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Synthesis and characterization of resorcinol–formaldehyde resin chars doped by zinc oxide

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ABSTRACT

Polycondensation polymerization of resorcinol–formaldehyde (RF) mixtures in water with addition of different amounts of zinc acetate and then carbonization of dried gels are studied to prepare ZnO doped chars. Zinc acetate as a catalyst of resorcinol–formaldehyde polycondensation affects structural features of the RF resin (RFR) and, therefore, the texture of chars prepared from Zn-doped RFR. The ZnO doped chars are characterized using thermogravimetry, low temperature nitrogen adsorption/desorption, Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM). At a relatively high content of zinc acetate (1 mol per 10–40 mol of resorcinol) in the reaction mixture, the formation of crystallites of ZnO (zincite) occurs in a shape of straight nanorods of 20–130 nm in diameter and 1–3 μm in length. At a small content of zinc acetate (1 mol per 100–500 mol of resorcinol), ZnO in composites is XRD amorphous and does not form individual particles. The ZnO doped chars are pure nanoporous at a minimal ZnO content and nano-mesoporous or nano-meso-macroporous at a higher ZnO content.

1. Introduction

Resorcinol–formaldehyde polymeric (RFP) materials such as resins, gels, adhesives, glues, *etc.* are of importance for industrial applications [1,2]. Porous and light RFP gels possessing unique properties can be also used for preparation of porous chars as precursors of highly porous activated carbons [3,4]. It is important that resorcinol is of little toxicity and has high activity in reactions with formaldehyde in aqueous solutions free of organic solvents. Addition of small amounts of acidic or basic catalysts can strongly affect resorcinol–formaldehyde polycondensation processes and structural features of RFP. Variations in content of reaction components and water as a solvent and changes in a catalyst type and content allow significant and controlled changes in the structural, morphological, and textural characteristics of the RFP gels and related materials, *e.g.* the products of RFP carbonization. Frequently, carbonates or hydroxides of sodium or potassium are used as catalysts to prepare RFP. The amounts of these catalysts estimated as a resorcinol/catalyst (R/C) ratio have been varied in a broad range from 10/1 to 2000/1 mol/mol [5].

Resorcinol–formaldehyde resins (RFR) are of interest as porous polymers or precursors of chars which can be used to prepare highly porous carbon materials [6–13]. The properties of the final carbon materials are mainly determined by the structure of polymeric precursors prepared by polycondensation of resorcinol with formaldehyde in the aqueous media. During RFR preparation, water can play a role of both a solvent and a template regulating the textural characteristics of RFR and chars [14].

On the basis of RFR, porous carbon composites containing different metals Fe, Co, Pt, Ag, Ni, Sn, Mn, *etc.* and their species have been synthesized to be used in electrochemical, catalytic, adsorption and other applications [15–19]. Metals and metal oxides in these composites can strongly affect the structural, textural and other characteristics of the materials [20]. Additionally, metal salts can play a role of a catalyst of the polycondensation processes on the RFR preparation, as well as the polymer carbonization. It is known that zinc acetate can be used as an ortho-orienting agent during the phenol-formaldehyde resin synthesis [21].

The aim of this paper is to study the influence of zinc acetate and its products (*e.g.* ZnO) on the morphological, structural, and textural

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Table 1
Initial ratio of components used to prepare RFR.

Series	Samples	Components ratio		
		R/F (mol/mol)	R/W (w/w)	R/C (mol/mol)
1	RF1	1:2.8	1:3.26	10:1
	RF2	1:2.8	1:4.00	20:1
	RF3	1:2.8	1:4.00	40:1
2	RF4	1:2.0	1:5.94	100:1
	RF5	1:2.0	1:5.94	200:1
	RF6	1:2.0	1:5.94	500:1

Note: R/F and R/C are the mole ratio of resorcinol (R), formaldehyde (F) and catalyst (C, zinc acetate); and R/W is the weight ratio of resorcinol and water (W) in the reaction mixture. R/C = 10:1 (mol/mol) ≈ 5:1 (w/w).

features of char-ZnO composites prepared by carbonization of RFR synthesized in the presence of different amounts of zinc acetate.

2. Materials and methods

2.1. Materials

Resorcinol (99.0%, pharm grade), 37% aqueous solution of formaldehyde, zinc acetate $Zn(COOCH_3)_2{\cdot}2H_2O$ and distilled water were used in the synthesis of RFR. In the first series of RF samples (used then in preparation of ZnO doped RF chars RFC1, RFC2, and RFC3), the amounts of zinc acetate were greater by an order of magnitude than that in the second series of samples (RF4, RF5, and RF6) (Table 1) as precursors of chars RFC4, RFC5, and RFC6. Zinc acetate and ZnO formed during sample preparation can catalyze the polycondensation and carbonization reactions.

Reaction compositions with zinc acetate were prepared by dissolution of a certain amount of resorcinol in distilled water with then added certain amount of zinc acetate dissolved. Then a certain amount of aqueous solution of formaldehyde was added and the mixtures were agitated for 2 min using a magnetic stirrer.

The first series of samples heated at 90 °C can fast transform into sol during 10–20 s. Samples of the second series were heated at 60 °C for 18 h to form the gel. For sample 4 (Table 1), the gel formation was already observed in 2.5 h. After gelation, all the samples were dried at room temperature for 5 days. Then ground dried samples were heated at 100 °C (first series) or 120 °C (second series) for 2 h.

Carbonization of the samples was carried out in an argon atmosphere with the gaseous products of the carbonization since a fixed bed reactor was used. The samples were heated at a rate of 5 °C/min to 780 °C (first series with RFC1, RFC2, and RFC3) or 800 °C (second series with RFC4, RFC5, and RFC6), and then they were heated at this temperature for 2 h.

2.2. Methods

ZnO doped chars were characterized using thermogravimetry (TG), low temperature nitrogen adsorption/desorption, Raman spectroscopy, XRD, scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM).

TG measurements were carried out in air using a Derivatograph C (MOM, Budapest) apparatus with 18–20 mg of samples placed in a ceramic crucible treated at a heating rate of 10 °C/min.

The textural characteristics of ZnO doped chars were determined using low-temperature nitrogen adsorption–desorption isotherms recorded using a Micromeritics ASAP 2420 analyzer or a Quantachrome Autosorb analyzer. The pore size distributions were calculated using nonlocal (NLDFT) or quenched solid (QSDFT) density functional theory (Quantachrome Software, http://www.quantachrome.com/) with a slit/cylindrical pore model. A complex model with slit/cylindrical pores and voids [22–25] between spherical nanoparticles (SCV) was used with a self-consistent regularization (SCR) procedure (SCV/SCR model) as described elsewhere [26–28].

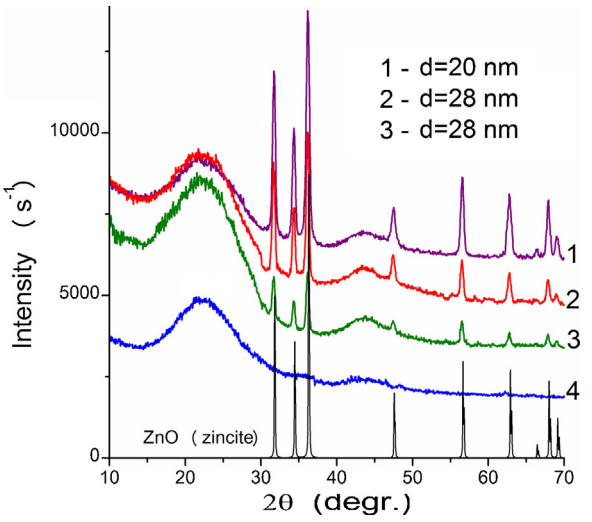

Fig. 1. XRD patterns of ZnO doped chars at the initial ratio R/C = 10/1 (curve 1), 20/1 (2), 40/1 (3) and 100/1 (4); *i.e.* for RFC1 (1), RFC2 (2), RFC3 (3), and RFC4 (4), and pure crystalline ZnO (zincite).

The X-ray diffraction (XRD) patterns of ZnO doped chars were recorded at room temperature using a DRON-4-07 (PO "Burevestnik", St. Petersburg) diffractometer with filtered Cu K_α ($\lambda = 0.15418$ nm) radiation in the 2θ range from 10° to 70° with a step of 0.1°. The average size of ZnO crystallites was estimated according to the Scherrer equation.

The Raman spectra of the studied materials were recorded using an inVia Reflex (Microscope DMLM Leica Research Grade, Reflex, Renishaw, UK) Raman microscope. The excitation was carried out by a laser at 514 nm.

SEM images were recorded using a JEOL JSM-6700F scanning electron microscope. HRTEM images were recorded using a JEOL JEM-2100F microscope with an X-ray microanalyzer (Oxford).

3. Results and discussion

XRD study of doped chars shows the presence of crystalline ZnO particles (zincite with hexagonal syngony according to JCPDS #79-206 [29]) in samples RFC1-RFC3 and of amorphous carbon phase observed in the XRD patterns at $2\theta = 22°$ and 44° (Fig. 1).

Clear, the content of crystalline ZnO (Fig. 1) decreases with decreasing amount of zinc acetate in the initial reaction mixture (Table 1). The ZnO lines in RFC1-RFC3 correspond to pure crystalline ZnO (zincite) shown in Fig. 1. The average size of ZnO crystallites (estimated using the Scherrer equation) is between 20 nm (RFC1) and 28 nm (RFC2, RFC3). These sizes correspond to minimal diameters of nanorods observed in SEM images of the composites (*vide infra*).

For RFC4 (Fig. 1, curve 4), as well as RFC5 and RFC6 (not shown here), only two halos of amorphous carbon phase are observed at $2\theta = 22°$ and 44°. These amorphous carbon phase features, besides lines of crystalline ZnO, are also characteristic for samples RFC1-RFC3. The crystallinity of RFC1 is 42% and an amorphous phase corresponds to 58% estimated from the ratio of integral intensity of all crystalline bands and two broad halos (at $2\theta = 22°$ and 44°), respectively. The crystallinity of RFC2 and RFC3 is much lower and corresponds to 17% and 9%, respectively.

It is known [30–32] that in hydrothermal synthesis or treatment, zinc oxide can form particles in the shapes of whiskers, tetrapods,

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