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Activated Carbon Modified with Different Chemical Agents as a Catalyst in the Dehydration and Dehydrogenation of Isopropanol

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Abstract Activated carbons modified with different chemical agents such as HNO_3, H_2SO_4, peroxyacetic acid (PAA), air, NH_3 and Cl_2 have been tested as catalysts in decomposition (dehydration and dehydrogenation) of isopropanol. The majority of the samples obtained have been characterised by well-developed microporous surface with a small contribution of mesopores (8–18%). The influence of the surface area of the samples on their catalytic performance has been insignificant. The carbon oxidation with oxidants in the liquid or gas phase leads to an increased catalytic activity and the dominant process is dehydration of the alcohol studied. Carbon modification by contact with gas ammonia or chlorine results in a decrease in the catalytic activity and a significant increase in the contribution of dehydrogenation of isopropanol. It has been shown that such behaviour of the catalysts has been a consequence of changes in the acid-base character of the carbons induced by their modification.

Keywords Decomposition of isopropanol · Activated carbon · Catalytic activity

1 Introduction

The processes of dehydration and dehydrogenation of alcohols are well-known and commonly used as model reactions for identification of acid-base active centres of solid catalysts [1–4]. These reactions lead mostly to olefins and ethers in the case of dehydration, or aldehydes and ketones in the process of dehydrogenation. As follows from literature data, decomposition of isopropanol via the first of these reactions in the presence of inorganic catalysts (metal oxides) runs with involvement of mainly acidic centres, whereas via the other preferentially with involvement of basic ones [5]. This rule is well satisfied for the basic catalysts such as MgO [6] or the acidic ones such as CrAPO-5 [2]. However, the reaction of isopropanol decomposition is not always so simple. Gervasini et al. [7] reported other possible mechanisms and active centres for the decomposition of isopropanol. According to the scheme proposed, propylene can be formed not only on the strong acidic Brönsted or Lewis centres, but also on the pair of a base and Lewis acid. In this last case the formation of diisopropyl ether can also occur. It is postulated that the process of isopropanol dehydrogenation towards acetone requires the presence of strong basic centres. On the other hand, Jacobs and Uytterhoeven suppose that to get acetone in the reaction of isopropanol decomposition the pair base-Lewis acid is needed [8]. However, it has been proved [1] that dehydrogenation to acetone over the catalysts based on metal oxides occurs also on the redox centres. Some reports show that dehydrogenation and dehydration of isopropanol are not only determined by surface acidic or basic properties of catalyst but also strongly affected by the reaction conditions employed, such as reaction temperature, isopropanol partial pressure and the oxidizing nature of the carrier gas [9, 10]. Despite the above presented ambiguities in the course of the reaction, the decomposition of isopropanol is assumed a useful method of investigation. Aramendia et al. [3] have compared the results of the isopropanol decomposition reaction with those of the other test reactions (transformations of 1-phenylathanol

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and 2-methyl-3-butyn-2-ol) and proved that they lead to concordant results on acid-base characteristic of catalysts.

So far the catalysts based on inorganic substances, such as metals and their oxides [7, 11–13] or zeolites [8, 14, 15], have been mainly studied by these reactions. The literature on the alcohol decomposition on activated carbons is rather scarce, although it has been proved that activated carbons can catalyse many chemical reactions [16] including alcohol decomposition. The most attention has been devoted to the reactions of butanol, isopropanol, ethanol or methanol [17–26]. It has been found that the dehydration activity of carbons results from the presence of carboxyl groups of varying acid strength, whereas the dehydrogenation activity results from the simultaneous presence of Lewis acid and Lewis base sites [17, 18]. Moreover, only those carboxyl groups that are characterised by low thermal resistance [21] or those that are easily accessible to the reagents [20] show catalytic activity in the reaction of dehydration. The dehydration has been shown to occur mainly on the external surface of the carbons, while dehydrogenation can take place also inside the pores [18, 22]. The products obtained as a result of the above processes can be involved in different secondary reactions, e.g. leading to formation of acetal in decomposition of ethanol [19] or to formation of methyl formate in decomposition of methanol [26].

Hitherto, the carbon catalysts used in the reactions of alcohol decomposition have been obtained from such precursors as olive stones [21, 22, 25], polyfurfuryl alcohol [17–20] or cellulose [23, 24], and the activation of the carbonisate has been realised by steam [21, 22] or carbon dioxide [17–20, 25]. The samples prepared in this way usually have been oxidised by different chemical agents [17–24]. These processes, applied to introduce oxygen functional groups on the surface of the material studied, cause an increase in the acidity of the catalysts and hence, an increase in the catalytic activity towards dehydration of alcohols.

The subject of this study was activated carbon obtained from brown coal by chemical activation with potassium hydroxide. Because of large surface area, the materials obtained in this way are also known as *super activated carbons* [27]. To the best of our knowledge, these materials have not been widely studied in the aspect of their catalytic properties in decomposition of alcohols. The activated carbon obtained was modified by oxidation with liquid agents (HNO_3, H_2SO_4, peroxyacetic acid) and gas agents (air) as well as treated with ammonia and chlorine. The main aim of our study was determination of the effects of the modifications applied on the catalytic activity of the carbon catalysts studied in the reactions of dehydration and dehydrogenation of isopropanol.

2 Experimental

2.1 Preparation of Catalysts

The precursor of all samples of activated carbon was Polish brown coal from the “Konin” colliery. The raw coal was ground in a ball mill and sieved to the mesh size $\leq$0.2 mm, then subjected to demineralisation by the Radmacher and Mohrhauer method using concentrated hydrochloric and hydrofluoric acids [28]. The demineralised coal obtained was activated using solid potassium hydroxide at the coal to KOH weight ratio of 1:4 [29]. The chemical activation was conducted for 45 min at 1,123 K under argon flow at the rate of 20 dm^3/min. To the product obtained a certain amount of a 5% HCl was added to get an acidic reaction, then it was washed with distilled water and dried at 383 K till constant mass. The initial materials are characterised in Table 1. The activated carbon (K) obtained was modified by oxidation with concentrated HNO_3, concentrated H_2SO_4, peroxoacetic acid (PAA—a mixture of acetic acid and hydrogen peroxide [30]) and air. Moreover modification of activated carbon with gas chlorine and gas ammonia has been performed. In the processes of wet oxidation the sample of 1 g of activated carbon was mixed with 50 cm^3 of the oxidant solutions and after completion of the process the product was carefully washed with warm distilled water and dried at 383 K overnight. The modification with the agents in gas phase was performed in a quartz reactor (heated by tube furnace) at the gas flow of 20–50 cm^3/min. All reagents used were of high-purity or analytical grade. The labelling of the catalysts samples, the modifying agents, conditions of the modification processes and the yields of the products obtained relative to the mass of the initial activated carbon are presented in Table 2.

2.2 Characterization of Catalysts

The activated carbon precursor, demineralised coal and the final activated carbon were subjected to proximate analysis including determination of the contents of ash, moisture and volatile matter. Moreover, all catalysts samples were subjected to elemental analysis on Elemental Analyser Vario EL III. The transmission FTIR spectra of some selected samples were acquired using a Bruker IFS 66v/S

Table 1 Proximate analyses of coals and activated carbon (wt %)

Sample	Moisture	Ash (dry basis)	Volatile matter (dry ash free)
Raw coal	17.0	22.6	33.3
Demineralised coal	0.0	0.9	37.0
Activated carbon (K)	0.0	3.3	0.0

Table 2 Sample naming, conditions of treatments of activated carbon (K) and yield of modified carbons obtained

Sample code	Modifying agent	Reaction time [h]	Reaction temperature [K]	Yield [%]
K/HNO_3/8 h	Conc. HNO_3	8	353	98.8
K/HNO_3/16 h	Conc. HNO_3	16	353	93.2
K/H_2SO_4/8 h	Conc. H_2SO_4	8	523	84.7
K/H_2SO_4/16 h	Conc. H_2SO_4	16	523	83.9
K/PAA/313 K	PAA	6	313	88.8
K/PAA/333 K	PAA	6	333	91.6
K/AIR/4 h	Air	4	673	87.0
K/AIR/8 h	Air	8	673	71.7
K/Cl_2/723 K	Cl_2	4	723	109.0
K/Cl_2/923 K	Cl_2	4	923	104.0
K/NH_3/1,073 K	NH_3	2	1,073	89.6
K/NH_3/1,223 K	NH_3	2	1,223	89.8

spectrometer by adding 256 scans at 2 cm^{-1} resolution. Pressed KBr pellets at a sample/KBr ratio of 1:1000 were used. The porous structure of the activated carbon samples was determined by a Micromeritics Sorptometr ASAP 2010 with nitrogen as adsorbate at 77 K. The total specific surface areas and pore volumes were calculated using the BET equation, whereas t-plot method was applied to calculate the micropore volume and micropore surface area [31].

2.3 Catalytic Tests

The catalytic tests of isopropyl alcohol decomposition were performed by the single reagent pulse method in a glass fixed-bed reactor in the temperature range 423–723 K and with the alcohol dose of 0.2 μL. The amount of carbon catalyst used was 0.02 g and the carrier gas was helium (99.99%, Linde) flown through reactor at the rate 30 cm^3/min. The products of isopropanol dehydration and dehydrogenation were analysed on a gas chromatograph, connected on-line to the reactor and equipped with a flame-ionisation detector. The column was 2 m long and was filled with 30% Emulphor O on Chromosorb W. The column temperature was kept at 383 K.

3 Results and Discussion

3.1 Samples Characterization

In order to minimise the influence of mineral substances on the catalytic test results, the raw coal was subjected to demineralisation. The raw and demineralised coal samples are characterised in Table 1. The comparison of ash content in both coals shows that the process of demineralisation by concentrated HCl and HF effectively removes the mineral substances. Despite such a significant demineralisation the content of volatile matter increased only from about 33 to 37% wt, which means that the process of demineralisation does not cause significant changes in the coal structure.

As follows from Table 2, all the reactions of activated carbon oxidation as well as its treatment with ammonia result in some loss of sample mass. The highest yield of the carbon modified by oxidation (98.8%) was obtained for the treatment of activated carbon with concentrated HNO_3 applied for 8 h. The lowest yield (and thereby the greatest mass loss) was noted for the sample oxidised with the air for 8 h, which can be a consequence of burn-off of part of the carbon substance. On the other hand, the modification of activated carbon with chlorine at 723 or 923 K, resulted in the yield increase above 100%, which can be explained by introducing a certain amount of chlorine atoms into the activated carbon structure. Papirer et al., on the basis of the XPS study of chlorinated carbon materials, reported that chlorine can be built into the carbon structure in different ways, mainly by addition or by substitution of hydrogen atoms. It is also supposed that the oxygen functional groups can be replaced by chlorine atoms [32].

Elemental composition of the samples studied is given in Table 3. These data show that demineralisation of the raw coal did not change significantly its elemental composition. However, significant changes in the elemental composition were noted after chemical activation of demineralised coal by KOH. The content of carbon increased significantly and that of all other elements decreased. It is a consequence of coal decomposition and a large mass loss in result of its activation (the yield of the reaction was 28.1% wt. only). The release of substantial amounts of volatile components taking place during this process leads to an increase in the content of ash. The treatment of activated carbon with the acids (HNO_3, H_2SO_4

Table 3 Elemental analyses of samples investigated (wt %)

Sample	Ash (dry basis)	C^{daf}	H^{daf}	N^{daf}	S^{daf}	Cl^{daf}	$^{a}O^{daf}$
Raw coal	22.6	60.3	5.3	1.0	2.0	–	31.5
Demineralised coal	0.9	64.3	4.8	0.7	2.4	–	27.8
Activated carbon (K)	3.3	96.8	0.9	0.1	0.4	–	1.8
K/HNO_3/8 h	1.1	65.8	0.9	0.9	0.2	–	32.2
K/HNO_3/16 h	1.0	61.2	0.2	0.9	0.1	–	37.6
K/H_2SO_4/8 h	1.5	93.5	0.9	0.2	0.2	–	5.2
K/H_2SO_4/16 h	0.3	85.9	1.0	0.3	0.4	–	12.4
K/PAA/313 K	1.5	90.3	0.6	0.4	0.4	–	8.3
K/PAA/333 K	3.3	90.1	0.6	0.3	0.3	–	8.7
K/AIR/4 h	2.4	90.5	0.8	0.6	1.4	–	6.7
K/AIR/8 h	5.1	89.9	1.0	0.3	1.0	–	7.8
K/Cl_2/723 K	1.9	84.3	1.1	0.4	0.9	8.0	5.3
K/Cl_2/923 K	5.9	90.1	1.0	0.2	0.8	7.3	0.6
K/NH_3/1,073 K	3.5	97.8	0.8	1.0	0.4	–	0.0
K/NH_3/1,223 K	2.7	98.1	0.7	0.8	0.4	–	0.0

[a] Calculated by difference

and PAA) usually leads to elimination of mineral compounds, while its treatment with gases (air, chlorine and ammonia) does not remove mineral compounds and that is why sometimes an increase in the content of ash is observed.

As expected, all the oxidation processes applied (by liquid and gas reagents) brought about an increase in the amount of oxygen with respect to that in the initial activated carbon (K). The content of oxygen in oxidised carbon samples is the greater the higher the temperature or the longer the time of the process. The greatest amount of oxygen was introduced into the carbon structure as a result of its reaction with concentrated HNO_3, while the oxidation with H_2SO_4 for 8 h proved the least effective. Analysis of the other results collected in Table 3 has shown that the reaction of activated carbon with H_2SO_4 does not increase the content of sulphur in the material obtained, which means that this process does not introduce sulphonic groups into the carbon structure, contrary to expectations [33]. The oxidation of activated carbon with HNO_3 leads to a small increase in the content of nitrogen, which is a result of attachment of this element to the carbon structure e.g. in the form of nitric groups [34]. The treatment of activated carbon with ammonia at temperatures 1,073 and 1,223 K also leads to an increase in the content of nitrogen, which can be related to formation of pyridinic, pyrrolic and quaternary nitrogen groups [35]. On the other hand, the samples treated with ammonia show a substantial oxygen removal, related to the decomposition of certain oxygen groups on the surface of the catalysts in so high temperatures. Moreover, it can be supposed that the removal of the oxygen functional groups is also a result of their contact with hydrogen produced in small amounts in the process of ammonia decomposition [36]. Table 3 data also indicate a high efficiency of activated carbon chlorination with gas chlorine, and show that greater amounts of this element were introduced to the carbon structure at the lower of the two temperatures applied.

The structural changes in the activated carbon taking place on its modification have been also followed by the FTIR spectroscopy (Fig. 1). For clarity of the figure, we show only the spectral analysis of the samples whose modifications by each of the modifying agents have been the most effective. The spectra of so selected carbon samples were analysed in the range of wavenumbers from 600 to 2,000 cm^{-1}, as in this range the differences between the spectra were the most pronounced. The band assignments made in this work were based on the literature data [34, 37–40].

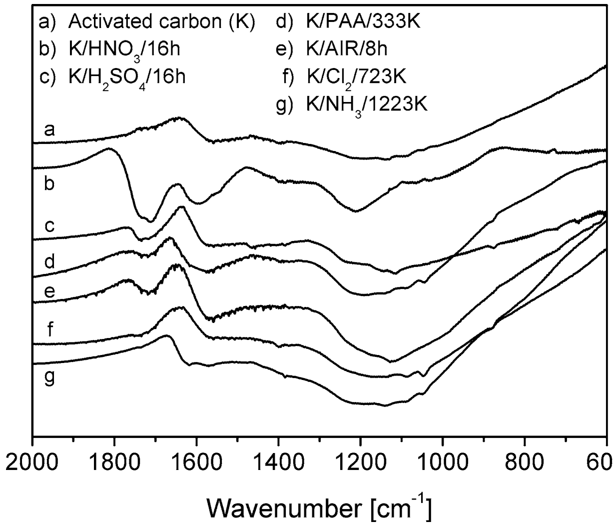

Fig. 1 FTIR spectra of selected samples

The spectrum of the initial activated carbon is poor in details; practically the only distinct signal is that at about 1,600 cm^{-1} (Fig. 1a). The band in this region can be assigned to aromatic structures (stretching vibrations) or to conjugated carbonyl systems. Since the unmodified activated carbon contains little oxygen (Table 3), the second possibility is rather unlikely. The carbon oxidation results in the appearance of the band at about 1,720 cm^{-1}. This band is well visible for the samples oxidised both in the solution of oxidising agents and in the gas phase. The band at 1,720 cm^{-1} can be assigned to the C=O stretching vibration from ketones, aldehydes or carboxyl groups. The most logical explanation for this signal would be the existence of carboxyl groups that are formed as a result of oxidation [40]. All types of the oxidation process applied are also responsible for an increase in the intensity of the band at about 1,600 cm^{-1}, which indicates the formation of carbonyl groups. The spectra also reveal a band in the range 1,000–1,300 cm^{-1}. The band in this region is difficult to assign because it is a result of the superposition of a number of broad overlapping bands ("fingerprint" together with C–O stretching, and O–H bending modes of alcoholic, phenolic, and carboxylic groups). In the spectra of the samples modified with HNO_3 or ammonia, some contribution to this band may come from the C–N vibrations [40]. As follows from further analysis of the spectra from Fig. 1, the highest intensity signals were recorded for the carbon oxidised by HNO_3 for 16 h. This observation can be explained on the basis of the data shown in Table 3, implying that in this mode of oxidation the amounts of oxygen introduced is by far the greatest.

Nitrogen adsorption study at 77 K proved that the activated carbon obtained by reaction of demineralised coal with KOH in solid state has well developed porous structure and large total specific surface area (S_{BET}) of about 2,800 m^2/g. Texture of all activated carbon samples is characterised in Table 4. The processes of modification had various but in general small effects on the surface area of the samples. The exceptions were the catalysts obtained as a result of the activated carbon reaction with concentrated HNO_3, for which a drastic decrease in the surface area was noted, suggesting a destruction of the porous structure of carbon upon its strong oxidation. The extension of the exposition of activated carbon to the oxidising agent or an increase in the reaction temperature lead to a small decrease in the surface area, which can also be a consequence of partial destruction of the porous system. This supposition is confirmed by the results of the total pore volume (V_{tot}) measurements, decreasing with increasing time and temperature of the modification process. The reverse situation is observed for the samples modified with chlorine and ammonia, for which the total pore volume slightly increases with increasing temperature of the process. It should be also noted that the reaction of activated carbon with ammonia gave samples of larger surface area and greater pore volume than those in the initial carbon. This observation can be explained by partial gasification of carbon with hydrogen, appearing in the reaction of ammonia decomposition. The process of gasification (but this time by oxygen and to a lesser extent) can be also observed for the sample oxidised with air for 4 h. The extension of the reaction time leads to a partial degradation of the porous structure and a decrease in the surface area. Because of the dominant contribution of micropores in the total surface area and the total pore volume (compare S_{micro} with S_{BET} and V_{micro} with V_{tot}, Table 4), all the catalysts obtained can be classified as microporous materials. The average size of the pores (D_{AV}) reach about 1.48 nm for the initial activated carbon. This value is close to the results obtained for similar carbons by more advanced methods by other authors. Illán-Gómez et al.

Table 4 Textural characteristics of carbon catalysts

Sample	S_{BET} [m^2/g]	S_{micro} [m^2/g]	V_{tot} [cm^3/g]	V_{micro} [cm^3/g]	D_{AV} [nm]
Activated carbon (K)	2,802	2,674	2.07	1.85	1.48
K/HNO_3/8 h	415	406	0.21	0.19	2.02
K/HNO_3/16 h	3	–	<0.01	–	2.28
K/H_2SO_4/8 h	2,369	2,260	1.41	1.24	2.39
K/H_2SO_4/16 h	1,952	1,889	1.10	0.99	2.26
K/PAA/313 K	2,746	2,638	1.92	1.73	2.79
K/PAA/333 K	2,457	2,356	1.71	1.54	2.79
K/AIR/4 h	2,826	2,708	1.94	1.74	2.75
K/AIR/8 h	2,639	2,533	1.78	1.60	2.69
K/Cl_2/723 K	2,374	2,293	1.60	1.46	2.70
K/Cl_2/923 K	2,498	2,417	1.69	1.56	2.71
K/NH_3/1,073 K	2,986	2,828	2.30	2.02	3.08
K/NH_3/1,223 K	2,967	2,719	2.34	1.91	3.15

[41] calculated the pore size distribution by the Horvath-Kawazoe method for the carbons obtained from the coal activated by KOH and found the dominant presence of the pores size 1–1.5 nm. A similar result (1–2 nm) was obtained by the DFT method for the KOH activated carbon fibres [42]. As follows from analysis of the data presented in Table 4, D_{AV} increases as a result of the all modifications applied. The increase is the greatest after the activated carbon modification with ammonia.

The nitrogen adsorption–desorption isotherms of selected samples are presented in Fig. 2. The shape of all isotherms is similar, but it is difficult to classify it as a certain IUPAC type [43]. The fact that 50–80% of the pore volume is filled with the adsorbate below $p/p_0 = 0.1$ indicates a microporous character of the carbons studied [34]. All the isotherms presented are characterised by a hysteresis loop that can be classified as H4 type [43]. This type of the hysteresis loop proves the presence of the slit-shaped pores, typical of many activated carbons. The occurrence of hysteresis loops also implies a certain contribution of mesopores to total porosity of the catalysts studied. Assuming that the total volume of pores is a sum of the volume of the micro- and mesopores, the contribution of mesopores to this total volume can be estimated from data presented in Table 4. For the initial activated carbon this contribution is close to 11%, whereas in the modified carbons it varies from 8 to 18%, depending on the method of modification. Further analysis of the isotherms presented in Fig. 2 proves that some of the hysteresis loops were not closed, like e.g. those for the carbons oxidised by HNO_3 and H_2SO_4. Open hysteresis loops are observed when the sizes of the pores are comparable with the size of the adsorbate molecule [43]. Their presence means that the carbon samples studied contain a certain amount of very small size pores (so-called ultramicropores).

3.2 Catalytic Activity of Carbons

The catalytic activity of the samples tested was determined on the basis of measurements of the degree of isopropanol conversion versus temperature. Interpretation of the results should be made taking into regard the possibility that the sample heating to the reaction temperature can change both its chemical composition (Table 3) and the texture of the samples surfaces (Table 4). The effect of temperature on the texture can be reliably assumed as insignificant for the two reasons. The first is that the initial activated carbon (K) was obtained at 1,123 K, so at the temperature much higher that used at the catalytic tests. The second reason is that although the modification of carbons was performed at different temperatures (313–1,223 K), the surface areas S_{BET} of the products obtained are relatively close. The only exceptions are the carbons oxidised by HNO_3 and H_2SO_4, however, for them the destruction of the porous structure should be related mainly to the aggressive character of the oxidising agent and not to the effect of temperature. The influence of temperature on the chemical composition of the samples cannot be neglected and has been regarded in interpretation of the results of the catalytic tests for particular carbon samples.

The results presented indicate that all the activated carbon samples obtained catalyse the reaction of dehydration of isopropanol to propylene and that of dehydrogenation to acetone, but with different selectivity (Figs. 3–9). When activated carbons are used as catalysts of isopropanol decomposition, Szymański et al. [18] proved that dehydration needs carboxyl groups of different strength, while dehydrogenation is a consequence of the simultaneous presence of Lewis basic and acidic centres. Another possible conversion of isopropanol is its dehydration towards diisopropyl ether. This reaction takes place on acidic

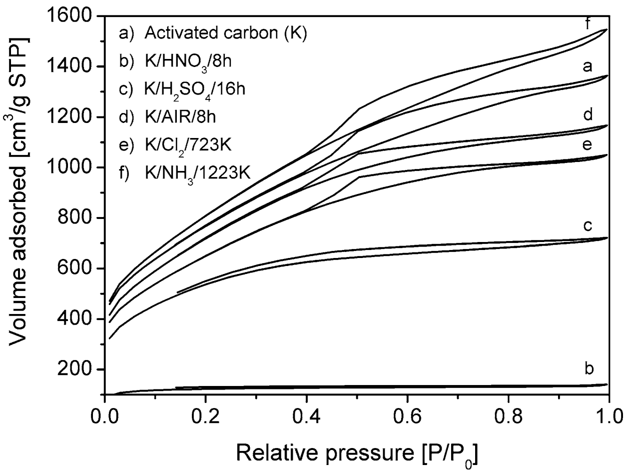

Fig. 2 Nitrogen adsorption–desorption isotherms of selected samples

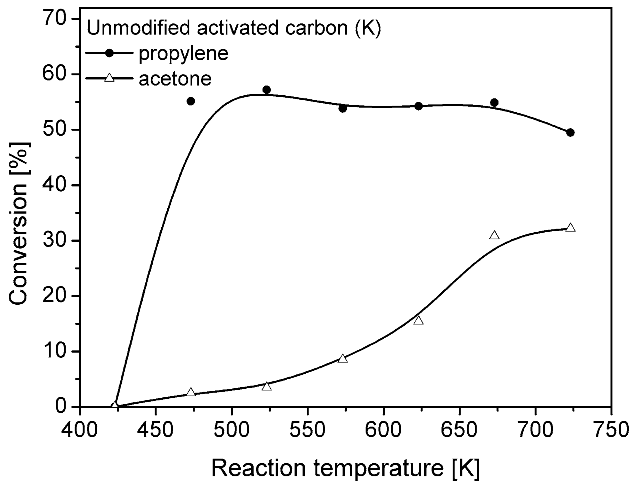

Fig. 3 Catalytic activity of unmodified activated carbon in the decomposition of isopropanol

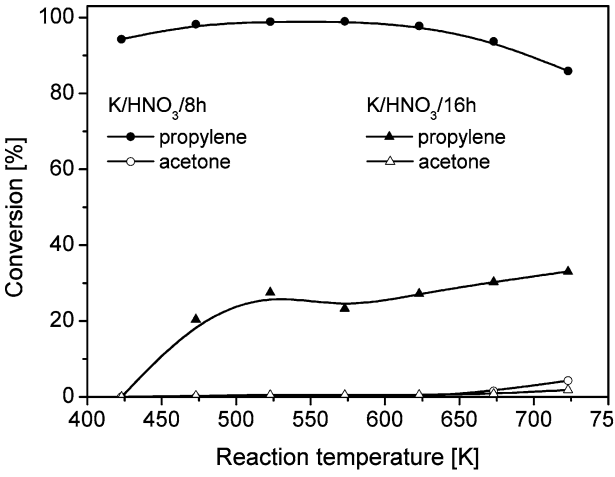

Fig. 4 Conversion of isopropanol over samples modified with nitric acid

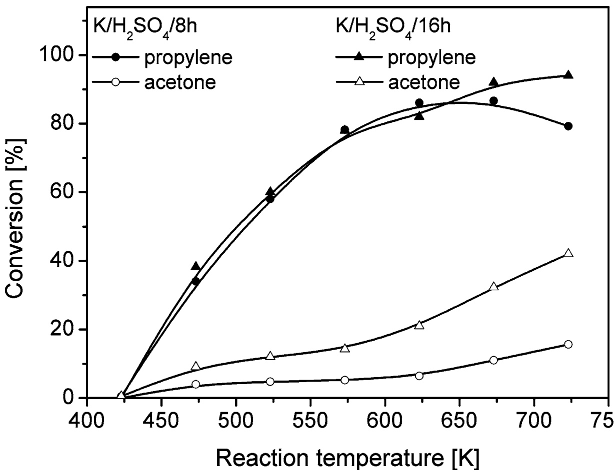

Fig. 5 Conversion of isopropanol over samples modified with sulphuric acid

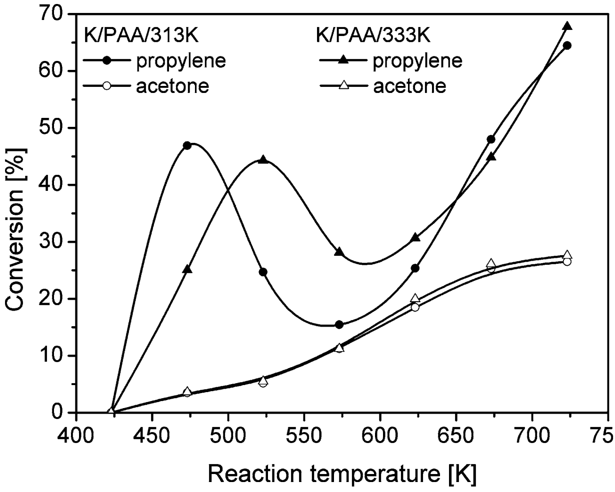

Fig. 6 Conversion of isopropanol over samples modified with peroxyacetic acid

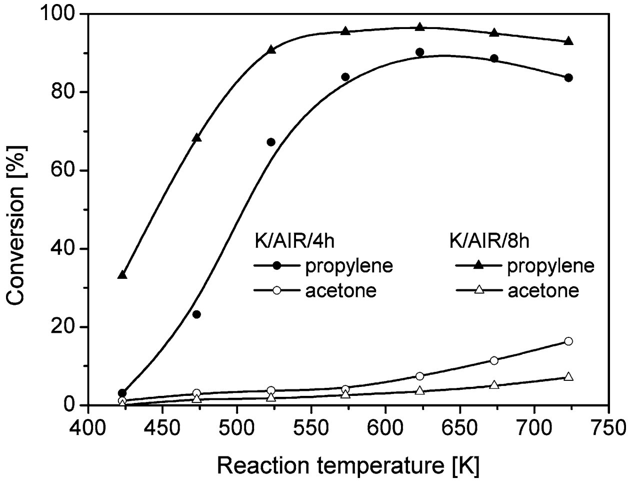

Fig. 7 Conversion of isopropanol over samples modified by contact with air

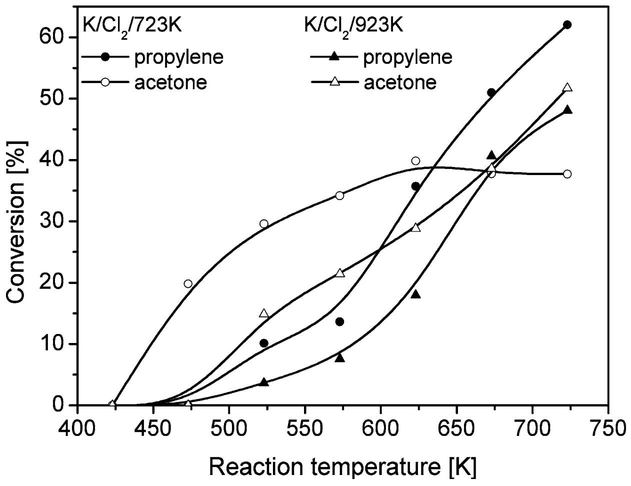

Fig. 8 Conversion of isopropanol over samples modified by contact with chlorine

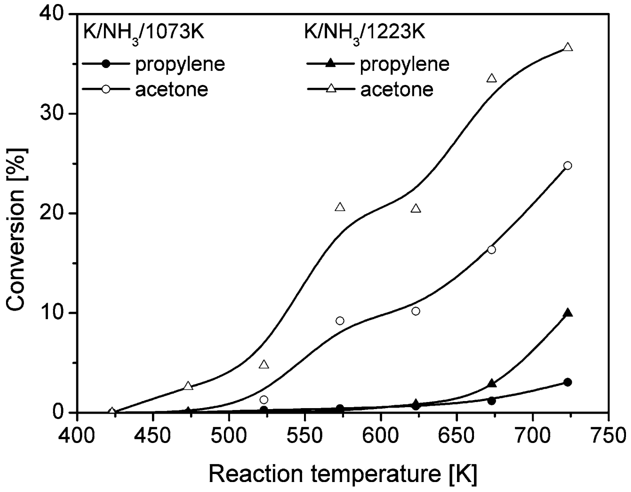

Fig. 9 Conversion of isopropanol over samples modified by contact with ammonia

centres, although a two-centre mechanism (involving acidic and basic centres) is also possible [7]. It should be noted that when the reactions were performed over the carbon catalysts tested in this study, only trace amounts of diisopropyl ether were observed, and the most active towards its production was the sample chlorinated at 723 K, for which the degree of isopropanol conversion to ether did not exceed 2.8%.

A comparison of the data presented in Fig. 3–9 proves that the method of modification of the activated carbon catalyst has a significant effect on the degree of conversion of isopropanol and on the selectivity of the reaction. The initial activated carbon (K) shows relatively high activity towards propylene formation and lower towards acetone formation (Fig. 3). So, it can be concluded that the activated carbon has both acidic and basic active centres. According to literature, the acidic properties of carbon are determined mainly by carboxyl groups but also other oxygen functional groups such as phenolic, carbonyl, lactone and lactol show weakly acidic character [44]. The chromene, pyrone, diketone or quinone groups on the one hand, and delocalized π-electrons of the basal planes, on the other, are assumed to have a basic nature. [45]. According to Fig. 3, the yield of acetone increases with increasing temperature of the reaction, while the yield of propylene (dehydration of isopropanol) initially fast increases with increasing temperature but starting from 500 K slowly decreases. This decrease can be a consequence of decomposition of oxygen groups induced by increasing temperature. This interpretation is confirmed by Szymański et al., who claim that the oxygen groups in carbons decompose with generation of H_2O, CO and CO_2, and that the carboxyl groups have the lowest thermal resistance [20].

For all samples oxidised either in a solution or in gas phase, the dominant process occurring in the course of the catalytic tests is dehydration of isopropanol to propylene (Figs. 4–7). This is a consequence of introduction of large amounts of oxygen to the carbon structure (Table 3, Fig. 1), however the wet oxidation process favours the formation of mainly carboxyl groups, while the oxidation by the air leads to formation of both carboxyl and hydroxyl (phenol) groups [46, 47]. Both these groups being Brönsted acids, act as active centres of isopropanol dehydration. The greatest degree of isopropanol conversion was obtained for the catalyst oxidised with concentrated HNO_3 for 8 h (Fig. 4), and the reaction occurred with almost 100% selectivity towards propylene and trifling selectivity towards acetone, which clearly points to the acidic character of the oxidised carbon. Although the extension of the process to 16 h caused the introduction of the greatest amount of oxygen, (Table 3), it also brought a significant decrease in the catalytic activity of the sample, which should be related to the destruction of its porous structure (Table 4). The samples oxidised with the air or concentrated H_2SO_4 are also characterised by high degrees of isopropanol conversion, in particular at high temperatures (Figs. 5 and 7). As follows from the plots presented, the time of activated carbon oxidation with H_2SO_4 does not have a significant effect on the degree of dehydration of isopropanol, while the extension of the time of oxidation with the air significantly increases the dehydrating properties of the catalysts. For the sample oxidised with PAA, dehydration of isopropanol to propylene runs through clear maxima of activity, which can be related to the earlier mentioned decomposition of certain oxygen functional groups (Fig. 6.). The fact that the highest degree of isopropanol conversion was obtained for the sample K/HNO_3/8 h, of very small surface area, means that this parameter does not determine directly the catalytic properties of the samples studied.

In contrast to the oxidised samples, the activated carbon subjected to chlorine treatment is characterised by enhanced selectivity towards acetone formation (Fig. 8). This phenomenon is well visible for both chlorinated samples, in particular in lower temperatures of isopropanol decomposition. The amount of acetone formed is greater for the sample chlorinated at 723 K than for that chlorinated at 923 K, which should be related with the amount of chlorine introduced into the catalyst structure (Table 3). According to literature data, chlorination of activated carbon increases the acidic character of its surface [25] and therefore the introduction of chlorine into the activated carbon structure should give an increase of amount of propylene obtained. However, as follows from our results and those reported by Pérez-Cadenas et al. [25], this is not the case. The authors of the latter paper have also proved that an increase in the total acidity of chlorinated carbons is a consequence of an increase in the acidity of Lewis centres accompanied by a decrease in the number of the Brönsted acidic centres. Thus, the observed increase in the selectivity of isopropanol decomposition towards acetone formation can be explained by the appearance of acidic Lewis centres, which—together with the basic centres present in the carbon—are considered to be the active sites of dehydrogenation [8, 18]. Further analysis of the results from Fig. 8 shows that the decomposition of isopropanol towards acetone and propylene generally increases with increasing temperature of the reaction.

The domination of the process of dehydrogenation over dehydration was also observed for the samples subjected to ammonia treatment (Fig. 9) and this domination is much better visible than for chlorinated samples. As already mentioned, the treatment of carbon with gas ammonia leads to total elimination of oxygen from the carbon structure (Table 3), so also from the carboxylic groups which are responsible for the process of dehydration. According to Barton et al. [48], the acidic and basic centres co-exist on the surface of the activated carbon but the concentration of the basic centres increases with decreasing acidic character of the surface. The basic active centres taking part in dehydrogenation of isopropanol can also be formed in the reaction of ammonia with the carbon. As already stated, this process leads to incorporation of nitrogen atoms into the carbon structure (Table 3), also in the form of basic pyridinium groups [35].

It should be emphasised that for the majority of the catalysts studied, the decomposition of isopropanol begins at relatively low temperatures (propylene starts appearing already at about 423 K).

4 Conclusions

The above discussed results have shown that all the carbon materials tested are catalytically active in dehydration and dehydrogenation of isopropanol, leading to formation of propylene and acetone as the main products, respectively. The modifying agent and conditions of the activated carbon modification have been found to have important effect on the catalytic properties of the products obtained. The carbon samples oxidised by the agents in the liquid or gas phase are more selective towards propylene formation, while those modified by ammonia or chlorine are more selective towards acetone. The sample oxidised with HNO_3 for 8 h was characterised by the highest activity in dehydration, which has been a consequence of introduction of large amounts of oxygen (mainly as carboxyl groups) into the carbon structure. The catalytic activity of the majority of the samples studied has been found to increase with increasing temperature of the isopropanol decomposition reaction. However, for certain oxidised carbon samples clear maxima of activity have been detected, which should be related to decomposition of certain oxygen functional groups on heating. An increase in the isopropanol conversion towards dehydrogenation noted for the samples subjected to chlorine or ammonia treatments is most probably a result of increased basicity of the carbon or formation of Lewis acidic centres.

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