Preparation of mesophase pitch from naphthalene by the aid of ZrO_2/SO_4^{2-} solid superacid as catalyst

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Introduction

Mesophase pitch as a better precursor for high performance carbon fiber and advanced binder pitch, is expected to possess high anisotropic content,low softening point and high solubility in some organic solvents.Preparation of mesophase pitch from aromatic hydrocarbon using acidic catalyst may be one of the satisfactory methods [1,2]. The aromatic hydrocarbon can link with each other through oligomerization reaction by the aid of Lewis acid.The derived products are rich in naphthenic rings which are very important for the succeeding pyrolysis process. In the present study, solid superacid ZrO_2/SO_4^{2-} was used as catalyst for the preparation of mesophase pitch from naphthalene.

Experimental

a) ZrO_2/SO_4^{2-}solid superacid catalyst was prepared using $ZrOCl_2 \cdot 8H_2O$ as initial material[3].

b) Naphthalene was catalytically modified at 210℃ under atmosphere pressure for 5 hours using above prepared solid superacid.

c) Mesophase pitch was obtained through pyrolysis of the modified product at 450℃ in N_2 flow under atmosphere pressure for 6 hours.

d) Elemental analysis,measurement of solubility, softening point and anisotropic content were characterized using traditional methods. Anisotropic texture was also investigated by the observation of polarized-light microscope.

The chemical structure of modified product and the pyridine soluble (PS) component of mesophase pitch were also investigated using EI-MS and ^{1}H-NMR.

Results and Discussion

Table1 shows some essential properties of modified product and mesophase pitch. Fig.1 and Fig.2 illustrate the EI-MS and the ^{1}H-NMR spectra of modified product, respectively.

From Fig.1, it can be found that modified product consists of dimer (m/e 256) ,trimer (m/e 384) ,tetramer (m/e 512) and a small amount of pentamer (m/e 636) of naphthalene and its derivatives. Fig.2 shows that modified product has about 19.4% of naphthenic groups with a few short aliphatic chains. Such saturated groups generated from modification of naphthalene, which has no saturated radicals, are superior in the preparation of mesophase pitch.This proves that ZrO_2/SO_4^{2-} has efficient catalytical ability at oligomerization of aromatic compounds.

Fig.3 and 4 give some chemical structure information of PS component of mesophase pitch. Comparing with Fig.1and 2, it can be found that mesophase pitch has few saturated groups.In spite of its high anisotropic content, mesophase pitch still exhibits low softening point. This could be attributed to its high content of PS component (Table1) which has some small molecules(Fig.3). Such small molecular constituents not only are good solvents for other large molecular constituents, but also can orient well by the aid of large aromatic layers. Polarized-light microscope observation shows that it possesses flow texture with large isochromatic domain .

ZrO_2/SO_4^{2-}solid superacid catalyst can be prepared and regenerated easily,and has no pollution to environment.The oligomerization reaction of naphthalene by the aid of ZrO_2/SO_4^{2-} can be carried out under atmosphere pressure. It can be considered that this method is worth further researching.

Reference

1. Isao Mochida et al. , High Temperature and High Pressure, Vol.22 , 671(1990) .
2. Feng wei , Lang Liu et al. , Fuel , Vol. 67 , 1653(1988) .
3. H. Matsuhashi et al. , Acid-Base Catalyst , Kodansha , Tokyo , 1988 , P357.

Table1 Some essential properties of naphthalene oligomers and mesophase pitch

	Elemental analysis(wt%)			Solubility(wt%)			S.P.	A.C.
	C	H	N	BS	BI-PS	PI	(℃)	(Vol.%)
Naphthalene oligomers	94.15	5.79	0	100	———	———	———	———
Mesophase pitch	95.79	3.91	0	34.96	12.54	52.50	222	95

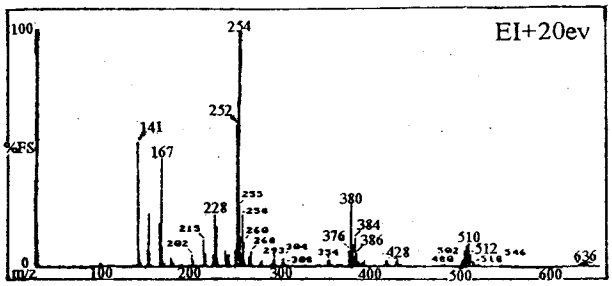

Fig.1 EI-MS spectrum of naphthalene oligomers

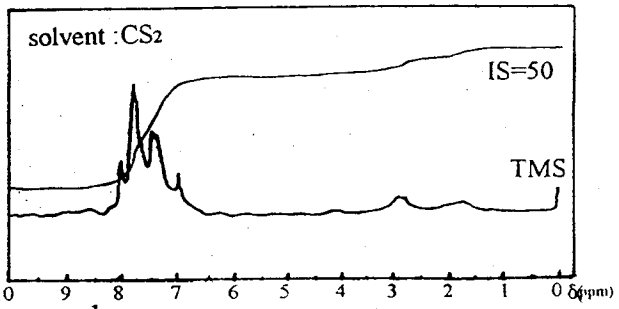

Fig.2 ^{1}H-NMR spectrum of naphthalene oligomers

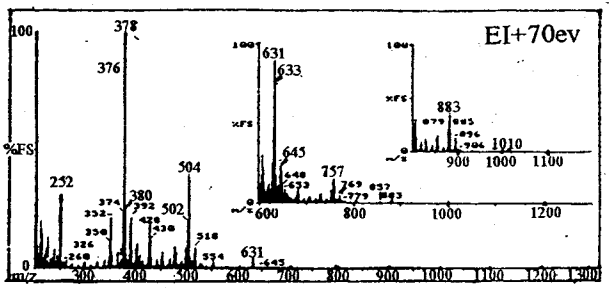

Fig.3 EI-MS spectrum of PS component of mesophase pitch

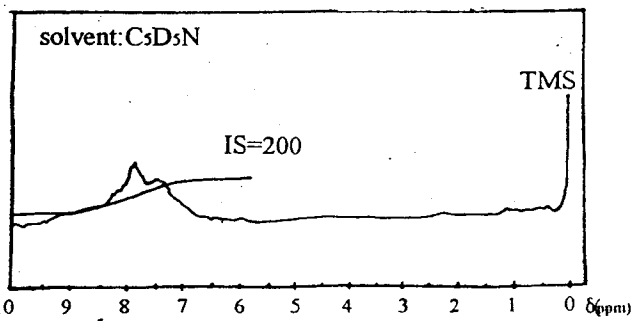

Fig.4 ^{1}H-NMR spectrum of PS component of mesophase pitch