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Oxidative Desulfurization of Coal Tar Pitch Using a Urea–Hydrogen Peroxide Complex/Carboxylic Anhydride System in THF

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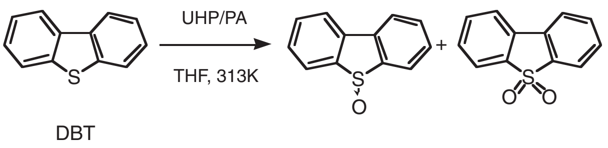
Oxidative desulfurization of coal tar pitch (CTP) using a urea–hydrogen peroxide complex with a carboxylic anhydride in THF was investigated. The sulfur content in CTP was reduced by more than 15% through the process.

Coal tar pitch (CTP) is the residue left by the distillation of coal tar, which is a by-product of coal when it is carbonized to make coke. CTP is a widely used precursor for many carbon materials such as graphite electrodes[1,2] and carbon fibers.[3,4] Recently, the use of high-sulfur coal has become increasingly prevalent, and this trend will result in the increase of the sulfur content in CTP. For the effective use of high-sulfur CTP, it is necessary to reduce the levels of sulfur. However, it is difficult to remove organosulfur compounds in CTP with conventional hydrodesulfurization, since CTP is chiefly composed of aromatic compounds, which would be susceptible to reduction under the reaction conditions. Reducing these aromatics would increase the processing costs by consuming additional hydrogen and further change the characteristics of the CTP. Therefore, the development of a novel desulfurization process for CTP is essential. Oxidative desulfurization would be a potential candidate since it does not require hydrogen. In this process, organosulfur compounds would be oxidized to more polar oxidation products, such as sulfoxides and sulfones, and could be removed by extraction or adsorption.[5–11] However, there have been few reports of the oxidative desulfurization of CTP. Jin et al. reported the oxidative desulfurization of CTP with hydrogen peroxide, catalyzed by trichloroacetic acid and ultrasonic waves: the sulfur content was reduced by more than 90%, although a significant increase in chloride content was observed.[12]

It is known that the system comprising the urea–hydrogen peroxide complex (UHP) with carboxylic anhydrides acts as an oxidizing agent for organosulfur compounds in MeCN.[13,14] We found that this system can also oxidize organosulfur compounds in THF. This would be useful for the oxidative treatment of CTP, which is soluble in THF but not in MeCN. In addition, the oxidation system would be favorable because the reaction can be carried out under anhydrous conditions, thus avoiding a reduction in the solubility of CTP due to the presence of water. Here, we report the oxidative desulfurization of CTP using the UHP/carboxylic anhydride system in THF.

Dibenzothiophene (DBT) was used as a model organosulfur compound, since most of the organosulfur compounds in CTP would be polycyclic aromatic sulfur heterocycles.[15] For a typical run, a solution of DBT (0.25 mmol) and UHP (2 mmol) in THF (50 mL) was warmed to 313 K with stirring, and then phthalic anhydride (PA; 4 mmol) was added. The disappearance of DBT was monitored using a previously reported HPLC method.[7] The major oxidation products were the corresponding sulfoxide and sulfone (Scheme 1). Oxidations of 5 mM DBT in MeCN at 313 K were carried out with 20 mM UHP and 80 mM of a carboxylic anhydride such as PA, maleic anhydride (MA), succinic anhydride (SA), glutaric anhydride (GA), and acetic anhydride (AA). The activities decrease in the order PA > MA > SA > GA > AA. PA and MA had the highest activities and hence were employed in further reactions. Figure 1 shows the oxidation of DBT with UHP and PA in MeCN or THF. The oxidation proceeded in THF as well as in MeCN, although the oxidation rate in THF was slower. The oxidation in THF was promoted by increasing the reaction temperature. Similar results were obtained using MA. These results suggested that the UHP/carboxylic anhydride system would be an effective oxidant for the oxidative desulfurization of CTP.



Scheme 1.

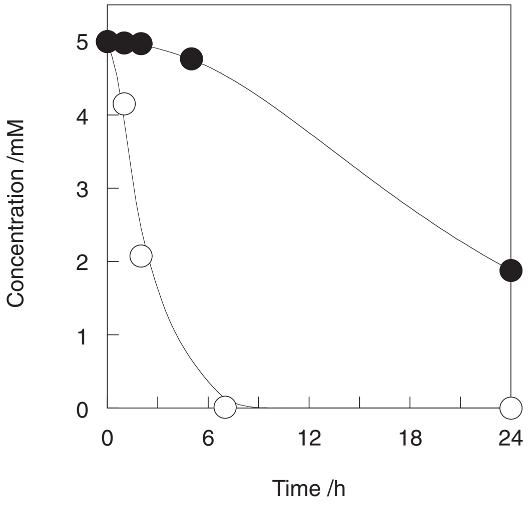


Figure 1. The disappearance of 5 mM DBT in MeCN (○) or THF (●) during the oxidation with 40 mM UHP and 80 mM PA at 313 K.

The oxidation system was applied to the oxidative desulfurization of CTP containing 0.35 wt% sulfur. A solution of CTP (1 g) and UHP (2 mmol) in THF (50 mL) was warmed to 313 K with stirring and then PA (4 mmol) was added. The ratio of UHP to sulfur in CTP is about 20 times greater than the stoichiometric amount. The mixture was stirred at 313 K for

Table 1. Oxidative desulfurization of CTP at 313 K for 24 h[a]

Entry	UHP /mmol	Carboxylic anhydride /mmol		Element/wt %					Sulfur removal[c] /%
		PA	MA	S	C	N	H	Total	
1	2	4	—	0.28	90.6	0.90	4.34	96.1	18
2	2	—	4	0.28	89.0	0.82	4.23	94.3	16
3	2	—	—	0.34	91.5	0.88	4.60	97.3	1
4[b]	—	—	—	0.35	93.2	0.99	4.17	98.7	—

[a]Reaction conditions: CTP, 1 g; THF, 50 mL. [b]CTP. [c]Calculated based on the change in the S/C ratio.

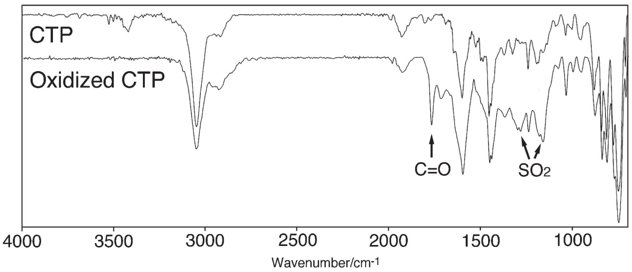


Figure 2. IR spectra of CTP and oxidized CTP.

24 h. After the oxidation, 250 mM aqueous Na_2CO_3 (50 mL) was added, and the THF phase was separated. The oxidized CTP was precipitated by the addition of water (50 mL) to the THF phase, separated by centrifugation, washed with water, and dried in vacuo. Elemental C, H, and N analysis was performed with a Yanaco CHN Corder MT-6. The sulfur content was measured using a Horiba SLFA-UV21 analyzer: the sample was prepared by dissolving the oxidized CTP (10 mg) in THF/phenyl acetate (9:1, 10 mL).

The results for the oxidative desulfurization of CTP are summarized in Table 1. The sulfur content was only slightly reduced in the absence of a carboxylic anhydride (Entry 3). On the other hand, the sulfur contents were remarkably reduced in the presence of PA or MA: more than 15% sulfur removal was observed (Entries 1 and 2). The oxidized organosulfur compounds would be removed from the reaction solution during extraction with aqueous Na_2CO_3. The oxidized organosulfur compounds in the CTP were identified by IR spectroscopy (Figure 2). The characteristic infrared absorptions of sulfones (ca. 1160 and 1300 cm^{-1}) appeared after oxidation, indicating their formation during the reaction. These results suggest that the UHP/carboxylic anhydride system would be effective for the oxidative desulfurization of CTP. The slight decrease in the total element content as a result of the oxidative treatment may have stemmed from the oxidation of polycyclic aromatics in CTP: the UHP/carboxylic anhydride system can also oxidize polycyclic aromatic compounds having more than three condensed rings, such as anthracene. The infrared absorption of carbonyl groups (ca. 1770 cm^{-1}) appeared after oxidation (Figure 2). The increase in oxygen content estimated from the elemental analysis data would be less than 5 wt %.

For the efficient reduction of the sulfur content in the oxidation product mixture, it is necessary to remove the oxidized organosulfur compounds that remain after the reaction by separation operations such as extraction and adsorption. Their removal from the oxidized petroleum fuels is rather facile.[5–11,16,17] However, it would be much more difficult to remove the oxidized organosulfur compounds from the oxidized CTP by extraction and adsorption due to their polarities. The oxidized CTP, as well as CTP itself, is sufficiently soluble only in polar solvents such as THF, pyridine, and 1-methyl-2-pyrrolidinone.[18] Additional investigations of the separation of the oxidized organosulfur compounds from the oxidized CTP are in progress.

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