Simultaneous synthesis of styrene and aniline over activated carbon catalysts. Influence of the surface chemistry

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ABSTRACT

Activated carbons prepared from different precursors and two commercial carbons were applied as catalysts of ethylbenzene dehydrogenation carried out in the presence of nitrobenzene as an oxidiser (ODE-N process). Using of nitrobenzene enabled obtaining not only styrene, but also second industrially important product – aniline. Prior to the reaction some activated carbon samples were modified by oxidation with an air/helium mixture in order to generate carbonyl (quinone) structures on their surfaces, which are expected to be active centres of the process. The results obtained show that all samples prepared catalysed the ODE-N reaction and both surface texture and surface chemistry are important in the catalytic behaviour of activated carbons in this process.

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1. Introduction

Styrene plastics such as polystyrene (PS), acrylonitrile-butadiene-styrene (ABS) or styrene-acrylonitrile (SAN), besides polyolefins and poly(vinyl chloride), are an important group of thermoplastics of a wide range of applications. Their widespread use is definitely related to their attractive physical and chemical properties, facility of their processing (in particular injection moulding) and possibility of copolymerisation of styrene with other monomers [1].

Over 90% of the world production of styrene is based on catalytic dehydrogenation of ethylbenzene (DE) [2]. This process is conducted in temperatures from 600 to 700 °C, under excess of steam [3]. Severe conditions of the reaction lead to a gradual deactivation of the catalyst and reduce the time of its use in industrial installations. This limitation has reduced economical attractiveness of this technology. Attempts at modification of this method have been made for many years and have been mainly concerned with the use of a proper oxidiser to perform oxidative dehydrogenation of ethylbenzene. As a result of introduction of oxidiser to the reaction system, the process of oxidative dehydrogenation of ethylbenzene can be performed at lower temperatures than DE and is practically irreversible. The most often used oxidising agents are oxygen or air (ODE process) [4,5]. The use of other compounds such as carbon dioxide [6–8], nitrogen oxide [9], sulphur dioxide [10] or

nitrobenzene [11–13] has also been tested. The use of nitrobenzene seems particularly interesting as its reduction leads to formation of aniline, which is a product of potential industrial use (e.g. for rubber industry, production of dyes or in pharmaceutical industry [14]).

The most often used catalysts in ODE are inorganic systems such as mixed oxides and oxides promoted with rare earth metals [15,16]. According to a number of literature reports, the use of activated carbons is also beneficial in this reaction, which is related to relatively high activity of such systems in ODE, availability and low cost of activated carbon precursors and facility of modification to ensure proper textural or chemical surface properties of activated carbon [17]. Guerrero-Ruiz and Rodríguez-Ramos [18], Drago and Jurczyk [19] and Pereira et al. [20] have found that the texture of catalyst's surface is an important parameter controlling the activity of catalysts. According to these authors, ODE reaction most probably takes place mainly in meso- and macropores, although no direct correlation has been found between the pore surface area and the catalytic activity of the catalysts tested.

Another important question is the nature of active centres involved in ODE. Iwasawa et al. [21], on the basis of a study with polynaphthoquinone as a catalyst, have suggested a redox mechanism of the process in which quinone groups play a substantial role. Results of the reaction performed in the presence of inorganic systems have revealed that the real catalyst of the process is the carbon deposit forming in the ODE reaction [22,23] and the reaction mechanism is the same as proposed by Iwasawa [21,24]. The study by Lisovski [22] has confirmed that gas oxygen reoxidises the surface of the reduced catalysts, or to be more exact – its hydroquinone groups. Pereira et al. and other authors [25–27] have confirmed that

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the active sites of ODE are carbonyl/quinone groups and reported that the yield of styrene is proportional to the concentration of such groups on the catalyst surface [25].

In our study we have decided to use nitrobenzene as an oxidiser (this compound is relatively rarely tested in this role in oxidative dehydrogenation of ethylbenzene [11–13]) and activated carbon as a catalyst (sporadically used in above process [13]). In view of the suggestions that oxygen groups (most probably carbonyl/quinone systems) are involved in the mechanism of ODE, it is justified to suppose that such structures will be also active in oxidative dehydrogenation of ethylbenzene performed in the presence of nitrobenzene as an oxidiser. In connection with the above, the aim of this study was to synthesise a series of activated carbons with different amounts of oxygen functional groups and establish their effect on the yield of styrene and aniline obtained in ODE-N reaction. As according to our preliminary results the activated carbon modified with gas oxidiser (air) show in most cases higher activity in ODE-N than those modified by wet oxidation [28], we decided to study activated carbons oxidised with helium/air mixture.

2. Experimental

2.1. Preparation of catalysts

Activated carbon precursors applied were pinewood (sawdust), cherry stones and waste poly(ethylene terephthalate) (PET). These materials were chemically activated with different activating agents.

The cherry stones were activated with solid potassium hydroxide at the weight ratio of the precursor to the activating agent of 1:1. The process was carried out in argon atmosphere in a reactor placed in a horizontal tube furnace at $800\,^\circ$C for 45 min. The material was washed with a 10% solution of hydrochloric acid and then with distilled water. The activated carbon obtained was dried overnight at $110\,^\circ$C and the sample was labelled as C(KOH).

The method of obtaining carbon from PET was a modified version of the procedure proposed by Przepiórski et al. [29]. Grounded PET was mixed with basic magnesium carbonate (BMC) of the molecular formula $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$, at the weight ratio of BMC to PET of 7:3. The mixture was placed in a crucible and heated in the furnace up to 290–295 $^\circ$C for 1 h. After cooling the melt was refined and carbonised at $850\,^\circ$C in argon atmosphere for 1 h. Upon heating BMC undergoes thermal decomposition with formation of MgO (of large volume) and evolution of gaseous products including CO_2 and H_2O, which is accompanied by the reaction of these gases with carbon material formed from PET. The product obtained was treated with a 10% solution of hydrochloric acid and dried overnight at $110\,^\circ$C. The activated carbon obtained was labelled as PET(BMC).

Pinewood sawdust was impregnated with an 18% solution of phosphoric acid at the ambient atmosphere for 2 h (the weight ratio of the precursor to the activating agent was 1:1). The impregnate was dried at $110\,^\circ$C, and then activated in a reactor placed in a tube furnace in argon atmosphere at $500\,^\circ$C for 1 h. The activated carbon was washed with distilled water and dried overnight at $110\,^\circ$C. The material was labelled as $P(H_3PO_4)$.

All activated carbon samples obtained were subjected to oxidation by a helium/air mixture containing 5% of oxygen. The reaction mixture was prepared by mixing air ($10\,cm^3$/min) and helium ($30\,cm^3$/min). The above flow rates were controlled by mass flow controllers. The oxidation was performed in a glass reactor placed in a vertical tube furnace at $450\,^\circ$C for 2.5, 5.0 or 10.0 h using 3 g of carbon sample. The oxidised activated carbons were labelled according to the scheme: AC_oxidation time (e.g. C(KOH)_2.5 h).

For comparative reasons two commercially available carbons were also used: RX 3 EKSTRA (NORIT) and WG-12 (GRYFSKAND in Hajnówka, Poland).

2.2. Characterisation of carbon catalyst

Textural properties of the carbon catalysts were determined on the basis of nitrogen adsorption at $-196\,^\circ$C, using a Micromeritics Sorptometer ASAP 2010. The BET equation permitted calculation of the apparent surface area (S_{BET}), while the micropore volume (V_{micro}) and external surface area (of meso- and macropores) (S_{ext}) were found using the t-plot method [30]. The total pore volume (V_{tot}) was obtained from N_2 amount adsorbed at a relative pressure close to unity. Quantitative elemental analysis CHNS was made by an Elemental Analyser Vario EL III. The transmission FTIR spectra of some selected samples were acquired using a Bruker IFS 66 v/S spectrometer by adding 256 scans at $2\,cm^{-1}$ resolution. Pressed KBr pellets at a sample/KBr ratio of 1:1000 were used. The temperature-programmed desorption (TPD) was performed in a quartz reactor using a 100 mg sample. Heating rate of $10\,^\circ$C/min up to $1050\,^\circ$C and helium flow rate of $10\,cm^3$/min were applied. The gases evolved were analysed on a Gas Analyser Thermo Star GSD 301 T2 (Pfeiffer Vacuum). Morphological appearance of the fresh and spent catalysts was studied by scanning electron microscopy (SEM) using a Philips 515 apparatus. Powder X-ray diffraction (XRD) measurements of selected samples have been carried out using a Bruker AXS D8 Advance apparatus, equipped with Johansson monochromator ($\lambda Cu\,K_{\alpha 1} = 1.5406\,Å$) and silicon strip detector LynxEye. XPS measurements were performed on an ESCALAB-210 spectrometer made by VG Scientific (GB), with the use of Al K_α radiation at the Constant Analyzer Energy CAE = 25 eV. The XPS spectra were smoothed and the Shirley background was subtracted. The calibration was carried out to the main C 1s peak at 284.8 eV. The concentration of the elements was calculated using the area of C 1s, O 1s, N 1s, S 2p peaks and cross-sections given by Scofield [31]. The XPS C 1s, O 1s and N 1s peaks were deconvoluted into individual spectral lines, treated as asymmetric sums of the Gauss–Lorentz functions. The ratio of the Gauss to the Lorentz lines of 20:80% was assumed. The following binding energies and their assignment to particular species was taken, according to literature data C 1s: 284.8 eV (C—C, C—H), 286.3 eV (C—O), 287.5 eV (C=O, O—C—O), 289.0 eV (O=C—O) and 291.3 eV (π–π^* transition) [32–34]; O 1s: 531.3 eV (C=O), 532.8 (C—O), 534.1 (O=C—O) [32]; N 1s: 398.8 eV (pyridinic nitrogen), 400.2 eV (pyrrolic nitrogen), 401.4 eV (quaternary nitrogen), 402.9 eV (oxidised nitrogen) [35–38].

2.3. Catalytic measurements

Catalytic properties of the activated carbons obtained were tested in oxidative dehydrogenation of ethylbenzene coupled with hydrogenation of nitrobenzene (ODE-N). The process was run in a glass reactor with a stationary bed of the catalyst of 50 mg at $400\,^\circ$C (as this is the optimum temperature of the process established in our earlier work [28]). Until reaching a desired temperature, argon was blown through the reactor. After reaching $400\,^\circ$C a mixture of ethylbenzene and nitrobenzene at the molar ratio of 3:1 (stoichiometric ratio) was introduced into the reactor by an infusion pump, at the rate of $0.5\,cm^3$/h. The reaction products and unreacted substrates were frozen in the U-tube and collected at every 12 min for 3 h. In order to obtain a homogeneous post-reaction mixture, the samples were mixed with isopropanol and then subjected to chromatographic analysis with the use of a capillary column MTX1 and FID detector.