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Fe-carbon nanoreactors obtained from molasses as efficient catalysts for limonene oxidation

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Abstract: Fe-carbon nanoreactors were prepared by the impregnation of carbon cages with iron nitrate. Carbon cages were obtained using molasses as a carbon precursor and silica spheres as a template. The porous structure of the carbon cages allows for uniform dispersion of Fe. Fe concentration was equal to 0.68, 1.32, and 2.64 wt% as Fe_3O_4. Obtained materials were characterized by nitrogen adsorption at 77 K, X-ray powder diffraction (XRD), and scanning electron microscope (SEM) method. Fe-carbon nanoreactors were very active in limonene oxidation. Fe-carbon nanoreactors were used as a catalyst in limonene oxidation by t-butyl hydroperoxide.

Keywords: carveol; catalyst; limonene oxidation; molasses; nanoreactors.

1 Introduction

A new methodology of porous carbons production in the presence of silica particles as template was described for the first time in 1998 [1]. Resorcinol and formaldehyde were used as carbon source. Different shapes of silica particles and different carbon sources (usually various polymers and biomass) used for porous carbons production were summarized in the review papers [2–4]. Porous carbon-based materials are regarded as one of the most interesting because of unique structure, surface properties, mass transfer capability, and various applications such as water purification, gas separation, catalyst supports, and electrodes [5–8]. Such materials were also applied for metal-carbon nanoreactors (MCNRs) production [9–11]. Authors used pyrolysis fuel oil pitch and nanosized silica template to production carbon cages (CCs). MCNRs were obtained by gold, copper, nickel, potassium, and manganese impregnation. Such MCNRs were used for hydrogen and ethylene adsorption and the heterogeneous catalytic oxidation of secondary alcohols.

Herein, we described Fe-carbon nanoreactors (FeCNRs) prepared with different amount of iron as precursor and hierarchical CCs obtained from molasses. Our team applied molasses as activated carbon precursor [12], but according to the our knowledge, molasses was not used as carbon precursor for porous carbon prepared using silica as template. The FeCNRs we produced were used for limonene oxidation. Catalysts contained commercial activated carbon, and we described iron for limonene oxidation earlier [13]. However, their catalytic activity was considerably different, taking into account the selectivities of the main products (1,2-epoxylimonene, carvone, carveol, and perillyl alcohol), the conversion of limonene, and the activity of the reused catalysts.

2 Materials and methods

The synthesis of the FeCNRs was performed in three steps: (i) SiO_2 (POCH Gliwice, Poland) nonporous solid spheres (SNSs) were obtained as described by Fang et al. [14], (ii) CCs were prepared by using the modified method described by Mayani et al. [11], and (iii) CCs were impregnated with iron nitrate as described by Młodzik et al. [13]. FeCNRs containing 0.68, 1.32, and 2.64 wt% of Fe as Fe_3O_4 (POCH Gliwice, Poland) were obtained.

The X-ray powder diffraction (XRD) patterns were recorded using PANalytical X-ray, Philips Analytical diffractometer (Amsterdam, Holand), with Cu Kα radiation ($\lambda=1.5418$ Å).

The values of interlayer spacing, layer diameter, stack height, effective dimension of crystallites, and average number of layers per stack were estimated on the basis of XRD results. The methods were described by Młodzik et al. [13].

The specific surface area (S_{BET}), the total pore volume (V_{tot}), the and micropore volume (V_{micro}) were calculated on the basis of nitrogen sorption experiments at 77 K conducted using Quadrasorb evo, Quantachrome. The scanning electron microscope (SEM) pictures

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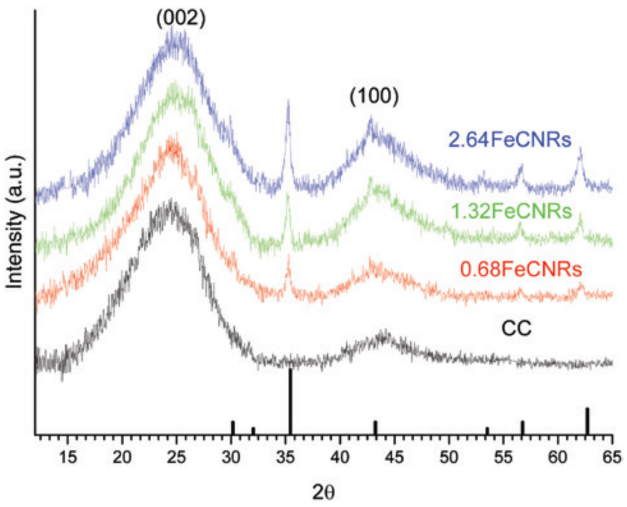

Figure 1: XRD patterns of CCs and FeCNRs. The peak positions of Fe_3O_4 from JCPDS (19-0629) database are indicated by vertical bars.

were obtained using ultra-high resolution field emission scanning electron microscope (UHR FE-SEM Hitachi SU8020, Tokyo, Japan) equipped with the secondary electron (SE) detectors and a photodiode-backscattered electron detector (PDBSE).

The determination of iron concentration was investigated by using the inductively coupled plasma atomic emission spectroscopy method.

The catalytic activity of the obtained FeCNRs was tested in the oxidation of limonene. The detailed description the method of limonene oxidation was presented in our previous work [13]. t-Butyl hydroperoxide was used as on oxidant.

3 Results and discussion

Figure 1 shows XRD patterns of CCs and FeCNRs. Two broad peaks (002) and (100) characteristic of partially graphitic carbon [15] were observed for CCs.

The breadth of the peaks and the lack of signals characteristic of high graphitized carbons suggest that the degree of graphitization of support is not high. Microcrystalline structural parameters of the support were estimated. The interlayer spacing, the layer diameter, the stack height, the effective dimension of crystallites, and the average number of layers per stack of CCs were equal to 0.352 nm, 3.56 nm, 1.16 nm, 3.40 nm, and 3.2, respectively.

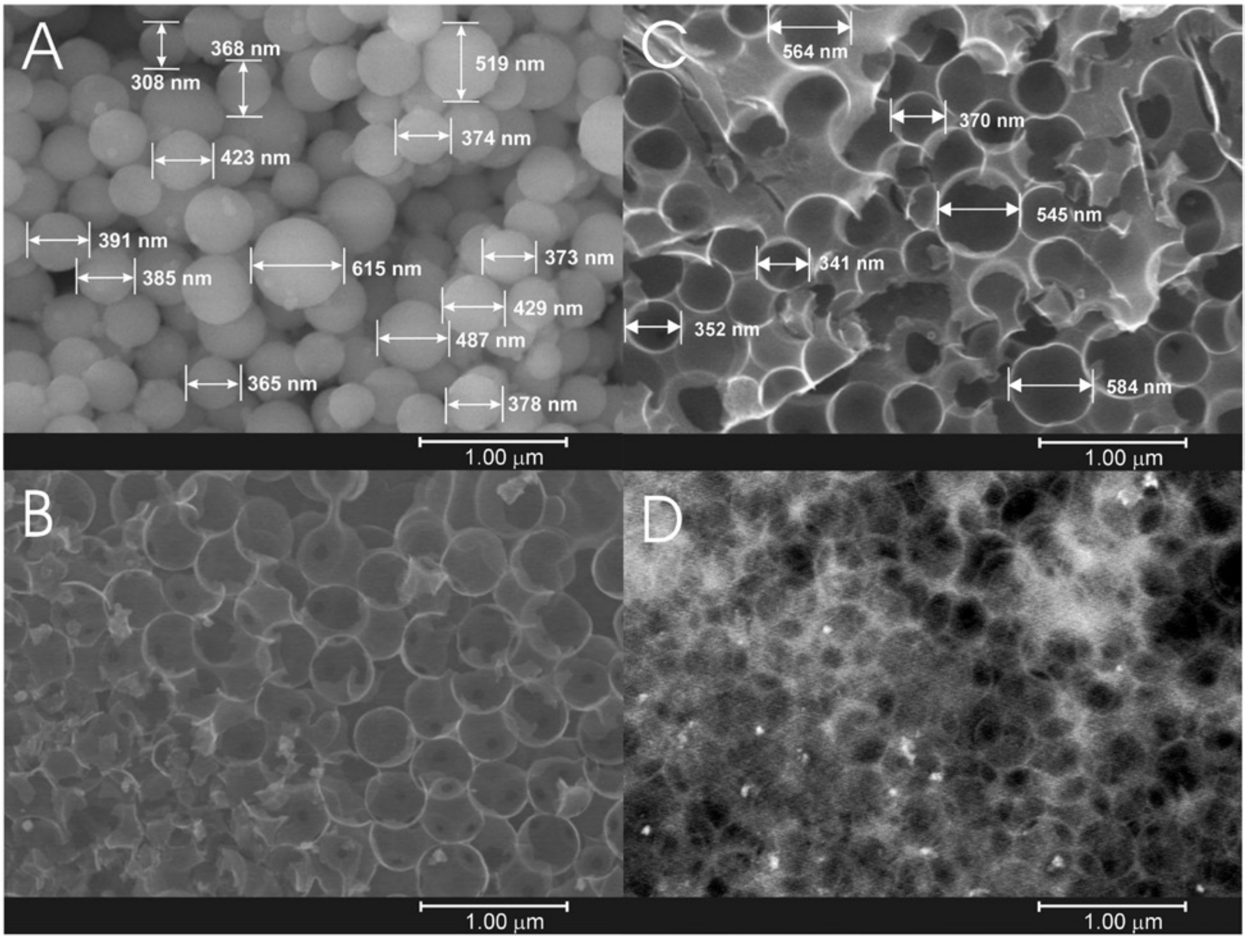

Figure 2: SEM pictures of (A) SNSs, (B) CCs, (C) 2.64FeCNRs using SE detector, and (D) 2.64FeCNRs using PDBSE detector.

Table 1: Textural parameters obtained from the N_2 adsorption data at 77 K.

Material	S_{BET} (m$_2$/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{micro}/V_{tot} (%)
CCs	386	0.391	0.128	33
0.68FeCNRs	440	0.338	0.149	44
1.32FeCNRs	424	0.322	0.146	45
2.64FeCNRs	377	0.289	0.126	44

FeCNRs showed similar diffraction patterns to CCs, but additional signals were observed at 35.40°, 57.00°, and 62.58°. These peaks can be indexed to Fe_3O_4 nanoparticles with inverse spinel structure matches well with the JCPDS Card No. 19-0629 [planes (311), (440), and (511)]. Fe(II) and Fe(III) with a 1 : 2 molar ratio were present. In contrast to the XRD results obtained when EuroPh was support [13], Fe_3O_4 patterns were observed even at an iron concentration equal to 0.68 wt%. The intensity of these peaks increased with the increase of Fe content. The influence of Fe_3O_4 concentration on the microcrystalline structural parameters cannot be estimated because peaks of CCs and Fe_3O_4 overlap each other. The average crystallite size of Fe_3O_4 was equal to 14 nm, as was estimated by Scherrer's equation.

Figure 2 shows SEM pictures of SNSs, CCs, and 2.64FeCNRs using SE detector and 2.64FeCNRs using PDBSE detector. The SNS image (Figure 2A) shows well-formed monodisperse spheres with an average particle size of 370 nm (range of 308–615 nm). CCs (Figure 2B) reveal a well-structured order with a hollow spherical center of carbon material.

The average diameter of the hollows was 377 nm (range of 316–584 nm). The shape of SNS template was well replicated in CCs. The introduction of iron did not damage CC structure (Figure 2C). SEM-backscattered electron image reveals bright particles sticking to the surface (Figure 2D). The micrograph obtained using the PD-BSE detector delivers information about the distribution of heavier elements on the surface iron. The distribution of Fe on CCs is uniform. Similar conclusions were drawn on the basis of 68FeCNR and 1.32Fe FeCNR pictures.

The values of S_{BET} and V_{micro} of the support were lower than those of 0.68FeCNRs, whereas V_{tot} was the highest (Table 1). By incorporating more amount of iron, the values of S_{BET}, V_{tot}, and V_{micro} decreased. S_{BET} and V_{micro} values were similar to those obtained for 2.64FeCNRs. The iron incorporation to the CC structure resulted in an increase in the micropore volume-to-total pore volume ratio. The V_{micro}/V_{tot} of the support and all FeCNRs were 33% and 44%–45%, respectively. Nanosized particles of Fe_2O_3 developed the microporosity of the materials.

On the basis on the density functional theory model fitting, it was found that the support was composed of cylindrical pores whereas FeCNRs were composed of slit and cylindrical pores.

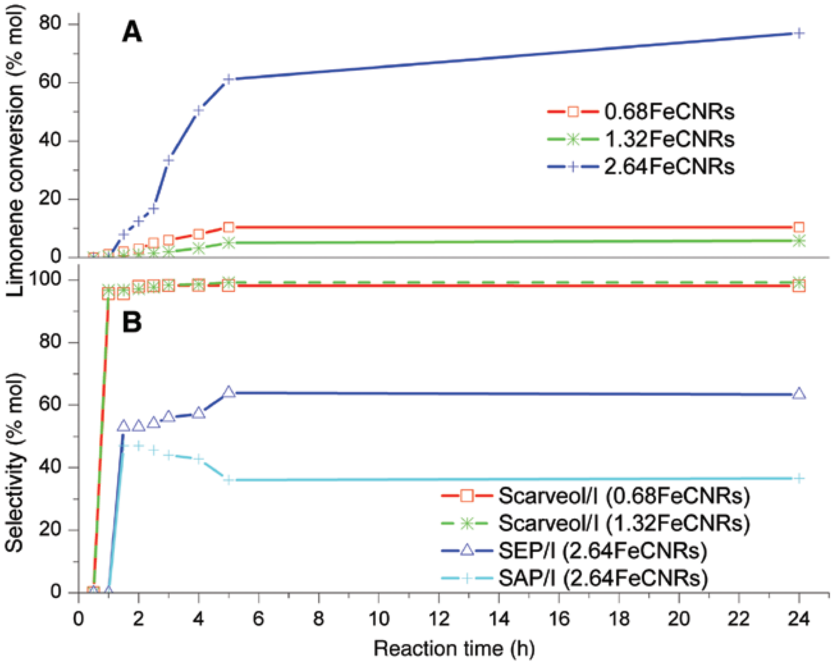

Figure 3: The results of the limonene oxidation on FeCNRs. (A) Conversions of limonene (CL) vs. time, (B) the selectivities (S) of the products (EP, 1,2-epoxylimonene; AP, perillyl alcohol).

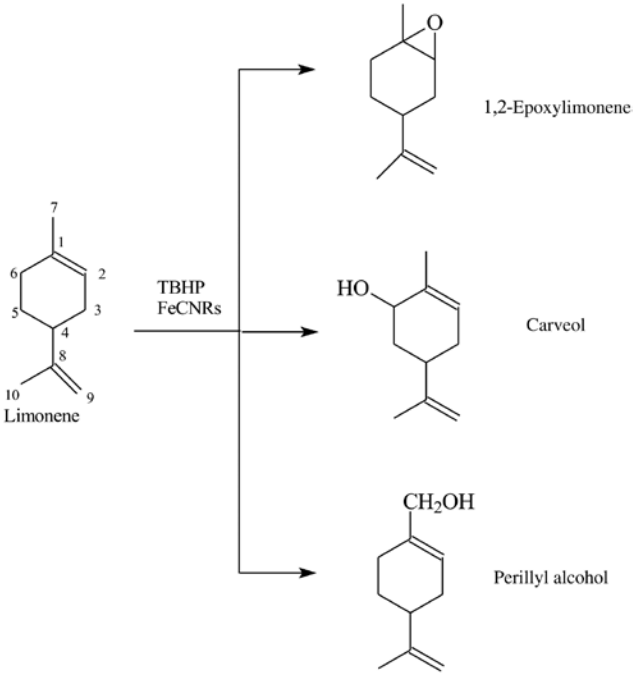

Figure 4: The formation the main products of limonene oxidation with TBHP on FeCNRs.

The studies on the catalytic activity FeCNRs showed that on the 0.68FeCNRs and 1.32FeCNRs, the almost only product of limonene oxidation was carveol – its selectivity amounted 96–98 mol%, independent of the reaction time (the second product was 1,2-epoxylimonene), and the conversion of limonene reached 10 and 6 mol% after 24 h, respectively (Figures 3A and B). The studies on the 2.64FeCNRs showed the change in the direction of limonene molecule oxidation because the main products were 1,2-epoxylimonene (its selectivity changed from 0 to 64 mol%) and perillyl alcohol (its selectivity changed from 0 to 47 and next 36 mol%) at limonene conversion from 0 to 75 mol% Figures 3A and B.

The scheme of the formation of the main products of limonene oxidation with t-butyl hydroperoxide (TBHP) on FeCNRs is presented in Figure 4.

The reused 0.68FeCNRs and 1.32FeCNRs were not active in oxidation limonene, but on the 2.64FeCNRs, the conversion of limonene achieved 25 mol% and perillyl alcohol was the only product of the limonene oxidation.

4 Conclusions

CCs were successfully synthesized by the simple method from molasses as the carbon source and silica spheres as the template. Fe nanoparticles were uniformly dispersed on CCs. The sizes of the CCs and FeCNRs depend on the SNS sizes. The porous structure make CC suitable as the support for FeCNRs – catalysts for limonene oxidation.

The obtained FeCNRs were active in limonene oxidation, and their activity was different from commercial activated carbon with iron, which we described earlier [13]. The main differences concern the selectivities of the main products (1,2-epoxylimonene, carvone, carveol, and perillyl alcohol) and the conversion of limonene. For 0.68FeCNRs and 1.32FeCNRs, it was possible to obtain almost one product (carveol), and for the 2.64FeCNRs, the formation of considerable amounts of 1,2-epoxylimonene (selectivity 64 mol%) at a very high conversion of limonene (approximately 77 mol%) was observed. Also, the reused 2.64FeCNRs was more active than the 2.64 EP we described earlier [13]. All products of limonene oxidation with TBHP on FeCNRs (carveol, 1,2-epoxylimonene, and perillyl alcohol) are very valuable intermediates used in the production of flavors, perfumes, cosmetics, food additives, drugs, agrochemicals, and polymers (e.g. “fragrant polymers”) [16]. Moreover, perillyl alcohol has been shown to be efficacious against the formation and progression of a variety of cancers. In animal studies, it has been shown to be therapeutic for pancreatic, mammary, and liver tumors and chemopreventive for colon, skin, and lung cancer [16]. It shows that the presented way of limonene oxidation should be further studied and developed.

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Bionotes

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Agnieszka Wróblewska, Professor at West Pomeranian University of Technology Szczecin, has a wide range of experience in the synthesis of zeolite-type microporous and mesoporous materials, in the epoxidation reactions of allylic compounds, and in the isomerization and oxidation of organic compounds of natural origin. She has a doctoral degree in Organic Chemical Technology.

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Jacek Młodzik graduated with a master’s degree in Chemical Technology in 2012. In October 2013, he started his PhD. He is a coauthor of many articles and patents, including a European patent for obtaining nanoporous carbon materials from beet molasses.

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Beata Michalkiewicz, Professor at West Pomeranian University of Technology Szczecin, has a wide range of experience in the investigation of catalytic selective methane oxidation, catalytic methane decomposition to carbon nanostructures, carbon dioxide adsorption, and photocatalytic reduction. She has an MSc in Inorganic Technology and a doctoral degree in Chemical Technology (catalysis). She is one of the leaders in the project “Post-combustion CO_2 Capture on New Solid Sorbents and Application in a Moving Bed Reactor” cofunded by the Polish-Norwegian Research Programme.