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Catalyzing mesophase formation by transition metals

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ABSTRACT

In this work, environmentally-benign mesophase pitches were prepared from feed stocks obtained from two different petroleum refinery processes namely 'clarified oil' (CLO) from fluid catalytic cracking (FCC) unit of Fuel Block and 'heavy extract' (HE) from solvent extraction unit of Lube Block by giving thermal treatment at 370 °C. The effect of thermal treatment and role of transition metal catalysts on development of mesophase in petroleum feed stocks have been discussed in this paper. Mesophase formation behavior in the feed stocks and microstructures of mesophase pitches produced were investigated by optical microscopic imaging. It was observed that mesophase formation in the feed stocks was slow under the influence of thermal soaking only. The addition of divalent transition metal salts of cobalt and nickel during thermal soaking accelerates the mesophase formation in pitches. The addition of 3 wt% of cobalt catalyst enhanced the mesophase content (MC) from below countable limit (BCL) to 16 vol% in CLO pitch and from 10 to 40 vol% in HE pitch and also reduced thermal soaking time in both the cases. The 3 wt% of nickel catalyst also showed similar behaviour and enhanced the mesophase content (MC) from below countable limit (BCL) to 13 vol% in CLO pitch and from 10 to 18 vol% in HE pitch in shorter thermal soaking time. The study further revealed that cobalt catalyst exhibited greater catalytic activity for mesophase formation than nickel catalyst. These catalysts also help to increase the yield of mesophase pitches. Pitch yield in case of uncatalysed pitch CLO-0-0 is 11.88 wt% which increases to 16.22 wt% (CLO-Co-3) and 15.08 wt% (CLO-Ni-3), whereas in case of heavy extract pitch yield increases from 24.41 wt% (HE-0-0) to 24.79 wt% (HE-Co-3) and 26.16 wt% (HE-Ni-3) by the addition of Co and Ni catalysts. The effect of transition metal catalysts on mesophase pitch properties such as elemental analyses (CHNS), softening point (SP), coking value (CV), toluene insolubles (TI) and quinoline insolubles (QI) have also been studied. The mesophase pitches were also characterized using NMR spectroscopy, FT-IR spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy, X-ray diffraction (XRD) and thermogravimetric analyses (TG/DTG).

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1. Introduction

In some petroleum refining processes aromatic rich streams are generated as by-product. clarified oil (CLO) and heavy extract (HE) are such by-products which are produced during fluidized catalytic cracking (FCC) process and Lube Base Oil refining process respectively. These aromatic streams have high C/H ratio and have potential for making industrial carbon materials like mesophase pitches and premium quality petroleum coke. It is well known that carbonaceous mesophase pitch has been extensively used as a precursor for making a variety of industrial as well as high performance carbonaceous materials such as premium quality needle coke, graphite electrodes [1–3], carbon fibres [4], C–C composites [5], fine-grained sintered carbons [6,7], Li-ion battery anodes [8], mesocarbon microbeads (MCMB) [9,10], carbon foam [11] and plasma-facing components for fusion devices [12].

Brooks and Taylor [10] first time observed formation of carbonaceous mesophase in pitch where liquid 'isotropic phase' and crystalline 'mesophase' remained in equilibrium. Since then, mesophase formation has seen many advances and is a subject of active research for carbon scientists and engineers because different feed stocks show different mesophase formation behavior. In literature, several studies have been reported in which mesophase pitches were prepared from different feed stocks (petroleum, coal tar, naphthalene and anthracene etc.) and under different experimental conditions such as thermal treatment temperature, heating rate, thermal soaking time and catalysts etc. [13].

Greinke and Singer [14] observed that during heat treatment of petroleum pitches chemical changes take place between isotropic and anisotropic phases. They also suggested that tiny

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mesophase spheres having round shape are formed due to polymerization of more reactive species present in the pitches. As thermal soaking time increases, the size of mesophase spheres also increases. Finally, the bigger mesophase spheres coalesce into bulk mesophase and finally converted into semicoke [10,15].

Generally, mesophase formation in the feed stocks and isotropic pitches takes long thermal treatment time of several hours which makes the mesophase pitch process more energy – intensive. Therefore, several researchers studied the effect of various catalysts to enhance mesophase formation in pitches and reduce thermal treatment time. Braun et al. [16] studied the effect of iron benzoate and naphthoate catalysts on coal tar mesophase pitches. They observed that the nucleation and growth of mesophase spheres are strongly influenced by the catalyst. Further, mesophase spheres formed are almost of equal size having a reduced tendency to coalesce with each other. The mesophase content (MC) in the pitches was also high. Braunhauer et al. [17] reported the catalysis of mesogen formation by ferric chloride and ferrocene catalysts. They found that these catalysts are effective to promote mesophase formation in the pitches.

Song et al. [18] reported that size of mesophase spheres increases by the addition of ferrocene catalyst and some of the mesophase spheres are converted into coalesced mesophase which indicate that the formation and transformation behavior of mesophase is accelerated by the addition of ferrocene. Carreira et al. [19] reported a different finding that addition of boron compound into petroleum residue initially enhances development of mesophase in the solid but as the concentration of boron exceeds to a certain limit the size of anisotropic structures decreases. Obara et al. [20] observed that as the concentration of inert silica gel is increased, the size of the mesophase spheres decreases during carbonization of a petroleum pitch. In some studies, catalysts were found to be effective for enhancing mesophase formation but catalyst recovery from pitch was a problem. The presence of catalyst particles in pitch may pose problems of deteriorating the final carbon product quality.

In literature, several researcher taken naphthalene and anthracene as a starting material and used $AlCl_3$ [21,22], $FeCl_3$ [23] and HF/BF_3 [24–26] as catalysts for making mesophase pitches. Mochida et al. [21] used aluminium chloride ($AlCl_3$) as a catalyst for making pitches which was very effective but main disadvantage of using $AlCl_3$ is difficulty in recovering it from pitch. Moreover, it is not recyclable. Mochida et al. [24] overcome the catalyst recovery and recyclability problems by using another gas phase catalyst $HF\text{-}BF_3$ for converting aromatic hydrocarbon feed stock into mesophase pitches. This strong Lewis acid catalyst ($HF\text{-}BF_3$) was found very effective to get high yield of mesophase pitches (up to 90%) as well as capable of producing mesophase in pitch as high as 100%. The further advantage of using $HF\text{-}BF_3$ catalyst is its easy recovery.

In literature, very few transition metals namely aluminium, iron have been used for catalyzing mesophase formation, therefore in the present study it was thought of using some unexplored transition metals such as cobalt and nickel for catalyzing mesophase formation in petroleum feed stocks. Further, in most of the prior research a very little or no work has been done on catalyst recovery aspect in spite of its importance in mesophase pitch application. In this work, we have also carried out work on recovery of catalyst (Co, Ni) used in preparation of pitches.

In the present work, we have prepared environmentally-benign mesophase pitches by thermal treatment of CLO and HE in presence of Co and Ni catalysts. Pitches prepared by providing different soaking time and in presence of different catalysts were examined to monitor the formation of poly-aromatics and increase of mesophase content. For detailed understanding of pitch composition mesophase pitches were characterized by various analytical techniques such as FT-IR, NMR, XRD, TG/DTG and scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDX) and optical microscopic imaging etc.

Table 1
Physico-chemical properties of clarified oil (CLO) and heavy extract (HE).

Characteristics	Test method	Clarified oil	Heavy extract
Density d_4^{15} gm/mL	IP 190	0.9251	0.9975
BMCI[a]	By calculation	51.00	81.00
Viscosity at 70 °C (cSt)	ASTM D 445	11.82	581.41
Asphaltenes wt%	IP 143	0.55	0.03
MCR[b] wt%	ASTM D 4530	1.01	5.79
Sulfur wt%	ASTM D 4294	1.28	4.91
Pour point (°C)	ASTM D 97	45	18

[a] Bureau of mines correlation index.
[b] Micro carbon residue.

2. Experimental

2.1. Raw materials and catalysts

In this study, two petroleum feed stocks namely CLO and HE sourced from different petroleum refineries were used for preparing mesophase pitches. Physico-chemical properties of CLO and HE are given in Table 1. Transition metal salts ($CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$) were used as catalysts. AR grade toluene and quinoline were used as solvents for determining insolubility in mesophase pitches.

2.2. Preparation of mesophase pitches

To prepare mesophase pitches 3 wt% percentage of transition metal salts ($CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$) were added in each feed stock (CLO and HE) and agitated at 150 °C. Thermal treatment of the mixtures was carried out in a laboratory glass reactor, taking 170 g of feed stock in the reactor consisting of arrangement of gas purging and measurement of reaction temperature. Thermal treatment was performed at 370 °C by maintaining heating rate of 5 °C/min for varying thermal soaking time from 2.20 to 21.00 h under continuous purging of nitrogen gas. All thermal treatment experiments were carried out at atmospheric pressure. The temperature was controlled with the help of a digital temperature indicator cum controller connected to a microcomputer controlled thermocouple immersed in the feed stock/pitch. The rate of nitrogen gas purging was maintained at 150 mL/min for 170 g of feed using wet gas flow meter to make reaction atmosphere inert, provide enough turbulence in viscous pitch. The mesophase pitches prepared from CLO were named as CLO-0-0, CLO-Co-3, CLO-Ni-3 and from HE were named as HE-0-0, HE-Co-3, HE-Ni-3. In the pitch nomenclature, first value denotes feed stock, second denotes transition metal catalyst and third denotes wt% percentage of catalyst. The physico-chemical properties of all prepared mesophase pitches in this study are given in Table 2.

2.3. Characterization of mesophase pitches

Mesophase pitches were characterized for their key physico-chemical properties like softening point (Mettler Toledo FP90, ASTM D-3104), coking value (ASTM D-4530), quinoline insolubles (ASTM D-2318), and toluene insolubles (ASTM D-4312) using American Society for Testing Materials (ASTM) test procedures. Physico-chemical properties are given in Table 2.

Elemental analyses of mesophase pitches were carried out using Elementar Vario Micro Cube instrument.

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