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Study on catalytic centres of activated carbons modified in oxidising or reducing conditions

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ABSTRACT

Three model reactions: decomposition of isopropanol, cyclisation of acetonylacetone and cumene decomposition have been used for characterisation of catalytically active centres in activated carbons modified in oxidising or reducing conditions. Oxidised activated carbon catalysts show high activity in isopropanol decomposition and the dominant product of this reaction is propene, which indicate that oxidation of activated carbons with liquid or gas agents stimulates formation of surface oxygen groups, mainly those of acidic character. Modification of activated carbon by reduction with hydrogen or by nitrogenation with ammonia causes partial removal of the oxygen functional groups leading to a decrease in the catalytic activity towards propene and a simultaneous increase in isopropanol conversion to acetone (basic centres formation). The influence of above modifications on the catalytic activity of activated carbons is confirmed by investigation of cyclisation of acetonylacetone. The dominant product of cumene decomposition performed over activated carbon samples studied is α-methylstyrene, which testifies to the presence of electron-transfer centres in these catalysts.

1. Introduction

Model reactions are commonly used for determination of chemical character of the surface of solid-state catalysts such as metals, metal oxides or zeolites [1–4]. The universality of model reactions follows from the fact that they are simple, usually take place at well-defined active centres (acidic, basic or redox) and are carried out in the conditions of catalyst work. Model reactions permit identification of the type and estimation of the strength of active centres on the catalyst surface. Exemplary model reactions include dehydration of alcohols or isomerisation of alkenes [5,6], taking place on weak acidic centres or cumene decomposition that needs strong Brönsted acidic centres [7–12]. The presence of basic centres is deduced from measurements of the rate of alcohol dehydrogenation to aldehydes.

So far model reactions have been used to characterise the catalytically active centres mainly on the surface of inorganic catalysts. However, it has been proved that such processes as alcohol decomposition [13–22] or Knoevenagel condensation [23] can be successfully used for identification of acidic/basic reaction centres in carbon materials. Decomposition of different alcohols over modified activated carbon catalysts have been studied by Szymański et al. [13–16]. On the basis of results of butan-2-ol [13] and isopropanol [14] decompositions, these authors claim that the activity of carbon catalysts towards dehydration is related to the presence of surface carboxyl groups of different strength, while the activity towards dehydrogenation is related to the simultaneous presence of acidic and basic Lewis centres. The activated carbons modified by oxidation have been shown to effectively catalyse isopropanol dehydration and dehydrogenation leading to diisopropyl ether and propene or acetone, respectively, and to be more active than unmodified carbons. Moreover, it has been established that dehydration takes place according to the mechanism of parallel or subsequent reactions on the outer surface of the catalysts, while dehydrogenation is realised inside the catalyst pores. According to literature, such model reactions as cyclisation of acetonylacetone or cumene decomposition have not been applied in investigation of catalytic centres in activated carbon materials. To the best of our knowledge, the cyclisation of acetonylacetone has been so far used only for characterisation of active centres of inorganic catalysts [24–26]. Depending on the nature of the catalyst applied, this process can lead to formation of 2,5-dimethylfuran (DMF) or 3-methylcyclopent-2-en-1-one (MCP), requiring Brönsted acid centres or basic centres, respectively [25]. Cumene decomposition has been used in investigation of fluorinated carbons and inorganic phase supported on carbon materials [27–29], but not activated carbons. This reaction can proceed in two directions. In the presence of strong Brönsted acidic centres it leads to benzene and

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Table 1
Proximate analyses of precursors (wt%).

Sample	Moisture	Ash (dry basis)	Volatile matter (dry ash free)
Raw brown coal from Konin colliery	17.0	22.6	33.3
Demineralized brown coal	0.0	0.9	37.0
Pinewood sawdust	11.9	2.4	83.3

propene (sometimes to m- and p-diisopropylbenzene), while in the presence of electron-transfer centres it gives styrene and α-methylstyrene and rarer n-propylbenzene and ethylbenzene (with involvement of Lewis acidic centres) [11,12]. Another possible product of this process is toluene, which can appear as a result of side chain cracking [10]. It is worth noting that cumene decomposition is interesting not only as a model reaction for characterisation of active centres but also, according to some authors, as a method for the production of α-methylstyrene – an important monomer for the use in petrochemical industry [27,30,31].

As the model reactions have been hitherto rarely applied in investigation of activated carbons, the main aim of this study was to determine the character of catalytically active centres in activated carbons, modified in oxidising or reducing conditions, by means of three selected model reactions: isopropanol decomposition, cyclisation of acetonylacetone and cumene decomposition.

2. Experimental

2.1. Preparation of activated carbon catalysts

The activated carbon samples studied were obtained from pinewood biomass (sawdust) and brown coal (from Polish colliery "Konin"). Parameters characterising the precursors (the contents of ash, moisture and volatile components) are given in Table 1. The precursors were subjected to preliminary mechanical processing (grinding and sifting to the mesh size of 0.4 mm), while the brown coal was also demineralised by the Radmacher and Mohrhauer method with the use of concentrated hydrochloric acid and hydrofluoric acid [32]. Then the samples obtained were subjected to chemical activation with potassium hydroxide (the weight ratio of KOH:precursor was 1:1) at 1073 K in a neutral gas atmosphere (argon) supplied at the flow rate of 50 $dm^3 h^{-1}$, for 45 min. The product was treated with a 5% HCl, washed with distilled water and dried at 383 K till constant mass. Because of the low content of mineral components, pinewood sawdust was not subjected to demineralisation.

The initial activated carbons were further subjected to chemical modifications using different times and temperatures of these processes. The oxidation was applied for introduction of new surface oxygen functional groups, while the aim of reduction was the partial removal of oxygen groups from the activated carbon surface. The oxidation was realised by exposure of carbon to liquid or gas oxidisers. The treatment in solution was performed with 30% H_2O_2, concentrated HNO_3, CH_3COOOH (peroxyacetic acid, PAA, a mixture of acetic acid and hydrogen peroxide [33]) or 2.5 M $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 (ammonium peroxydisulphate, APS) [34]. In the processes of wet oxidation the sample of 3 g of activated carbon was mixed with 90 cm^3 of the oxidant solution and after completion of the process the product was carefully washed with warm distilled water and dried at 383 K overnight. The oxidising agent used in gas phase was the atmospheric air. The reduction of activated carbons was realised by their reaction with hydrogen, ammonia or by high temperature annealing in argon atmosphere of carbon samples previously oxidised with ammonium peroxydisulphate at 303 K. The modification of samples (0.3–1.0 g) with the agents in gas phase was performed in a quartz reactor (heated by a tube furnace) at the gas flow of 20–50 $cm^3 min^{-1}$. The samples obtained were sieved to the grain size ≤0.06 mm and labelled to include the following information: *initial carbon-modifying agent-time of modification-modification temperature*.

2.2. Catalyst characterisation

Textural properties of the carbon catalysts were determined on the basis of nitrogen adsorption at 77 K, 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 by using the *t*-plot method [35]. The total pore volume (V_{tot}) was obtained from N_2 amount adsorbed at a relative pressure close to unity. The approximate average pore diameter was calculated using the formula $D_{av} = 4V_{tot}/S_{BET}$. Quantitative elemental analysis CHNS was made by an Elemental Analyser Vario EL III. The total acidity of the activated carbon samples was determined by potentiometric titration.

2.3. Catalytic measurements

The catalytic tests in the reaction of isopropanol decomposition were performed by the pulse method in a glass reactor with a fixed bed catalyst (0.02 g) at temperatures from 423 to 723 K. Isopropanol was dosed by a microsyringe in the amount of 0.2 μl. The products of dehydration and dehydrogenation were analysed using a gas chromatograph (connected on-line with reactor) equipped with a FID detector and a 2 m column packed with 30% Emulphor O supported on Chromosorb W. The carrier gas was helium.

Cyclisation of acetonylacetone was conducted in a glass reactor with a fixed bed catalyst (0.05 g) at 623 K using procedure of Michalska et al. [36]. Upon increasing temperature and during the reaction helium was blown through the reaction system (30 $cm^3 min^{-1}$). After reaching a desired temperature, acetonylacetone (0.5 cm^3) was introduced into the reaction system by an infusion pump at the flow rate of 0.5 $cm^3 h^{-1}$. These conditions correspond to liquid hourly space velocity (LHSV) of about 1.52 h^{-1} (or 10.0 $cm^3 g_{cat}^{-1} h^{-1}$). The outlet of the reactor was connected to a glass U-shaped tube submerged in a cooling mixture of isopropanol-dry ice, in which the reaction products were condensed. After introduction of the whole amount of acetonylacetone the contents of the U-shaped tube was analysed on a gas chromatograph equipped with a FID detector and a 3 m SE-30 column. The carrier gas used was helium.

Cumene decomposition tests were performed for the activated carbon catalysts obtained from brown coal from "Konin" colliery. This process was realised by the pulse method in a glass reactor with a fixed bed catalysts (0.05 g) at 623 K. After reaching a desired temperature, cumene was dosed by a microsyringe in the amount of 1 μl to the reactor. The outlet of the reactor was connected to the chromatograph. The products were analysed using a FID detector and a 3 m column packed with 5% SE-30 deposited on Chromosorb G AW-DMCS. Helium was used as a carrier gas.

For all model reactions used in this study the blank experiments (without catalyst) have been performed. The results obtained indicate that the extent of the noncatalytic reactions is negligible as only traces of products were obtained.

3. Results and discussion

3.1. Catalyst characterisation

The results of proximate analysis of raw brown coal, demineralised brown coal and pinewood sawdust are given in Table 1. The raw

Table 2
Elemental analyses of samples prepared from demineralized brown coal (wt%, dry basis).

Sample	Ash	C	H	N	S	O[a]
KD	5.5	87.4	0.8	0.5	1.5	4.3
KD-PAA-4h-333 K	1.8	85.2	1.7	0.4	0.4	10.5
KD-PAA-8h-333 K	2.8	85.4	1.6	0.5	0.5	9.2
KD-H_2O_2-24h-303 K	2.1	84.6	1.0	0.6	0.9	10.8
KD-H_2O_2-24h-333 K	2.0	82.5	1.0	0.4	0.4	13.7
KD-HNO_3-4h-333 K	1.2	79.0	0.9	1.0	0.3	17.6
KD-HNO_3-8h-333 K	1.2	76.3	1.3	0.9	0.3	20.0
KD-APS-24h-303 K	1.2	70.5	1.5	0.7	0.6	25.5
KD-APS-24h-333 K	1.3	67.5	1.5	0.8	0.4	28.5
KD-AIR-4h-573 K	4.0	88.6	0.6	0.9	0.4	5.5
KD-AIR-8h-573 K	2.1	87.2	0.6	0.8	0.4	8.9
KD-NH_3-4h-923 K	2.0	92.1	0.8	3.3	0.4	1.4
KD-NH_3-4h-1123 K	1.5	92.7	0.9	3.1	0.1	1.7
KD-H_2-4h-923 K	2.1	95.4	0.8	0.6	0.1	1.0
KD-H_2-8h-923 K	3.1	95.2	0.8	0.8	0.1	0.0
KD-APS-Ar-4h-1123 K	1.9	94.4	0.8	1.3	0.3	1.3

[a] Calculated by difference.

brown coal shows a high content of mineral components (22.6%), so to eliminate a possible catalytic effect of mineral compounds it was subjected to demineralisation. Inorganic substances are removed from coal upon its exposure to concentrated acids as evidenced by a low content of ash in demineralised coal (0.9%).

Moreover, this process causes only a small increase in the content of volatile matter (from 33.3% to 37%), which means that demineralisation does not introduce significant changes in the coal structure. Pinewood sawdust shows high content of volatile matter (83.3%) and high moisture content (11.9%) when compared to the corresponding contents in demineralised brown coal. As it shows low content of ash, no demineralisation was performed.

To get materials of different chemical structures, the initial activated carbons (KD and S) were subjected to modifications such as oxidation with liquid or gas agents, nitrogenation with ammonia, reduction with hydrogen or thermal treatment in argon atmosphere of carbon samples previously oxidised with ammonium peroxydisulphate. Results of elemental analysis and ash content in all catalyst samples studied are collected in Tables 2 and 3.

As follows from the results, all processes of oxidation (realised with liquid or gas agents) lead to an increase in the amount of oxygen relative to that in the initial activated carbons. The content of oxygen in the samples subjected to oxidation was found to depend on the type of oxidising agent, temperature and duration of oxidation. According to literature, the higher the oxidation temperature and the stronger the oxidiser, the more oxygen atoms are introduced into the carbon structure [37]. The results obtained in our study confirmed the above relations as the content of oxygen increased with increasing temperature of oxidation. The influence of reaction time on results of oxidation is not so well defined and extension of the reaction time only slightly affects the content of oxygen in the oxidised samples. The greatest increase in the content of oxygen was noted after the reaction of the initial activated carbon samples (KD and S) with a solution of ammonium peroxydisulphate at 333 K for 24 h, while the lowest amount of oxygen was introduced by exposing these carbon samples to air for 4 h. The second most effective oxidiser was concentrated nitric acid. Our results differ from those reported by the group of Moreno-Castilla [38], who claims that the greatest amount of oxygen is incorporated into the carbon structure by oxidation with concentrated nitric acid and the lowest – by oxidation with ammonium peroxydisulphate. The differences can originate from different conditions of oxidation and the use of different precursors and different activation methods (KOH vs. steam). The data presented in Tables 2 and 3 also show that the content of oxygen introduced upon the oxidation of activated carbon samples with different oxidisers decreases as APS > HNO_3 > H_2O_2 > PAA > AIR. Our earlier investigations prove that type of oxidising agent determines not only the amount of oxygen introduced to the carbon structure but also the type of oxygen structures formed [39,40]. The oxidation in solutions of oxidisers leads mainly to formation of surface carboxyl groups, while oxidation with air leads to formation of both carbonyl and hydroxyl (phenolic) groups. Similar conclusions have also been drawn by other scientists [16,41].

Table 3
Elemental analyses of samples prepared from pinewood sawdust (wt%, dry basis).

Sample	Ash	C	H	N	S	O[a]
S	4.0	88.8	1.7	0.2	0.0	5.3
S-PAA-4h-333 K	2.1	84.5	1.9	0.9	0.0	10.6
S-PAA-8h-333 K	3.9	85.6	1.6	0.6	0.0	8.3
S-H_2O_2-24h-303 K	1.6	83.7	1.0	0.2	0.1	13.4
S-H_2O_2-24h-333 K	2.2	81.4	1.1	0.4	0.1	14.8
S-HNO_3-4h-333 K	2.0	75.2	2.4	0.5	0.0	19.9
S-HNO_3-8h-333 K	3.3	74.7	3.8	0.5	0.0	17.7
S-APS-24h-303 K	1.3	69.0	1.7	0.5	0.3	27.2
S-APS-24h-333 K	1.8	62.8	1.5	0.7	0.2	33.0
S-AIR-4h-573 K	2.5	87.6	0.8	0.6	0.1	8.4
S-AIR-8h-573 K	3.0	86.9	0.8	0.4	0.1	8.8
S-NH_3-4h-923 K	5.0	91.1	0.8	3.0	0.1	0.0
S-NH_3-4h-1123 K	5.1	91.2	0.9	2.7	0.1	0.0
S-H_2-4h-923 K	5.1	93.4	0.7	0.7	0.1	0.0
S-H_2-8h-923 K	5.7	93.2	0.6	0.5	0.0	0.0
S-APS-Ar-4h-1123 K	2.1	94.8	0.9	0.9	0.1	1.2

[a] Calculated by difference.

As expected, annealing of oxidised carbon in a high temperature in an argon atmosphere leads to a significant removal of oxygen from the carbon structure, which should be interpreted as a result of thermal decomposition of the oxygen functional groups. Even more pronounced decline of the oxygen content (particularly great in the samples based on pinewood sawdust) is detected for the samples treated with ammonia and hydrogen. In such samples the decrease in the content of oxygen is a consequence of thermal decomposition of oxygen functional groups and their reduction by hydrogen [42] (direct reaction with hydrogen applied or with hydrogen generated by partial decomposition of ammonia [43]).

Further analysis of the results shows that besides introduction of significant amount of oxygen the oxidation with nitric acid also leads to a small increase in the content of nitrogen, which is a result of incorporation of this element into the carbon structure (among others in the form of nitro groups [44]). Increase in the content of nitrogen is also observed as a result of modification of activated carbon samples with ammonia at a high temperature, which can be explained by formation of pyridine and pyrrole groups or quaternary systems [45]. According to the data from Tables 1 and 2, the reactions of oxidation with liquid oxidisers usually remove mineral compounds, while modification with gas agents (air, ammonia or hydrogen), in contrast to the effects of wet treatment, does not lead to washing out of mineral compounds and sometimes even an increase in the content of ash after such a treatment is observed.

Trace amounts of sulphur (0.1–0.3%) were noted in the samples from pinewood sawdust, while in the samples from brown coal the content of sulphur was slightly greater (0.1–1.5%). The content of hydrogen in all the samples was low; in the samples originating from brown coal it varied in the range 0.6–1.7%, while in the samples from pinewood sawdust – in the range 0.6–3.8%.

The texture of the activated carbon samples studied is characterised in Tables 4 and 5. As follows, the chemical activation by potassium hydroxide gives activated carbons of highly developed microporous structure and large specific surface area (close to 950 m^2/g for the samples originated from brown coal and almost 1160 m^2/g for the samples prepared from pinewood sawdust).

Table 4
Textural characteristics of carbon catalysts prepared from brown coal.

Sample	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	D_{av} (nm)
KD	953	22	0.48	0.44	2.00
KD-PAA-4h-333 K	1041	22	0.52	0.49	2.00
KD-PAA-8h-333 K	980	21	0.49	0.46	2.00
KD-H_2O_2-24h-303 K	938	17	0.48	0.45	2.04
KD-H_2O_2-24h-333 K	958	20	0.50	0.46	2.09
KD-HNO_3-4h-333 K	856	18	0.43	0.40	2.00
KD-HNO_3-8h-333 K	881	20	0.44	0.41	2.02
KD-APS-24h-303 K	744	17	0.38	0.35	2.02
KD-APS-24h-333 K	415	14	0.22	0.19	2.09
KD-AIR-4h-573 K	999	22	0.50	0.46	1.99
KD-AIR-8h-573 K	1100	27	0.55	0.51	2.00
KD-NH_3-4h-923 K	1041	23	0.52	0.48	1.99
KD-NH_3-4h-1123 K	1426	32	0.72	0.66	2.01
KD-H_2-4h-923 K	1082	22	0.54	0.50	2.00
KD-H_2-8h-923 K	1087	25	0.54	0.50	2.00
KD-APS-Ar-4h-1123 K	924	22	0.46	0.42	1.98

Thus, the type of precursor seems to have little effect on the textural properties of activated carbon catalysts.

According to the data displayed in Tables 4 and 5, the effect of the processes of modification applied was different but nevertheless small. The exceptions were the catalysts obtained from brown coal and pinewood sawdust subjected to a reaction with ammonium peroxydisulphate at 333 K, for which a drastic decrease in the surface area was observed, suggesting a destruction of the porous structure of these samples upon their strong oxidation. Another possible explanation of this phenomenon is that carbon pores can be blocked by bulky oxygen functional groups, e.g. carboxyl groups (these samples have the highest content of oxygen, see Tables 2 and 3). This supposition has been confirmed by results of TPD and FTIR measurements (presented in our other papers [40,46]), which prove that the content of carboxylic groups in the discussed carbons is definitely the highest for the samples oxidised with ammonium peroxydisulphate and decreases in the sequence APS > HNO_3 > H_2O_2 > PAA > AIR. Similar relations have been obtained by our group for activated carbons prepared from peach stones [39]. Moreover, the partial "regeneration" of porous structure of the APS oxidised carbons after heat treatment in argon atmosphere (decomposition of most of the oxygen groups) also suggests that the decrease in S_{BET} observed for oxidised samples results in some extent from the limited accessibility of nitrogen molecules to pores during porosity measurements.

For the samples originating from pinewood sawdust (Table 5), increase in the time of oxidation or in the reaction temperature leads to a small decrease in the specific surface area, which can be related to partial destruction of the pore system and/or discussed above limited accessibility to pores. This interpretation is confirmed by the fact that the total pore volume also decreases with increasing time of the reaction and with its temperature. For the samples obtained from brown coal the analogous relations are less pronounced (Table 4). It should be mentioned that exposure of activated carbons to gas reagents gives samples of surface area and pore volume greater than in the initial material (KD and S). This phenomenon can be explained by partial gasification of carbon by oxygen, hydrogen or the hydrogen coming from decomposition of ammonia. Thus, it can be assumed that the final surface area and pore volume are resultants of the two opposite processes: decrease of porosity caused by pore destruction or their limited accessibility and increase in pore volume as a result of carbon gasification.

All activated carbon samples have well developed microporous structure as indicated by average pore diameter (D_{av}), which is very close to 2 nm, and a dominant contribution of micropores in the total surface area of the samples and a dominant contribution of micropore volume in the total pore volume of the samples.

3.2. *Catalytic activity of carbons in isopropanol conversion*

Catalytic activity of the activated carbon samples studied was assessed on the basis of the measured yield of products of isopropanol conversion versus the reaction temperature (Figs. 1–9). According to the results obtained, all activated carbon samples show catalytic activity in isopropanol dehydration to propene and its dehydrogenation to acetone, while the degree of isopropanol conversion to particular products depends on the mode of carbon

Table 5
Textural characteristics of carbon catalysts prepared from pinewood sawdust.

Sample	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	D_{av} (nm)
S	1157	23	0.57	0.54	1.99
S-PAA-4h-333 K	1178	22	0.59	0.55	2.00
S-PAA-8h-333 K	1154	24	0.58	0.54	2.01
S-H_2O_2-24h-303 K	1131	19	0.58	0.54	2.05
S-H_2O_2-24h-333 K	1057	23	0.57	0.52	2.14
S-HNO_3-4h-333 K	1067	21	0.53	0.50	1.99
S-HNO_3-8h-333 K	1058	22	0.52	0.49	1.98
S-APS-24h-303 K	951	25	0.48	0.44	2.00.
S-APS-24h-333 K	462	16	0.24	0.21	2.04
S-AIR-4h-573 K	1217	29	0.61	0.57	2.01
S-AIR-8h-573 K	1159	20	0.58	0.54	2.01
S-NH_3-4h-923 K	1197	23	0.60	0.56	2.00
S-NH_3-4h-1123 K	1424	44	0.74	0.66	2.08
S-H_2-4h-923 K	1199	26	0.61	0.56	2.02
S-H_2-8h-923 K	1186	26	0.60	0.56	2.02
S-APS-Ar-4h-1123 K	1052	26	0.52	0.48	1.98

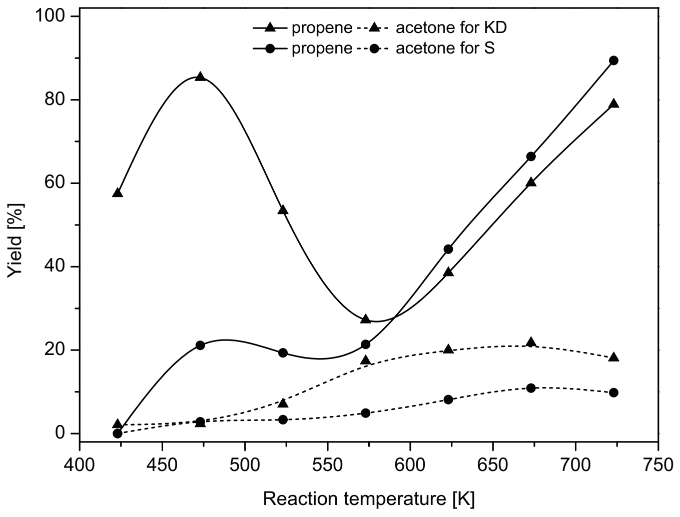

Fig. 1. Decomposition of isopropanol over initial activated carbons prepared from brown coal (KD) or from pinewood sawdust (S).

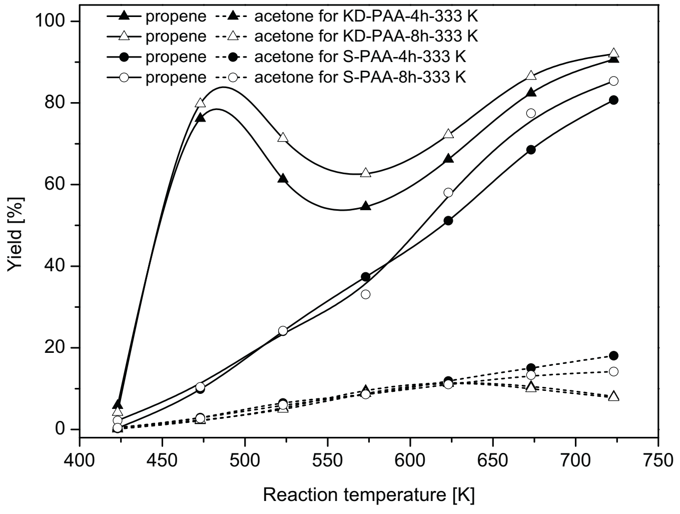

Fig. 2. Decomposition of isopropanol over activated carbons oxidised with peroxyacetic acid.

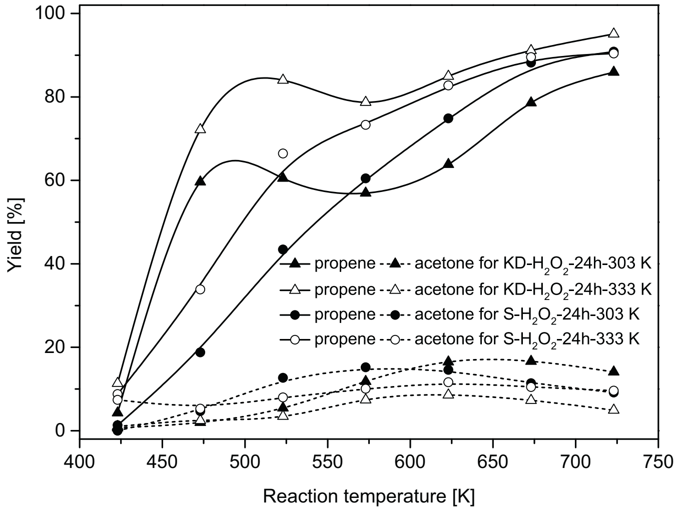

Fig. 3. Decomposition of isopropanol over activated carbons oxidised with hydrogen peroxide.

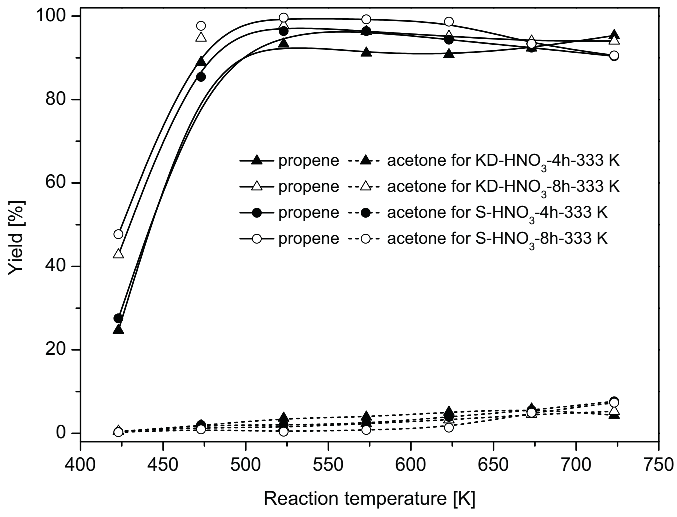

Fig. 4. Decomposition of isopropanol over activated carbons oxidised with nitric acid.

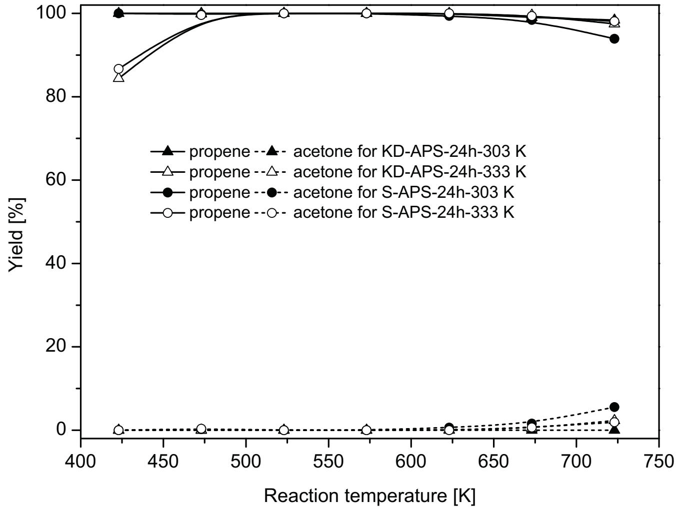

Fig. 5. Decomposition of isopropanol over activated carbons oxidised with ammonium peroxydisulphate.

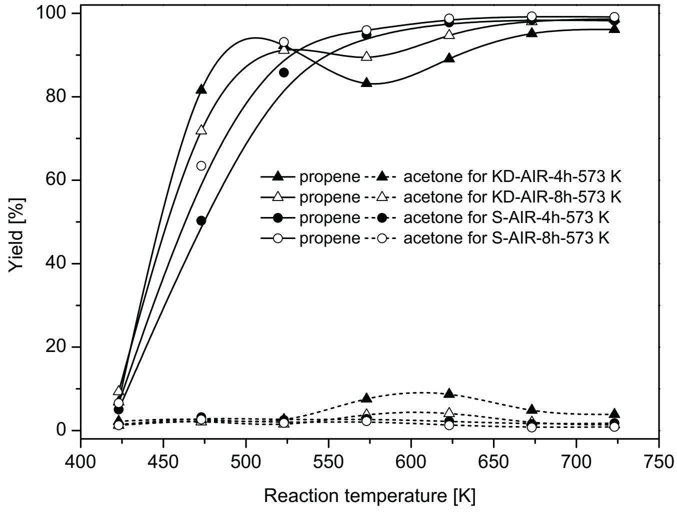

Fig. 6. Decomposition of isopropanol over activated carbons oxidised with air.

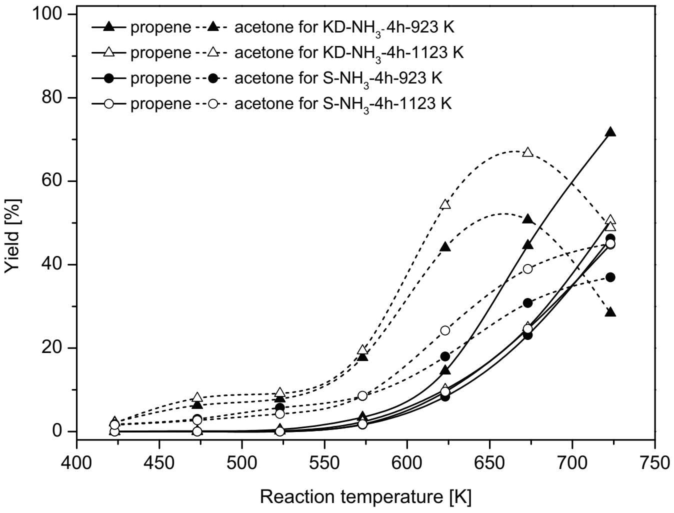

Fig. 7. Decomposition of isopropanol over activated carbons modified with ammonia.

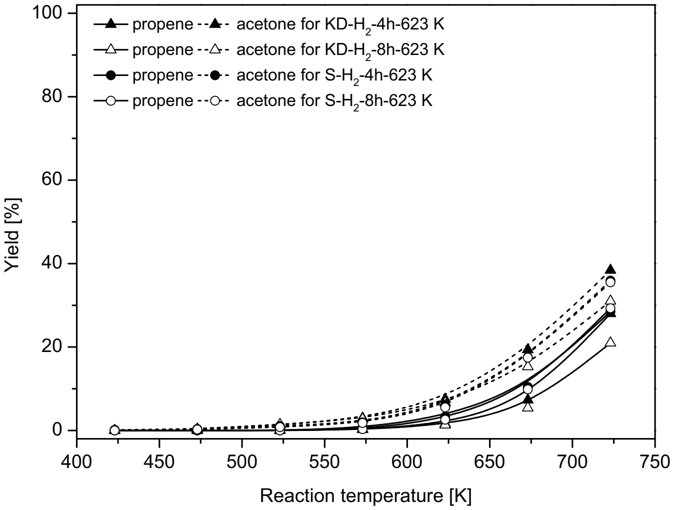

Fig. 8. Decomposition of isopropanol over activated carbons modified with hydrogen.

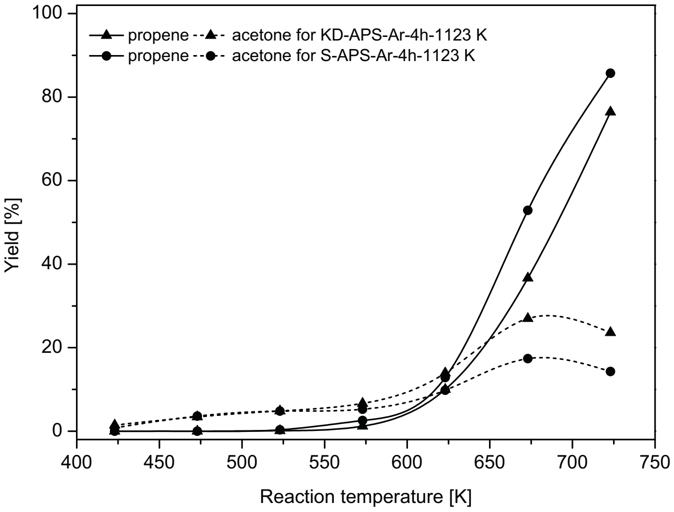

Fig. 9. Decomposition of isopropanol over activated carbons oxidised with ammonium peroxydisulphate and subsequently thermally treated in argon.

samples modification. In the reactions over the catalysts studied no diisopropyl ether was detected among the reaction products.

Fig. 1 presents isopropanol conversion in the reactions over the initial activated carbon samples originating from brown coal and pinewood sawdust. The results indicate that isopropanol decomposition over unmodified activated carbon samples runs mainly towards propene, which testifies to the presence of acidic centres in this catalyst. According to literature data, mainly carboxyl groups are responsible for acidic properties of carbons, although weak acidic properties are also shown by certain other types of oxygen functionalities: hydroxyl (phenol), carboxylic anhydrides, lactone and lactol [47]. For both KD and S samples, the yield of propene increases with increasing reaction temperature and both curves reveal a distinct maximum at about 475 K (more pronounced for KD) and for higher temperatures their activity slowly decreases, probably because of thermal decomposition of surface active centres of acidic character, mainly carboxyl groups. This supposition has been confirmed by Szymański et al. [16], who reported that carboxyl groups decompose in the range 373–673 K. As the maximum is higher for the carbon sample obtained from brown coal, it can be supposed that this sample contains more acidic groups than that from pinewood sawdust. This has been confirmed by results of potentiometric titration, which prove that total acidity of KD sample is 0.78 mmol H^+/g, whereas for S sample it amounts to 0.58 mmol H^+/g. After drop in the propene yield, this parameter again increases to form some minima in the propene yield curves. This increased activity of carbons can originate from other than carboxyl groups of acidic character, e.g. mentioned earlier hydroxyl (phenol), lactone, lactol groups and carboxylic anhydrides. These functionalities are more thermally stable than carboxyl groups [16] and they can originally occur in carbons investigated but can also appear as a result of carboxyl groups decomposition. For example adjacent carboxyl groups undergo dehydration to anhydrides, whereas carboxyl and phenolic groups can react to form lactones [34].

The activated carbon samples originating from both precursors also catalyse isopropanol decomposition towards acetone, but the yield of this product is much smaller than that of propene. The degree of isopropanol conversion to acetone slightly increases with increasing temperature. The above results prove that the activated carbon samples besides acidic active centres (which dominate) contain also basic active centres. According to literature data, the basic properties of carbons are mainly determined by the presence of chromene, pyrone, diketone and quinone structures but they are also related to the presence of a system of delocalised π electrons from graphene layers [48].

Figs. 2–6 present results of measurements of the catalytic activity of activated carbon samples obtained from brown coal or pinewood sawdust and then modified with liquid or gas oxidising agents. Oxidation was carried out either in “mild” conditions (low temperature or short reaction time) or in “drastic” conditions (high temperature or long reaction time). As indicated by the data shown in Fig. 2, the main direction of isopropanol decomposition over activated carbon samples oxidised with peroxyacetic acid is dehydration to propene. It should be noted that the curves illustrating the yield of propene are only slightly different from those showing catalytic activity of unmodified activated carbon samples. A possible explanation is that peroxyacetic acid is a weak oxidiser and introduces a small number of carboxyl groups into the activated carbon structure. This supposition is confirmed by elemental analysis results, which indicate that the samples oxidised with peroxyacetic acid show the lowest content of oxygen from among the samples modified by liquid oxidisers, see Tables 2 and 3. Comparison of the effects of oxidation with peroxyacetic acid in “mild” and “drastic” conditions reveals only small differences in the catalytic activity of the activated carbon tested (a bit higher activity is observed for the samples modified in “drastic” conditions, i.e. at a longer time of the reaction). For the samples obtained from brown coal, clear maxima and minima of activity are observed, whose appearance can be related to the mentioned earlier thermal decomposition of certain acidic functional groups (carboxyl groups). It is worth noting that the reaction temperature responsible for these maxima (about 480 K) is very close to the temperature at which CO_2 release starts in TPD experiments [40]. It additionally confirms the supposition on decomposition of carboxyl groups of the catalysts during catalytic test. The above maxima are absent in the case of curves obtained for the samples prepared from pinewood sawdust. A possible explanation is that the concentration of carboxyl groups is higher in oxidised brown coal-originated samples than in oxidised samples obtained from pinewood sawdust.

Results of isopropanol decomposition over activated carbon samples oxidised with hydrogen peroxide are presented in Fig. 3 and show that the catalytic activity of these samples is somewhat higher than that of the samples oxidised with peroxyacetic acid. The increased degree of isopropanol conversion to propene means that the oxidation with H_2O_2 is more effective in introduction of oxygen functional groups of acidic character than the oxidation with PAA, which is in agreement with the results of elemental analysis (Tables 2 and 3).

The results from Fig. 3 also imply that in the “drastic” conditions (higher temperature of oxidation) the yield of propene obtained from dehydration of isopropanol is much higher. This observation is in agreement with the results of elementary analysis showing that at higher temperatures of oxidation with H_2O_2 the amount of oxygen incorporated into the carbon structure is greater. Another observation following from Fig. 3 is that the maxima of catalytic activity of the carbon samples obtained from brown coal and oxidised with H_2O_2 become less pronounced than those observed for the initial sample (KD) and the samples oxidised with peroxyacetic acid.

Fig. 4 presents results concerning isopropanol decomposition over the activated carbons oxidised with concentrated nitric acid (which belongs to the group of the strongest oxidisers, along with ammonium peroxydisulphate [37,40]). The treatment with the solutions of the above oxidising agents leads mainly to formation of carboxyl groups [37,39,44,46]. As has been established, the higher the oxidation temperature and the stronger the oxidiser, the more oxygen atoms are incorporated into the carbon structure [37]. In view of the above, the activated carbon samples oxidised with nitric acid were expected to be highly effective in dehydration reaction. Indeed, high yield of propene (80–95%, obtained at temperature as low as 473 K) points to strongly acidic character of these carbon samples. This character has been confirmed by results of potentiometric titration (total acidity of the above samples was in the range 1.99–2.52 mmol H^+/g). The degree of isopropanol conversion to propene fast increases up to 473 K and for higher temperatures the catalytic activity of activated carbon samples modified with nitric acid gets stabilised or slowly decreases. A small decrease in the catalysts activity observed for activated carbon samples obtained from pinewood sawdust and oxidised with HNO_3 is probably a consequence of decomposition of some acidic oxygen functional groups.

The data on the degree of isopropanol conversion to propene over the activated carbon samples oxidised with solution of ammonium peroxydisulphate (APS) are presented in Fig. 5. As mentioned above, this compound is a very strong oxidiser, which is evidenced by the results of elementary analysis (the samples oxidised with it show the highest content of oxygen from among all oxidised ones, Tables 2 and 3). Also total acidity of the above samples was the highest (3.09–3.81 mmol H^+/g). In the reactions over carbon catalysts oxidised with APS nearly 100% conversion of isopropanol to propene was obtained, indicating almost totally acidic character of their surfaces. Analysis of the data obtained for the initial and the oxidised activated carbon samples (shown in Figs. 1–5) reveals a strong dependence between propene yield and the content of oxygen introduced into the carbon structure. The content of oxygen was the lowest in the initial samples (KD and S), and in the samples oxidised with liquid oxidisers the content of oxygen increased in the order: PAA < H_2O_2 < HNO_3 < APS and in the same order the catalytic activity of the oxidised samples increased.

Fig. 6 presents the catalytic activity in isopropanol decomposition of activated carbons modified by oxidation in gas phase (air). The character of the curves in this figure is slightly different from that recorded for the carbons oxidised with APS or HNO_3. The samples oxidised with air show initially very low activity towards isopropanol decomposition to propene, which increases with increasing temperature. It is known from literature that the oxidation of carbon with liquid oxidisers favours formation of carboxyl groups, while the oxidation with air leads mainly to formation of carbonyl and hydroxyl (phenol) groups [41,49]. Of the latter two only hydroxyl groups are Brönsted acids and can act as active centres in dehydration of isopropanol.

To sum up the results concerning isopropanol decomposition over oxidised activated carbon samples, the oxidation by liquid as well as gas agents leads mainly to formation of surface oxygen functional groups of acidic character. This conclusion is based on the significant activity of oxidised samples in the reaction towards isopropanol dehydration whose main product is propene. The highest degree of isopropanol conversion to propene was obtained for the samples prepared from both precursors and oxidised by ammonium peroxydisulphate or concentrated nitric acid. The results are in agreement with the elemental analysis data showing that oxidation with these oxidisers leads to the greatest increase in the content of oxygen. Our results have also shown that the type of oxidation conditions (“mild” or “drastic”) also influences the degree of isopropanol dehydration. Usually the samples oxidised in “drastic” conditions revealed higher catalytic activity. This observation is related to the fact that the “drastic” conditions generally favour introduction of a greater amount of oxygen into the carbon structures than the “mild” ones (the content of oxygen in the oxidised carbon samples increases with increasing temperature of oxidation; the effect of increasing reaction time is not so clear as increase in the reaction time has only small influence on the contents of oxygen). The exceptions are the samples oxidised with APS at 333 K for 24 h. Although they have the greatest content of oxygen, the yield of propene in the reactions at 423 K with their use is by 25% lower than that in the presence of the samples oxidised with APS at 303 K. However, the catalytic activity of the former samples rapidly increases and then remains at a very high level (close to 100%). The most pronounced influence of the oxidation temperature on the catalytic activity of carbons in isopropanol dehydration was observed for the samples oxidised with hydrogen peroxide. Extension of the time of oxidation with HNO_3, PAA or air only slightly improves the catalytic activities of the respective samples in isopropanol dehydration. As follows from our results the type of precursor used for preparation of activated carbon has no significant influence on the degree of isopropanol conversion to propene. Only for the samples obtained from brown coal and oxidised with PAA (both in mild and drastic conditions) and with H_2O_2 at elevated temperature, the catalytic activity in isopropanol dehydration was much better than that of the samples obtained from pinewood sawdust.

The effect of carbon modification in reducing conditions on the catalytic activity in isopropanol decomposition is illustrated in Figs. 7–9. As follows from these results, modification of activated carbons by reduction with hydrogen and nitrogenation with ammonia leads to a decrease in the catalytic activity towards

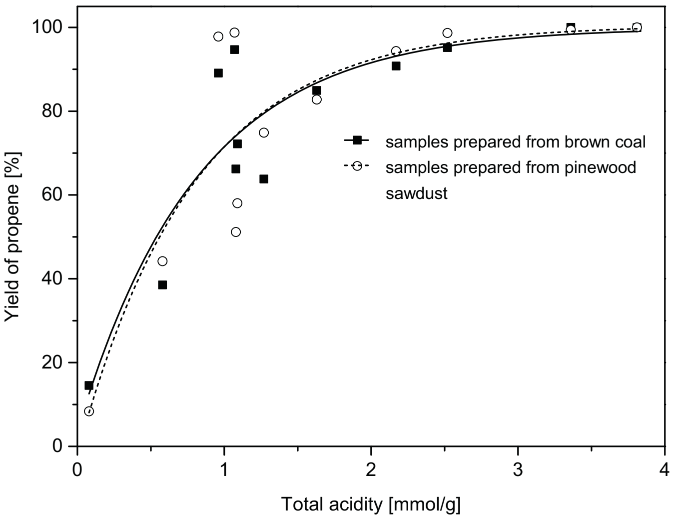

Fig. 10. Yield of propene in the decomposition of isopropanol reaction versus the total acidity of the activated carbon samples studied.

propene and the domination of acetone in the products of isopropanol decomposition. It is a consequence of partial (or in some samples even total, see Tables 2 and 3) removal of oxygen functional groups whose majority show acidic character (see the results in Fig. 1). The appearance of acetone in the products of isopropanol decomposition testifies to the presence of basic centres on the surface of activated carbon samples [14]. In the samples modified with ammonia the basic centres can be amine or pyridine nitrogen functionalities [50]. This supposition is confirmed by an increased content of nitrogen in the samples after this modification (Tables 2 and 3). It is difficult to surmise what is responsible for the basic properties of the samples reduced with hydrogen. Surely not the basic oxygen groups because these samples show no or very little content of oxygen. A possible explanation is that the basic character of these samples is related to the presence of some unsaturated sites [42] or π electrons in graphene layers [51].

As indicated by the presence of two products of isopropanol decomposition (propene and acetone) the thermal treatment in neutral gas atmosphere at 1123 K of carbon samples oxidised with ammonium peroxydisulphate gives catalysts having both acidic and basic active centres (Fig. 9). The presence of basic centres in the samples studied can be related to the occurrence of thermally stable oxygen groups of basic character, e.g. mentioned earlier pyrone functionalities (which decompose only above 1173 K [16]), and with the presence of π electrons from graphene layers. The yield of propene is low up to about 573 K but above this temperature it rapidly increases. As acidic oxygen groups do not exist at temperature of 1123 K [16] and thermal decomposition of isopropanol is negligible (blank test), some other phenomenon has to be responsible for the rapid increase in propene yield above 573 K. It cannot be excluded that some mineral substances contained in the carbons investigated (see Tables 2 and 3) are involved in decomposition of isopropanol towards propene. According to Gervasini et al. [52] this process can proceed not only on Brönsted acids but also on Lewis acidic centres (which are present on the surface of certain mineral compounds).

Fig. 10 shows the correlation of carbons activity at 623 K in the reaction of isopropanol conversion to propene with the catalyst total acidity. Analysis of these data indicates that the activity of the catalysts studied in the above reaction shows a tendency to increase with increasing of their acidity, although some clearly marked deviations from this tendency are noted.

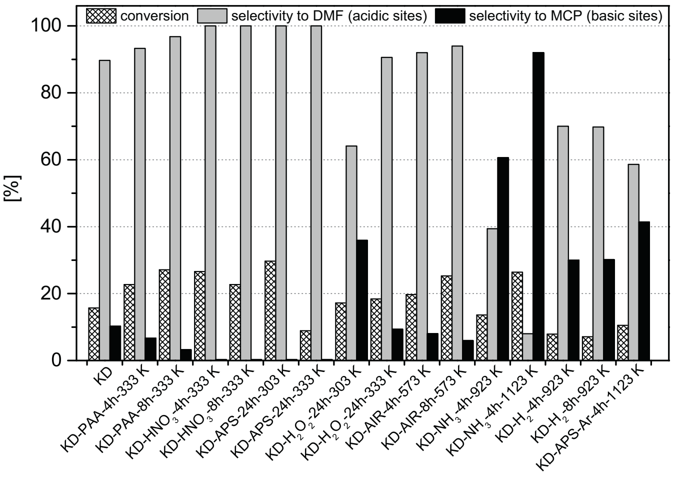

Fig. 11. Acetonylacetone transformation over carbons prepared from brown coal.

3.3. Catalytic activity of carbons in acetonylacetone conversion

Results illustrating catalytic activity of the activated carbon samples studied in cyclisation of acetonylacetone are presented in Figs. 11 and 12. As follows, cyclisation of acetonylacetone over all oxidised carbon samples gives 2,5-dimethylfuran (DMF) as the main product. This fact confirms literature reports claiming that oxidation increases the acidic character of carbon as a result of incorporation of oxygen in the form of different functional groups [53]. The highest selectivity of acetonylacetone cyclisation to DMF (close to 100%), indicating the presence of almost only acidic sites, was obtained for the samples prepared from both precursors and oxidised with ammonium peroxydisulphate at different temperatures or with concentrated nitric acid at two different modification times. On the other hand, high selectivity towards MCP was observed for the samples reduced with hydrogen or subjected to thermal treatment, however, much prevalence of the concentration of basic centres over acidic ones was noted only for the samples modified with ammonia. The above relations are well pronounced for the samples obtained from both precursors used and are similar to those obtained for isopropanol decomposition.

On the basis of measurements of the total degree of acetonylacetone conversion it can be concluded that the greatest number of active centres (both acidic and basic) occurs in the samples oxidised with ammonium peroxydisulphate at 303 K. The number of active centres is the lowest in the samples modified with APS at 333 K

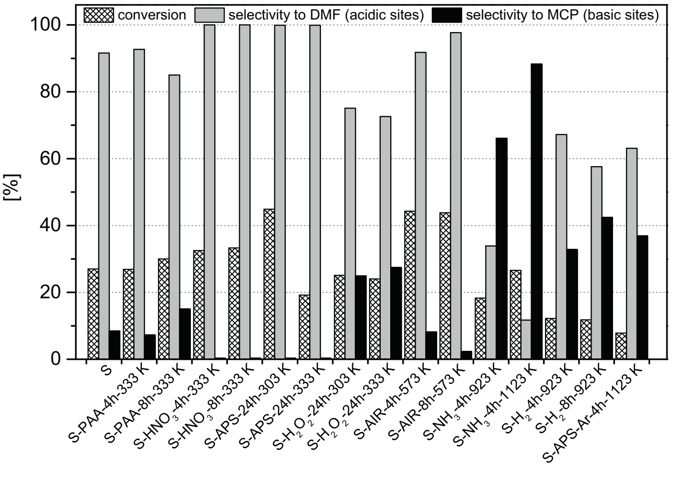

Fig. 12. Acetonylacetone transformation over carbons prepared from pinewood sawdust.

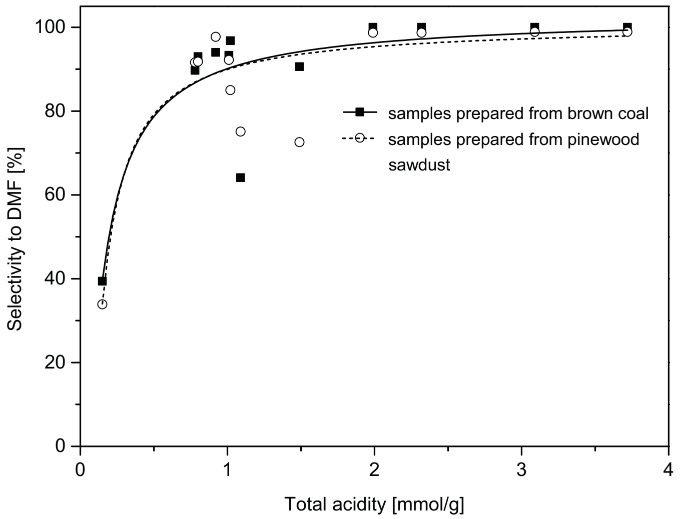

Fig. 13. Selectivity to DMF versus the total acidity of the activated carbon samples studied.

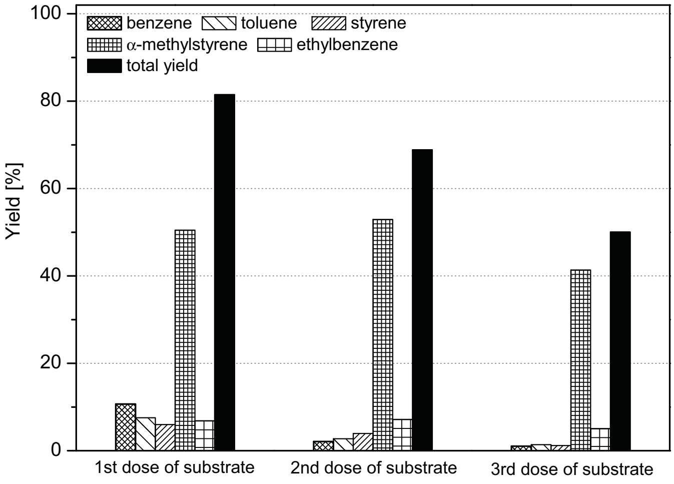

Fig. 14. Results of cumene decomposition over initial activated carbon prepared from brown coal versus the number of substrate pulses.

(in particular the sample obtained from brown coal), the samples reduced with hydrogen and those whose oxidation with APS was followed by thermal treatment. The relatively low degree of total conversion of acetonylacetone observed for the carbons oxidised with ammonium peroxydisulphate at 333 K can be explained taking into regard the textural parameters of these samples. Although the oxidation with APS in "drastic" conditions (333 K) leads to the introduction of the greatest amount of oxygen (Tables 2 and 3), it also causes a significant decrease in the specific surface area and in the total pore volume (Tables 4 and 5), related to destruction of the porous system of carbon samples or/and to limited pore accessibility caused by bulky carboxyl groups. The low total number of acidic and basic centres in the other above discussed samples can be explained by destruction of the oxygen functional groups under the effect of thermal treatment and/or hydrogen.

The catalytic activity of carbons in acetonylacetone conversion to 2,5-dimethylfuran as a function of catalyst total acidity is presented in Fig. 13. Similarly as in the case of isopropanol dehydration, the activity of the catalysts studied in the above reaction shows a tendency to increase with increasing of their acidity, although some clearly marked deviations from this tendency are noted. This result means that besides the acidity also other factors influence the catalytic performance of the activated carbons. In consistence with earlier discussed observations, such a factor can be the texture of the catalyst surface.

3.4. *Catalytic activity of carbons in cumene decomposition*

The catalytic activities of activated carbon samples obtained from brown coal in the process of cumene decomposition performed by the pulse method are characterised in Figs. 14–18. As follows from Fig. 14, the yields of the majority of cumene decomposition products decrease from the first to the third substrate pulse. This tendency was observed for all carbon catalysts tested in this study and can be explained by the formation of carbonaceous deposit blocking the active centres of the catalysts. For this reason in the following part of the paper only the results for the first pulse injection of cumene are presented, so as to analyse the results for the catalysts surface almost not covered with carbonaceous deposit. Analysis of the results obtained after the first injection of cumene indicates that the surface of unmodified activated carbon is characterised by the presence of different types of active centres. The high yield of α-methylstyrene (close to 50%) evidences the domination of electron-transfer centres, while the yield of benzene oscillating near 10% informs about the presence of a low number of strong Brönsted acidic centres. The yields of the other products do not exceed 7%. As there are no literature reports on cumene decomposition over activated carbon, it is difficult to establish which parts of carbon structure are responsible for its catalytic properties in this reaction. It can only be supposed that the electron-transfer centres are various defects in the carbon structure, such as dislocations, voids, atoms with free valencies. The presence of catalytically active sites of this type has been postulated by e.g. Muradow's group [54]. Similar conclusions have been drawn by Fiedorow et al. [28] who studied fluorinated carbon materials and suggested that possible carbon active centres towards α-methylstyrene are the paramagnetic centres appearing as a result of cleavage of the C—C bonds. Also the nature of strong Brönsted acidic centres in carbons has not been resolved yet. It cannot be excluded that the presence of these centres is related (at least in part) to the mineral compounds found in small amounts in the carbon samples studied (Tables 2 and 3) or to the remains of HCl strongly adsorbed on the carbon surface during sample preparation (see Section 2).

Figs. 15 and 16 present the yields of the particular products of cumene decomposition over the activated carbon samples subjected to oxidation with liquid agents, Fig. 17 gives the results of cumene decomposition over the carbon sample oxidised with

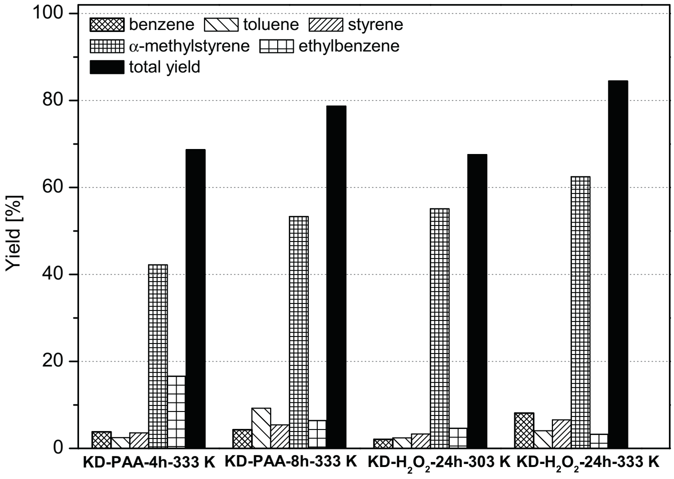

Fig. 15. Cumene decomposition over activated carbons prepared from brown coal and oxidised with peroxyacetic acid or hydrogen peroxide.

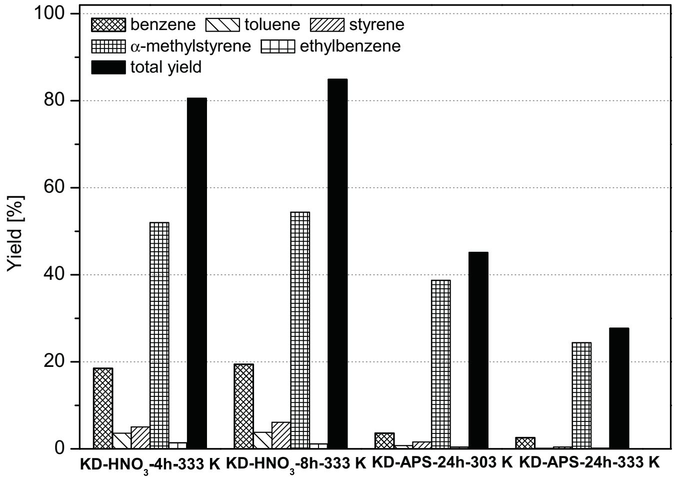

Fig. 16. Cumene decomposition over activated carbons prepared from brown coal and oxidised with nitric acid or ammonium peroxydisulphate.

air, whereas Fig. 18 illustrates changes in the catalytic activity of activated carbon samples subjected to modification with ammonia, hydrogen or oxidised with APS at 303 K and then annealed in argon atmosphere. Analysis of these data shows that the dominant direction of cumene decomposition over all carbon samples investigated is dehydrogenation and the main product is α-methylstyrene. This observation means that the carbon catalysts have a prevailing content of electron-transfer centres. The greatest amount of α-methylstyrene was obtained over the carbon treated with ammonia at 923 K and for the sample oxidised with hydrogen peroxide at 333 K, which suggests that these samples have a high content of the earlier mentioned structural defects. The lowest amount of α-methylstyrene was obtained over a carbon sample subjected to oxidation with APS at 333 K. However, the low catalytic activity of this sample can be related to its small specific surface area (Table 4), and thus a limited contact of reagents with the active centres of the catalyst.

The greatest number of strong Brönsted acidic centres was found in the activated carbon samples oxidised with nitric acid (the yield of benzene close to 18–20%). This result suggests that the presence of strong Brönsted acidic centres can be partly related to the remains of small amounts of the modifying agent (HNO_3 is a strong Brönsted acid), strongly adsorbed on the carbon surface. Oxidation with the other oxidising liquids leads to lower number of strong Brönsted acidic centres. This observation means that carbon samples modified by oxidation contain mainly weak acidic centres. On the other hand, no cumene conversion to benzene over the carbon samples modified by treatment with hydrogen or by thermal treatment in the argon atmosphere means that these modifications lead to total removal of strong Brönsted acidic centres. Nitrogenation with ammonia also leads to the removal of the majority of strong acidic centres as the conversion to benzene over the relevant samples does not exceed 2%. Most probably this effect is related to the influence of high temperature causing decomposition of the majority of strong Brönsted acidic centres.

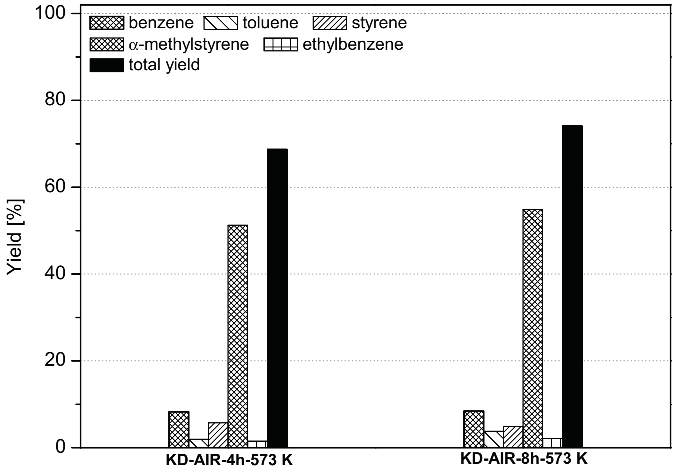

Fig. 17. Cumene decomposition over activated carbons prepared from brown coal and oxidised with air.

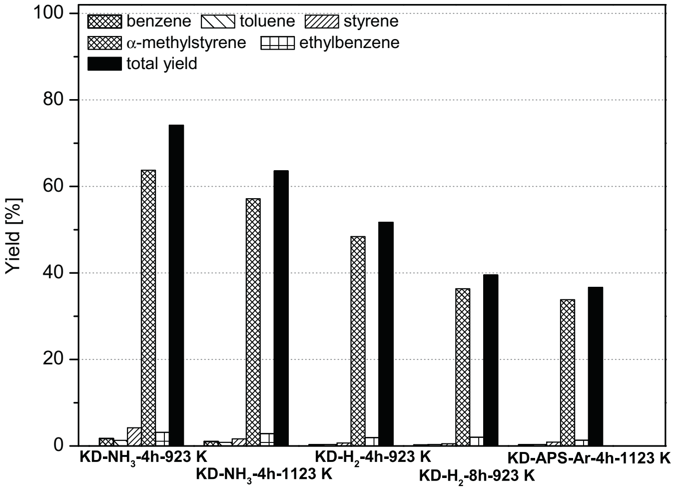

Fig. 18. Cumene decomposition over activated carbons prepared from brown coal and modified with ammonia, hydrogen or by thermal treatment.

The greatest total yield of cumene decomposition products was observed for the activated carbon samples over which the highest degree of conversion to α-methylstyrene was obtained, i.e. the sample oxidised with H_2O_2 at 333 K, the sample treated with ammonia at 923 K and for the initial KD sample. The lowest total yield of cumene decomposition products was noted for the sample oxidised with APS at 333 K over which the lowest conversion to α-methyl-styrene was established. As follows from analysis of our results, there is correlation between the total yield of all products and the conditions of carbon modifications. On the one hand, for the oxidised samples the total yield increases with increasing time and temperature of oxidation. The exception is the sample oxidised with APS at 333 K for which the total yield is lower than for the sample oxidised with APS at 303 K. On the other hand, a reverse tendency was observed for the samples treated with ammonia and hydrogen, i.e. with increasing time and temperature of modification the total yield of cumene decomposition products decreased.

4. Conclusions

All activated carbon samples studied were found to show catalytic activity in the model reactions of isopropanol decomposition and cyclisation of acetonylacetone. Oxidation of activated carbon samples was proved to lead to their increased acidity, while the treatment with ammonia, hydrogen or thermal treatment lead to increased basicity of the carbon. The carbon samples oxidised with ammonium peroxydisulphate or concentrated nitric acid showed almost fully acidic character. The type of precursor used to obtain activated carbon samples had insignificant effect on the results of these model reactions. The results concerning the catalytic activity of carbon samples in cumene decomposition proved the dominance of electron-transfer centres over the strongly acidic Brönsted ones. The highest number of electron-transfer centres was found in the sample oxidised with H_2O_2 at 333 K and in the sample treated with ammonia at 923 K, while the lowest for the sample oxidised with ammonium peroxydisulphate at 333 K. The greatest number of strong acidic Brönsted centres was found in the samples oxidised with nitric acid, whereas the thermal treatment or reduction with hydrogen resulted in their total removal.

Acknowledgement

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References

[1] M.A. Aramendía, V. Boráu, I.M. García, C. Jiménez, A. Marinas, J.M. Marinas, A. Porras, F.J. Urbano, Appl. Catal. A 184 (1999) 115–125.
[2] C. Lahousse, J. Bachelier, J.-C. Lavalley, H. Lauron-Pernot, A.-M. Le Govic, J. Mol. Catal. 87 (1994) 329–332.
[3] G. Zadrozna, E. Souvage, J. Kornatowski, J. Catal. 208 (2002) 270–275.
[4] D. Martin, D. Duprez, J. Mol. Catal. A: Chem. 118 (1997) 113–128.
[5] H. Lauron-Pernot, F. Luck, J.M. Popa, Appl. Catal. 78 (1991) 213–225.
[6] M. Guisnet, Stud. Surf. Sci. Catal. 20 (1985) 283–297.
[7] S.E. Tung, E. McIninch, J. Catal. 4 (1965) 586–593.
[8] K. Brückman, J. Haber, React. Kinet. Catal. Lett. 10 (1979) 173–177.
[9] Z. Sarbak, Appl. Catal. A: Gen. 159 (1997) 147–157.
[10] N.N. Binitha, P.P. Silija, V. Suraj, Z. Yaakob, S. Sugunan, IOP Conf. Ser. Mater. Sci. Eng. 17 (2011) 012018.
[11] D. Best, B.W. Wojciechowski, J. Catal. 47 (1977) 11–27.
[12] A. Corma, H. Farag, B.W. Wojciechowski, Int. J. Chem. Kinet. 13 (1981) 883–895.
[13] G.S. Szymański, G. Rychlicki, Carbon 29 (1991) 489–498.
[14] G.S. Szymański, G. Rychlicki, Carbon 31 (1993) 247–257.
[15] G.S. Szymański, G. Rychlicki, A.P. Terzyk, Carbon 32 (1994) 265–271.
[16] G.S. Szymański, Z. Karpiński, S. Biniak, A. Świątkowski, Carbon 40 (2002) 2627–2639.
[17] F. Carrasco-Marín, A. Mueden, C. Moreno-Castilla, J. Phys. Chem. B 102 (1998) 9239–9244.
[18] C. Moreno-Castilla, F. Carrasco-Marín, C. Parejo-Pérez, M.V. López Ramón, Carbon 39 (2001) 869–875.
[19] E. Jasińska, B. Krzyżyńska, M. Kozłowski, Catal. Lett. 125 (2008) 145–153.
[20] J. Jasińska, B. Krzyżyńska, M. Kozłowski, Cent. Eur. J. Chem. 9 (2011) 925–931.
[21] J. Bedia, J.M. Rosas, J. Márquez, J. Rodríguez-Mirasol, T. Cordero, Carbon 47 (2009) 286–294.
[22] J. Bedia, R. Ruiz-Rosas, J. Rodríguez-Mirasol, T. Cordero, J. Catal. 271 (2010) 33–42.
[23] E. Perozo-Rondón, V. Calvino-Casilda, R.M. Martín-Aranda, B. Casal, C.J. Durán-Valle, M.L. Rojas-Cervantes, Appl. Surf. Sci. 252 (2006) 6080–6083.
[24] J. Weitkamp, M. Hunger, U. Rymsa, Microporous Mesoporous Mater. 48 (2001) 255–270.
[25] S. Carre, B. Tapin, N.S. Gnep, R. Revel, P. Magnoux, Appl. Catal. A: Gen. 372 (2010) 26–33.
[26] J. Gościańska, M. Ziółek, E. Gibson, M. Daturi, Catal. Today 152 (2010) 33–41.
[27] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, T. Suzuki, Catal. Lett. 69 (2000) 59–64.
[28] P. Fiedorow, A. Krawczyk, R. Fiedorow, K.T. Chuang, Mol. Cryst. Liq. Crys. A 354 (2000) 435–442.
[29] P.M. Boorman, K. Chong, R.A. Kydd, J.M. Lewis, J. Catal. 128 (1991) 537–550.
[30] S.M. Bradley, R.A. Kydd, J. Catal. 141 (1993) 239–249.
[31] F. Patrick, S. Sugunan, React. Kinet. Mech. Catal. 103 (2011) 125–131.
[32] W. Radmacher, P. Mohrhauer, Brennstoff-Chemie 37 (1956) 353–358.
[33] R. Pietrzak, H. Wachowska, Fuel 82 (2003) 705–713.
[34] C. Moreno-Castilla, F. Carrasco-Marín, A. Mueden, Carbon 35 (1997) 1619–1626.
[35] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982.
[36] A. Michalska, M. Daturi, J. Saussey, I. Nowak, M. Ziółek, Microporous Mesoporous Mater. 90 (2006) 362–369.
[37] T.J. Bandosz, J. Jagiełło, J.A. Schwarz, Anal. Chem. 64 (1992) 891–895.
[38] C. Moreno-Castilla, M.V. López-Ramón, F. Carrasco-Marín, Carbon 38 (2000) 1995–2001.
[39] I. Gniot, P. Kirszensztejn, M. Kozłowski, Appl. Catal. A 362 (2009) 67–74.
[40] B. Krzyżyńska, A. Malaika, P. Rechnia, A. Tolińska, P. Kirszensztejn, M. Kozłowski – to be sent.
[41] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Carbon 37 (1999) 1379–1389.
[42] J.A. Menéndez, J. Philips, B. Xia, L.R. Radovic, Langmuir 12 (1996) 4404–4410.
[43] H.P. Boehm, G. Mair, T. Stoehr, A.R. de Rincón, B. Tereczki, Fuel 63 (1984) 1061–1063.
[44] I.I. Salame, T.J. Bandosz, J. Colloid Interface Sci. 240 (2001) 252–258.
[45] J. Przepiórski, M. Skrodzewicz, A.W. Morawski, Appl. Surf. Sci. 225 (2004) 235–242.
[46] B. Krzyżyńska, A. Malaika, P. Rechnia, M. Kozłowski – to be sent.
[47] J. Lahaye, Fuel 77 (1998) 543–547.
[48] M.A. Montes-Morán, D. Suárez, J.A. Menéndez, E. Fuente, Carbon 42 (2004) 1219–1225.
[49] V. Strelko Jr., D.J. Malik, M. Streat, Carbon 40 (2002) 95–104.
[50] C.L. Mangun, K.R. Benak, J. Economy, K.L. Foster, Carbon 39 (2001) 1809–1820.
[51] J.P. Chen, S. Wu, K.-H. Chong, Carbon 41 (2003) 1979–1986.
[52] A. Gervasini, J. Fenyvesi, A. Auroux, Catal. Lett. 43 (1997) 219–228.
[53] B.K. Pradhan, N.K. Sandle, Carbon 37 (1999) 1323–1332.
[54] N. Muradov, F. Smith, A. T-Raissi, Catal. Today 102–103 (2005) 225–233.