

Chemically Modified Activated Carbons as Catalysts of Oxidative Dehydrogenation of *n*-Butane

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Commercial availability and low price of light alkanes make them very attractive in many branches of industry. Potentially interesting is their use in the process of oxidative dehydrogenation leading to production of olefins. This study was undertaken to characterise the oxidative dehydrogenation of *n*-butane to 1,3-butadiene (important substrate in production of synthetic rubber and polyamides) taking place over the modified carbon catalysts obtained from peach stones precursor. The catalytic tests were performed in the temperature range 250–450 °C at oxygen/*n*-butane ratio of 1:1. For the majority of the activated carbon samples studied at the lowest temperature the only product was CO₂. At 300 °C the products of dehydrogenation of *n*-butane and side products appeared. With increasing temperature the amount of compounds generated increased and in the group of C₄ hydrocarbons the dominant were 1-butene and 1,3-butadiene. The most effective catalyst was the sample oxidised with air, the least effective was the sample modified with ammonium peroxydisulphate.

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1. Introduction

Research work on methods of production of 1,3-butadiene has been intensified in the last years because of its importance as a raw material for chemical industry — 1,3-butadiene is the most important monomer in synthesis of rubber (SBR, NBR and others) and polyamides [1, 2]. Because of commercial availability and relatively low price of light alkanes, dehydrogenation of *n*-butane to 1,3-butadiene has been generally accepted as a good way to produce this compound. However, this method has a few drawbacks — dehydrogenation is a reversible and endothermic reaction, so requires high operation temperature to obtain the optimum substrate to product conversion level. Catalytic oxidative dehydrogenation (ODH) of *n*-butane is expected to reduce the costs of 1,3-butadiene production relative to those of non-oxidative process, as it is irreversible and exothermic and can be carried out at lower temperatures. Moreover, the presence of oxygen limits coking and extends the catalyst lifetime. Many papers have been devoted to ODH of light alkanes, but most of them concerned the use of inorganic catalysts in the process. The catalysts most often studied were vanadium or molybdenum-containing ones which showed high activity for this reaction [3–7]. However, as proved by the study of the oxidative dehydrogenation of ethylbenzene to styrene, the real catalyst of this reaction is the carbonaceous deposit forming *in situ* on the surface of the inorganic system [8–10]. Similar conclusions were reached by Maldonado-Hódar et al., who studied ODH of

n-butane over the Ni–Mo–O catalyst [11]. As the chemical structure of the carbonaceous deposits is very similar to that of activated carbons, we decided to check the behaviour of activated carbons modified in different ways in this reaction.

The main advantages offered by activated carbons follow from the possibility of their modification to get desired textural properties and chemical character of the surface. Literature survey has brought only one paper on ODH of *n*-butane over carbonaceous materials but the carbon catalysts were not modified in any way [12]. The authors of this paper have reported that the unmodified coals of different degree of metamorphism show high catalytic activity in the reaction studied. The highest yield of C₄ products was obtained for high volatile (hv) bituminous coal. The main parameters determining the activity of these catalysts indicated by the authors were the type of porous structure, content of mineral substances and number of active sites.

As follows from presented literature, activated carbons could be potential catalysts of ODH of *n*-butane, but have not been hitherto tested in this process. In view of the above, the aim of this study was to obtain activated carbon, subject it to different modifications and test the effect of the modification on the catalytic properties of the material obtained in the ODH reaction of *n*-butane.

2. Experimental

2.1. Samples and their characterisation

The peach stones were used as a precursor of the activated carbon samples tested in ODH of *n*-butane. They

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were activated with KOH at 800 °C [13], and the material obtained was modified to change the character of its surface. Oxygen groups were introduced into the carbon structure with the help of the following liquid or gas agents: hydrogen peroxide, ammonium peroxydisulfate (APS), nitric acid, peroxyacetic acid (PAA), air. The other types of treatment applied were reduction with hydrogen, nitrogenation with ammonia and thermal treatment in an argon atmosphere (the carbon sample previously oxidised with APS), which resulted in decrease in the oxygen content in the carbon samples. The samples were labelled as follows: AC/modifying agent/temperature/time of modification. Detailed information on the preparation and properties of the catalysts obtained is given in Gniot et al. [14].

All carbon samples obtained were subjected to elementary analysis on an Elemental Analyser Vario EL III and their texture was characterised on the basis of N₂ adsorption/desorption isotherms determined at -196 °C with a Micrometrics Sorptometer ASAP 2010 apparatus. The apparent surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation, whereas micropore volumes (V_{micro}) were determined by the t -plot method [15]. The total pore volumes (V_{tot}) were obtained from the N₂ amount adsorbed at a relative pressure close to unity.

2.2. Catalytic tests

The catalytic tests were carried out in a continuous-flow fixed-bed reactor at atmospheric pressure using a glass wool as a catalyst support on which about 100 mg of

material was placed. The temperature was measured by a thermocouple inserted into the catalyst bed. The post-reaction gas mixture was analysed by chromatographic methods. The chromatograph was equipped with two columns: Restek CarboBlack C with 0.19% picric acid (determination of C4 hydrocarbons and CO₂) and the second one — molecular sieve 5A column (oxygen, nitrogen and CO). The temperature used in the standard catalytic tests was in the range 250–450 °C and the feed composition was obtained by mixing of air and *n*-butane (oxygen to *n*-butane ratio = 1:1). Diluent was helium and the flow rate of gas reagents was 20 cm³/min.

3. Results and discussion

3.1. Characterization of materials

Selected physical and chemical properties of the activated carbon samples unmodified and modified in different ways are collected in Table I. As follows from analysis of these data, the use of an oxidising agent in the process of carbon treatment gives an increase in the content of oxygen in the carbon structure. For a given modifying agent, this increase significantly depends on the temperature of modification; the higher the temperature the greater the amount of oxygen groups introduced. The effect of changes in the time of modification was rather small. The most effective oxidising agent proved to be APS, while the least effective was the treatment of initial activated carbon with air.

TABLE I

Selected parameters of activated carbons tested.

| Sample | S_{BET} [m ² /g] | V_{tot} [cm ³ /g] | V_{micro} [%] | O^{d} [wt%] |
|--|--------------------------------------|---------------------------------------|------------------------|----------------------|
| AC | 1248 | 0.61 | 86.9 | 5.9 |
| AC/H ₂ O ₂ /30 °C/24 h | 1223 | 0.61 | 95.1 | 10.6 |
| AC/H ₂ O ₂ /60 °C/24 h | 1103 | 0.58 | 91.4 | 13.6 |
| AC/APS/30 °C/24 h | 824 | 0.41 | 92.7 | 25.4 |
| AC/APS/60 °C/24 h | 416 | 0.21 | 90.5 | 31.6 |
| AC/PAA/60 °C/4 h | 1169 | 0.58 | 94.8 | 9.8 |
| AC/PAA/60 °C/8 h | 1204 | 0.60 | 95.0 | 9.5 |
| AC/HNO ₃ /60 °C/4 h | 1132 | 0.56 | 94.6 | 18.9 |
| AC/HNO ₃ /60 °C/8 h | 1162 | 0.57 | 94.7 | 20.1 |
| AC/air/300 °C/4 h | 1270 | 0.63 | 95.2 | 8.5 |
| AC/air/300 °C/8 h | 1256 | 0.62 | 95.2 | 7.7 |
| AC/NH ₃ /650 °C/4 h | 1139 | 0.55 | 96.4 | 0.9 |
| AC/NH ₃ /850 °C/4 h | 688 | 0.34 | 94.1 | 1.1 |
| AC/H ₂ /650 °C/4 h | 936 | 0.46 | 93.5 | 2.1 |
| AC/APS-30 °C/Ar/850 °C/4 h | 1179 | 0.59 | 94.9 | 4.0 |

The type of the oxidising agent used was found to influence not only the amount but also the character of oxygen groups introduced into the sample. According to our results published in [14] and the results from [16, 17], the oxidation of activated carbon samples with the modifying agent in solution generates mainly carboxyl groups, whereas the treatment with a gas oxidising agent generates mainly hydroxyl (phenol) groups and carbonyls/quinones.

Some samples of the carbon were subjected to modifications aimed at elimination of oxygen groups from their structure. According to the data presented in Table I, all these modifications were effective. The lowest level of oxygen was achieved in the sample subjected to high temperature treatment with ammonia, but the temperature applied was proved to have small effect on the efficiency of the process. According to literature, the samples treated at high temperature show the presence of stable carbonyl/quinone groups, although the presence of basic groups, such as pyrones and chromenes in them is also possible [14, 18].

The initial activated carbon was evidenced to have relatively large surface area (Table I). The treatment of the initial carbon with air leads to a small increase in this parameter, while the other types of treatment produce a decrease in the surface area, the most pronounced after modification with APS at 60 °C and little less after modification with hydrogen or ammonia. All carbon samples have microporous structure as follows from the values of V_{tot} and V_{micro} . Other details on the samples characterization by different techniques are presented in paper of Gniet et al. [14].

3.2. Catalytic properties of carbons

Catalytic activity in the oxidative dehydrogenation of *n*-butane as a function of reaction temperature was analysed in terms of the effects of the types of treatment of the initially activated carbon. According to the chromatographic data, ODH of *n*-butane over activated carbon leads to generation of the following C4 hydrocarbons: 1-butene, *cis* and *trans* isomers of 2-butene, 1,3-butadiene and CO_x (that can appear as a result of combustion of *n*-butane as well as unsaturated hydrocarbons formed in the reaction).

Figures 1–8 present the yields of particular products versus the temperature of the process for all activated carbon samples obtained, implying some general conclusions. For the majority of the activated carbon samples tested at the lowest temperature applied (250 °C) the only product was CO_2 . With increasing temperature of the process the formation of *n*-butane dehydrogenation products and side products is observed. The yields of *cis* and *trans* isomers of 2-butene are comparable at each temperature applied. Also at each temperature considerable part of the substrate undergoes oxidation to carbon oxides of which the contribution of CO_2 is greater than CO. The contribution of particular products increases with growing temperature and the greatest amounts of C4 products are generated at 450 °C. At

high temperatures the dominant reaction products are 1,3-butadiene and 1-butene, while in lower temperatures the amounts of all C4 hydrocarbons obtained are comparable. For the majority of modified carbon samples the harsher the modification conditions (higher temperature or longer time of treatment) the lower the yields of C4 products (except for carbon samples modified with PAA and APS).

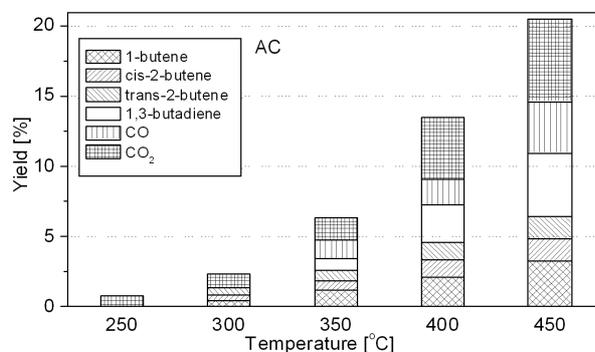


Fig. 1. Yields of the products of ODH of *n*-butane versus the temperature of the process over unmodified activated carbon.

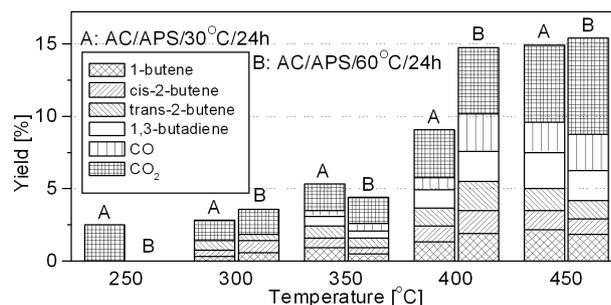


Fig. 2. Yields of the products of ODH of *n*-butane performed over the catalysts modified with ammonium persulfate (APS).

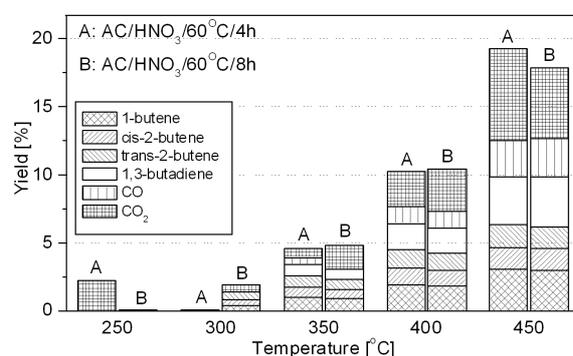


Fig. 3. Yields of the products of ODH of *n*-butane performed over the catalysts oxidised with nitric acid.

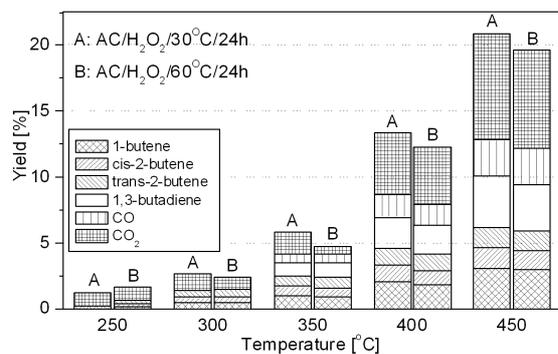


Fig. 4. Yields of the products of ODH of *n*-butane performed over the catalysts oxidised with hydrogen peroxide.

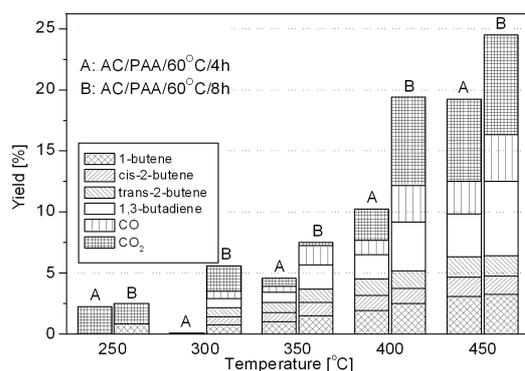


Fig. 5. Yields of the products of ODH of *n*-butane performed over the catalysts oxidised with peroxyacetic acid (PAA).

As follows from Fig. 1, the use of unmodified carbon in ODH of *n*-butane permits getting relatively high yields of C4 olefins. At the lowest temperature studied (250 °C) the only product is carbon dioxide. Starting from 300 °C, besides the product of deep oxidation also 1-butene and its isomers *cis*-2-butene and *trans*-2-butene are formed. The most desirable 1,3-butadiene

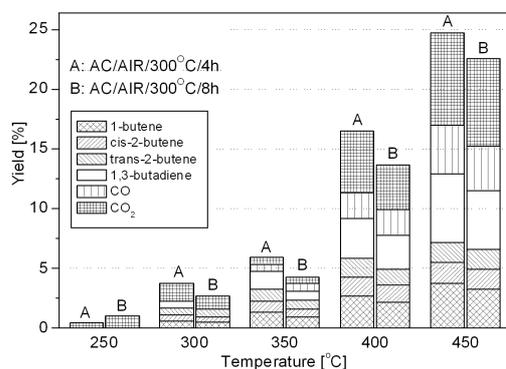


Fig. 6. Yields of the products of ODH of *n*-butane performed over the catalysts oxidised with air.

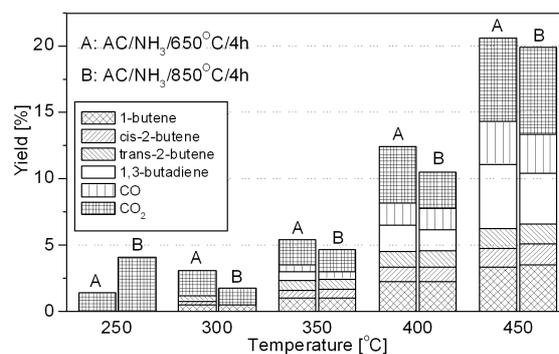


Fig. 7. Yields of the products of ODH of *n*-butane performed over the catalysts modified with ammonia.

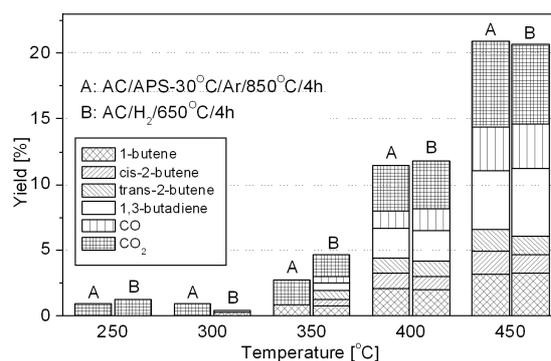


Fig. 8. Yields of the products of ODH of *n*-butane performed over the catalysts subjected to thermal treatment or reduction with hydrogen.

starts forming only in higher temperatures (≥ 350 °C). Similar behaviour was observed for the samples oxidised with APS and HNO_3 (Figs. 2 and 3), and also for the samples $\text{AC}/\text{NH}_3/650$ °C/4h, $\text{AC}/\text{AIR}/300$ °C/8 h and $\text{AC}/\text{PAA}/60$ °C/4h (Figs. 5–7). The situation is different for both samples oxidised with hydrogen peroxide (Fig. 4) and for those oxidised with PAA for 8 h, for which already in the lowest temperature studied small amounts of 1-butene and the products of its isomerization are formed. When using the latter sample (and sample oxidised with air for 4 h), in relatively low temperature of ODH of *n*-butane (300 °C), along with 1-butene and 2-butene isomers the desired 1,3-butadiene is formed (Figs. 5 and 6). When using the samples subjected to nitrogenation with ammonia at 850 °C or to thermal treatment, 1,3-butadiene starts appearing only from 400 °C (Figs. 7 and 8).

In order to compare the catalytic activity of all activated carbon samples obtained, the yields of all C4 products appearing as a result of ODH of *n*-butane performed at 450 °C (at which the best results were achieved) are collected in Table II. According to these data, for each of the catalysts applied the dominant C4 products of ODH of *n*-butane were 1-butene and 1,3-butadiene. Apart from them also the products of isomerization of 1-butene: *cis*-

-2-butene and *trans*-2-butene were generated. As follows from literature, isomerization can occur according to three mechanisms: ionic, radical [19] and with involvement of a pair of acid-base centres as proposed by Ghorbel et al. [20]. According to the first mechanism, the isomerization takes place on acidic or basic centres. When the reaction is catalysed by acid sites, the amounts of *cis* and *trans* 2-butene are comparable (the *cis/trans* ratio ≈ 1), but when by basic centres then the amount of *cis*-2-butene is by about one order of magnitude greater than that of *trans*-2-butene (the *cis/trans* ratio ≈ 10). When the reaction runs with the involvement of neighbouring acidic and basic sites, the ratio of *cis* and *trans* isomers is intermediate between the above two [20]. In our catalytic tests the amounts of 2-butene isomers formed were similar, so the isomerization reaction is supposed to take

place on acidic centres. The strongest acids that can be formed in the carbon structure are the carboxyl groups. According to our earlier studies [14], the greatest number of these groups contain the catalysts modified with APS. However, using these carbon samples as catalysts leads to low yields of 2-butene isomers. This result can be explained by instability of carboxyl groups that decompose already in the range 100–400 °C [16, 21]. For the other samples the yields of *cis*- and *trans*-2-butene are relatively high. Most probably in the other samples the role of acidic active sites is played by more thermally stable acidic hydroxyl groups, present either originally in the modified carbon samples or formed as a result of oxygen introduction into the system during the process of ODH of *n*-butane.

TABLE II

Yields of C4 products obtained in ODH reaction of *n*-butane over different carbon catalysts at 450 °C.

| Sample | Yield of products [%] | | | | Total yield of C4 hydrocarbons [%] |
|--|-----------------------|----------------------|------------------------|---------------|------------------------------------|
| | 1-butene | <i>cis</i> -2-butene | <i>trans</i> -2-butene | 1,3-butadiene | |
| AC | 3.28 | 1.56 | 1.56 | 4.55 | 10.95 |
| AC/H ₂ O ₂ /30 °C/24 h | 3.10 | 1.54 | 1.49 | 3.95 | 10.08 |
| AC/H ₂ O ₂ /60 °C/24 h | 2.96 | 1.43 | 1.50 | 3.49 | 9.38 |
| AC/APS/30 °C/24 h | 2.14 | 1.37 | 1.53 | 2.49 | 7.53 |
| AC/APS/60 °C/24 h | 1.86 | 1.09 | 1.25 | 2.01 | 6.21 |
| AC/PAA/60 °C/4 h | 3.38 | 1.65 | 1.57 | 4.37 | 10.97 |
| AC/PAA/60 °C/8 h | 3.21 | 1.49 | 1.74 | 6.08 | 12.52 |
| AC/HNO ₃ /60 °C/4 h | 3.07 | 1.62 | 1.62 | 3.52 | 9.83 |
| AC/HNO ₃ /60 °C/8 h | 3.00 | 1.55 | 1.62 | 3.66 | 9.83 |
| AC/air/300 °C/4 h | 3.76 | 1.70 | 1.73 | 5.72 | 12.91 |
| AC/air/300 °C/8 h | 3.27 | 1.66 | 1.66 | 4.94 | 11.53 |
| AC/NH ₃ /650 °C/4 h | 3.35 | 1.38 | 1.48 | 4.90 | 11.11 |
| AC/NH ₃ /850 °C/4 h | 3.53 | 1.56 | 1.53 | 3.76 | 10.38 |
| AC/H ₂ /650 °C/4 h | 3.21 | 1.43 | 1.40 | 5.15 | 11.19 |
| AC/APS-30 °C/Ar/850 °C/4 h | 3.19 | 1.68 | 1.68 | 4.52 | 11.07 |

As indicated by the data from Table II, the worst catalytic properties in ODH of *n*-butane shows the sample modified with APS at 60 °C, leading to the least yield of 1,3-butadiene and the lowest total yield of C4 products. As follows from Table I, this sample shows the greatest content of oxygen from among the catalysts tested. As mentioned earlier, this oxygen occurs mainly in the form of carboxyl groups, not catalytically active in the ODH reaction. The greatest yield of C4 hydrocarbons and one of the greatest yields of 1,3-butadiene is noted for the activated carbon oxidised with air for 4 h. According to literature data, oxidation with air leads mainly to formation

of hydroxyl groups and carbonyls/quinones [16, 17]. The latter are commonly known as the active sites of ODH [8, 22–24]. Relatively high yields of 1,3-butadiene can also be reached over the catalyst subjected to reduction with hydrogen and having little oxygen content (Table I). This result is probably related to the fact that certain carbon substances after reduction show enhanced susceptibility to oxidation [25]. Velásquez et al. also reported formation of a great number of carbonyls/quinones during ODH on the samples reduced with hydrogen [26].

4. Conclusions

For the majority of the carbon samples obtained and applied as catalysts of ODH of *n*-butane, the reaction performed at the lowest temperature tested (250 °C) leads to generation of small amounts of CO₂. At 300 °C besides CO_x, also the products of dehydrogenation are formed (1-butene, isomers of 2-butene and 1,3-butadiene). With increasing temperature of the reaction the yield of these C4 hydrocarbons increases, and the dominant products are 1-butene and 1,3-butadiene. The results obtained have proved that the best catalyst of ODH of *n*-butane is activated carbon oxidised with air for 4 h as the reaction over this catalyst gives the highest yield of C4 hydrocarbons and one of the highest yields of 1,3-butadiene. The lowest total yield of C4 products and the lowest yield of 1,3-butadiene was obtained for the sample modified with ammonium peroxydisulfate at 60 °C for 24 h. The catalytic activity of the carbon samples obtained can be explained by the differences in the content of carbonyls/quinones, considered as the catalytically active sites of ODH of hydrocarbons. These oxygen functional groups can originally occur in carbons but they can also be formed as a result of the contact of carbon and oxygen in the ODH process.

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