metal chlorides removed significantly amounts of dinonyl sulphide at 200°C which was not the case 25°C. The ethyl mercuric chloride quantitatively removed the sulphide at the higher temperature and over half of the dibenzothiophene as well.

Thus treatment at the higher severity leads to increased removal of both nitrogen and sulphur model compounds. Possibly competition for metal ions at the higher temperature in the metal coordination sphere accounts for the decreased activity of the

Table 2. Removal of Nitrogen and Sulphur Compounds from Syncrude with Metal Chlorides

% Removal at 25°C for 1 hr

Metal chloride	Carbazole	2-Methyl indole	7,8-Benzo quinoline	N-Ethyl carbazole	Benzo-thiophene	Dodecyl mercaptan	Dibenzo-thiophene	Dinonyl-sulphide	Total N + S
$CuCl_2 \cdot 2H_2O$	26	0	32	33	0	18	0	2	11.5
$FeCl_3 \cdot 6H_2O$	36	65	44	35	0	36	0	0	23.0
$SnCl_2$	24	0	38	30	5	25	0	5	14.1
$ZnCl_2$	34	25	12	34	9	16	15	0	16.9
C_2H_5HgCl	0	0	0	0	0	-	6	14	5.5
C_6H_5HgCl	4	18	7	0	0	-	0	0	3.1

% Removal at 200°C for 2 hr

Metal chloride	Carbazole	2-Methyl indole	7,8-Benzo quinoline	N-Ethyl carbazole	Benzo-thiophene	Dodecyl mercaptan	Dibenzo-thiophene	Dinonyl-sulphide	Total N + S
$CuCl_2 \cdot 2H_2O$	58	95	98	0	3	21	0	18	27.4
$FeCl_3 \cdot 6H_2O$	52	100	92	14	2	31	3	19	30.9
$SnCl_2$	0	44	31	5	4	15	0	40	20.7
$ZnCl_2$	0	62	83	3	0	3	1	65	27.8
C_2H_5HgCl	52	4	2	0	3	-	53	100	44.9
C_6H_5HgCl	16	100	10	0	0	-	0	44	14.7

ethyl carbazole. Since only small amounts of the metal chlorides were used, competition of the model compounds for metals could cause less reactive ligands in particular the ethyl carbazole to be displaced by more reactive ligands.

Carbazole also appears to be affected by the competitive processes for metal ions. At the high severity the requirements of metal ions for the more reactive indole (100%) and quinoline (92%) were satisfied with the copper and iron chlorides and therefore increased removal of the carbazole was possible. In the case of the tin and zinc chlorides requirements of the more reactive nitrogen compounds were not satisfied, in particular when the dialkylsulphide also required significant portions of the metal ions and consequently no carbazole was removed. It is interesting that of the nitrogen compounds, only the carbazole was significantly removed by the ethyl mercuric chloride. Therefore this must be ascribed to its acidity.

At the high severity the methyl indole and benzoquinoline were affected similarly by the metal chlorides with the exception of reaction with phenyl mercuric chloride. It would appear that the nitrogen of the benzoquinoline was more sterically hindered by the benzo group than in the case of the indole by the methyl group.

It was unexpected that the dibenzothiophene with the more shielded sulphur would be more reactive with the metal chlorides than the benzothiophene. A small amount reacted with the zinc chlorides at the low severity but at the higher severity their was no reaction possibly due to competition from the dialkyl sulphide, the indole and quinoline.

The ethyl mercuric chloride removed only a small amount of the dibenzothiophene and dialkylsulphide at the low severity but large and quantitative amounts respectively at the higher severity. The ethyl mercuric chloride possibly reacted to such an extent with these sulphur compounds because it being soluble in the medium and also due to the fact that the mercury is a soft Lewis acid (low positive charge and high polarizability) that has affinity for soft (low electronegativity and high polarizibility) bases (14). Finally the phenyl mercuric chloride also had some affinity for the sulphide at high severity.

The results for removal of the nitrogen and sulphur compounds with the metal carbonyls are shown in Table 3. It should be mentioned that the mercaptans did not survive these treatments and therefore are not included in the tables. At the low severity the iron pentacarbonyl removes only small amounts of N-ethyl carbazole, benzothiophene and the dialkyl sulphide and nothing of the other compounds. The di-iron nonacarbonyl removes significant amounts of the thiophenes and sulphides but no nitrogen compounds

Table 3. Removal of Nitrogen and Sulphur Compounds from Syncrudes by Treatment with Metal Carbonyls

% Removal at 25°C for 30 min.

Metal carbonyl+	Carbazole	2-Methyl indole	7,8-Benzo quinoline	N-Ethyl carbazole	Benzo-thiophene	Dibenzo-thiophene	Dinonyl-sulphide	Total N + S
$Fe(CO)_5$	0	0	0	8	8	0	12	6.1
$Fe_2(CO)_9$	0	0	0	0	17	20	26	13.6
$CO_2(CO)_8$	32	51	4	0	41	66	100	56.8
$Mn_2(CO)_{10}$	4	2	0	0	44	100	100	53.1
$HCo(CO)_4$	78	0	40	0	9	8	10	13.5
$HMn(CO)_5$	100	100	100	0	21	25	10	36.5

% Removal at 100°C for 10 min.

Metal carbonyl+	Carbazole	2-Methyl indole	7,8-Benzo quinoline	N-Ethyl carbazole	Benzo-thiophene	Dibenzo-thiophene	Dinonyl-sulphide	Total N + S
$Fe(CO)_5$	38	0	16	0	31	0	25	16.1
$Fe_2(CO)_9$	0	0	0	0	0	0	0	0
$CO_2(CO)_8$	4	7	0	0	44	100	100	53.7
$Mn_2(CO)_{10}$	0	2	0	0	44	100	100	52.8
$HCo(CO)_4$	20	0	24	18	3	0	18	11.7
$HMn(CO)_5$	50	43	100	0	0	0	0	15.7

The cobalt carbonyl removes significant amounts of carbazole, methyl indole, large amounts of the thiophenes, and the dialkyl sulphide quantitatively, but little of the benzoquinoline and ethyl carbazole. The manganese carbonyl removed practically nothing of nitrogen compounds but large to quantitative amounts of the sulphur compounds. The hydrido cobalt carbonyl removed much of the carbazole and benzoquinoline, but little of the other compounds, while the hydrido manganese carbonyl quantitatively removed the carbazole, methyl indole and benzoquinoline, no ethyl carbazole and small but significant amounts of the sulphur compounds.

At the more severe treatment the results are considerably different. The iron pentacarbonyl now removed a significant amount of carbazole, a small amount of benzoquinoline and ethyl carbazole and increased amounts of benzothiophene and dialkyl sulphides. Whereas the nonacarbonyl removed some sulphides at the low temperature, it was completely ineffective at the high temperature probably because of decomposition. The cobalt and manganese carbonyls were less or almost ineffective for nitrogen removal at the higher temperatures, but even slightly better for the sulphur compounds. The hydrido carbonyls became less effective in most cases probably due to decomposition.

The fact that the dibenzothiophene in case of the cobalt and manganese carbonyls as well as zinc and ethyl mercuric chlorides reacts to a larger extent than the benzothiophene would seem to indicate that larger aromatic system are prefered in complexation. Then the possibility of complexation with tricyclic aromatic hydrocarbons should be considered. These hydrocarbons comprise 1.32% of the Syncrude light distillate medium while the dibenzothiophene comprises only .057%. Thus, if the tricyclic hydrocarbons competed with the nitrogen and sulphur compounds, the quantitative removal of the dibenzothiophene and the dinonyl sulphide as well as a large portion of the benzothiophene in the presence of the limited amounts of a metal carbonyls or chlorides would not be possible. Of course, the sulphur compounds might undergo reactions involving cleavage of carbon-sulphur bonds (15,16).

CONCLUSIONS

The copper, iron, tin and zinc chlorides can remove significant amounts of all nitrogen compounds, mercaptans and dialkyl sulphides even when used in limited amounts. However, there is evidence for competition between the nitrogen compounds for these metal chlorides. The ethyl and phenyl mercuric chlorides removed significant amounts of some of these compounds at higher temperatures. With the exception of ethyl mercuric chloride these chlorides did not remove the large amount of thiophenes. Cobalt and manganese carbonyls removed large amounts of benzo- and dibenzothiophene and the cobalt carbonyl also removed significant quantities of some of the nitrogen compounds. These thiophenic compounds are difficult to separate from corresponding aromatic hydrocarbons by conventional methods and the use of metal carbonyls could have relevance to analytical and processing applications.

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