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Influence of activated carbon modifications on their catalytic activity in methanol and ethanol conversion reactions

Research Article

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Abstract: Activated carbons containing different surface functionalities have been investigated as catalysts in conversion reactions of ethanol and methanol. These carbon materials were prepared from Polish brown coal by chemical activation with potassium hydroxide and modified by the oxidation or reaction with ammonia or chlorine. The main process upon ethanol decomposition was its dehydrogenation, while in the process of methanol decomposition only a few samples were catalytically active, and the only product was dimethyl ether (a product of dehydration).

Keywords: *Dehydration • Dehydrogenation • Alcohols • Activated carbon • Catalytic activity*

1. Introduction

One of the catalytic processes taking place on acid/base active centres is the decomposition of alcohols. From among reactions of this type described in literature, much interest has been devoted to dehydration and the dehydrogenation of aliphatic alcohols (mainly isopropanol [1,2]). Taking into regard the selectivity of these reactions towards acid or base catalytic centres, these processes are classified as the so-called models and often used for characterisation of the chemical character of the surface [3-5]. These processes are of interest regarding their cognitive aspect as well as their prospective applications [6,7] due to the significant industrial importance of the products obtained in ethanol and methanol decompositions (such as ethylene, acetaldehyde, diethyl ether, dimethyl ether and formaldehyde) [6,7].

A large number of catalytic systems has been studied in the reactions of methanol and ethanol decomposition, starting from the catalysts based on metal oxides [8-10] (transient metals included [7]), through zeolites [11-13] to metals or metal oxides supported on activated carbon [14-22]. There are only a few reports on the decomposition of ethanol and methanol on activated carbon which is used as catalyst in its own right [22-27]. Szymański *et al*. [23] carried out the process of ethanol decomposition over different carbon catalysts obtained from poly(furfuryl alcohol). Apart from the fundamental products of ethanol decomposition (ethylene, diethyl ether and acetic aldehyde) they also obtained 1,1'-diethoxyethane. The same authors proved that those samples oxidised with concentrated nitric acid showed greater activity and selectivity towards dehydration, than those with the addition of Ni^{2+} ions which resulted in the appearance of new centres active in dehydrogenation. According to authors, the dehydrogenation occurred with simultaneous participation of Lewis acid and base sites. Catalytic activity increases with increasing temperature of the process, but for temperatures higher than 593 K, a drop in the catalytic activity caused by thermal decomposition of surface oxygen groups is observed. Grunewald and Drago [24] who checked the behaviour of carbon molecular sieves in the reaction of ethanol decomposition noted that when this process is conducted exclusively in the neutral gas atmosphere the catalytic activity decreases, and the main reaction product is ethylene. The catalyst activity can be recovered when a mixture of the carrier gas and air is used; then the dominant products are ethyl acetate and acetic aldehyde. The dehydrogenation of ethanol was established to take

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place on Lewis acid sites; their activity decreased with time at the neutral gas flow through the catalyst bed. The other major product observed (ethyl acetate) was the result of a secondary condensation reaction.

Ethanol decomposition has also been studied by the research group of Carrasco–Marín [25]. They studied the effect of active carbon oxidation with $(NH_4)_2S_2O_8$ on their activity and selectivity in ethanol decomposition reaction. As follows from their results, the activated but unoxidised carbon is able to catalyse exclusively the dehydrogenation reaction whose main product is acetic aldehyde. Dehydrogenation takes place on both acid and base centres. This reaction can also be catalysed by ether groups on the surface of the carbon catalysts. When oxidised activated carbons are used, alcohol decomposition can result in its dehydration and dehydrogenation. The dehydration process increases with an increased total acidity of the carbon surfaces and takes place mainly at the active centres of the Brönsted type. The main product of the reaction is ether which easily converts to ethylene.

Not many authors have been interested in the decomposition of methanol on carbon materials. Zawadzki *et al*. revealed that the pure, unoxidised carbon itself is unreactive in the decomposition of methanol [22]. Catalytic activity appeared only after carbon oxidation by gas oxygen. The results provided evidence for the participation of methoxides and formaldehyde intermediates in the decomposition of methanol. The reaction of methanol decomposition catalysed by activated carbons oxidised by different oxidising agents was studied by Moreno–Castilla *et al*. [26,27]. They reported that activated carbons oxidised with $(NH_4)_2S_2O_8$ have the strongest acid groups and are the most active in the dehydration reaction of methanol to dimethyl ether. An increase in the catalyst heating temperature results in a rapid decrease in its activity in methanol dehydration. The reason is a gradual decomposition of carboxyl groups present on the catalyst surface which already becomes unstable at 453 K.

As follows from the survey of literature, reactions of ethanol and methanol decompositions can be a source of information on the chemical nature of the carbon surface. Moreover, to the best of our knowledge, these reactions have not been performed over carbon catalysts obtained by chemical activation by KOH and modified by concentrated H_2SO_4, peroxyacetic acid, ammonia or chlorine. The aim of the study was to establish the effect of the initial activated carbon modification (liquid or gas phase oxidation and ammonia or chlorine treatment) on its catalytic properties in ethanol and methanol decompositions.

2. Experimental procedure

The precursor used to obtain the 13 samples of different surface carbon catalysts was Polish brown coal from the Konin colliery. The initial procedure to obtain the activated carbon catalysts included grinding of the precursor to the size ≤0.2 mm, its demineralisation by the concentrated HCl and HF and chemical activation by potassium hydroxide at 1123 K. The activated carbon was then treated with various chemical reagents such as nitric acid, sulphuric acid, peroxyacetic acid (PAA), air, gas ammonia and chlorine. The aim of these modifications was to introduce new surface functional groups or change (as to the type and abundance) of the present active centres. Details on the conditions of precursor activation and modification as well as full characterisation of the samples obtained (elemental analysis, FTIR results, porous structure) have been given in our previous paper [28]. The samples obtained were labelled to include the following information: K / modifying agent / time of modification / modification temperature.

The catalytic tests in the decomposition of ethanol and methanol were performed in a glass fixed-bed reactor. Small volumes (0.2 μL) of ethyl or methyl alcohol were introduced in pulses into the reactor containing a layer of a carbon catalyst (0.02 g). The reaction temperature varied from 423 to 723 K. The carrier gas was helium at a flow rate of 30 cm^3 min^{-1}. Products of ethanol and methanol decomposition were analysed on a gas chromatograph connected on-line with the reactor and equipped with flame-ionisation detector (FID) and a 2 m long column packed with 30% Emulphor O on Chromosorb W.

3. Results and discussion

3.1. Catalyst characterization

The most important data characterising the catalysts tested (ash content, presence of heteroatoms, specific surface area, pore volume and area contributions) are shown in Table 1. The ash content in carbon decreases as a result of its treatment with concentrated acids: nitric acid (samples K/HNO_3/8 h/353 K, K/HNO_3/16 h/353 K), sulphuric acid (samples K/H_2SO_4/8 h/523 K, K/H_2SO_4/16 h/523 K), and even after contact with peroxyacetic acid (sample K/PAA/6 h/313 K). According to literature [29], treatment with acids also results in increased acidity and hydrophilous character of the carbon surface. Modifications of the initial activated carbon performed by reagents in the gas phase do not remove mineral components but to the contrary, for the majority of samples, lead to an increased ash content.

Further analysis of data shown in Table 1 proves that oxidation of activated carbon by oxidising agents both in gas and liquid phase brings an increase in the oxygen content relative to that in the initial sample. According to the literature, carbon oxidation in the gas phase increases mainly the concentration of hydroxyl and carbonyl groups, while the wet oxidation leads mainly to an increased content of carboxyl groups [30]. The unmodified activated carbon obtained from brown coal by the chemical activation with potassium hydroxide shows a slight content of heteroatoms (O, H, N, Cl, S) [28]. The number of oxygen groups significantly increases with an increasing oxidation temperature and an extended duration of the process (Table 1). The most effective oxidising agent proved to be concentrated nitric acid as the treatment with this acid resulted in the incorporation of the greatest number of oxygen groups into the carbon structure. As follows from literature data, the carbon oxidation with concentrated nitric acid enhances the acidity of the active centres while decreasing the number of basic centres [31]. On the other hand, oxidation with nitric acid leads to the formation of weakly acidic functional groups [32]. According to Shim *et al.* [33], these weakly acidic groups are carboxyl, lactone and phenol ones. Moreover, the oxidation process with nitric acid besides oxygen incorporation leads to a nitrogen attachment to the carbon structure (Table 1). Nitrogen can be attached in the form of nitric groups [34]. Oxidation of the initial activated carbon with concentrated sulphuric acid, peroxyacetic acid or air led to a much smaller increase in the oxygen content (Table 1).

The treatment with ammonia (Table 1) results in the deep removal of oxygen from the structure of activated carbon and the introduction of considerable amounts of nitrogen (e.g. in the form of pyridine functionalities [35]). The full elimination of oxygen is explained by the fact that upon heating in high temperatures, the oxygen functional groups present on the surface of the catalysts undergo thermal decomposition. The modification of the activated carbon with gas chlorine was effective, and a greater amount of chlorine was introduced into the carbon structure at the lower modification temperature (Table 1). It is assumed that chlorine is incorporated into the carbon structure mainly through addition or by substitution of hydrogen or oxygen atoms [36].

Porous structure of the carbon catalysts was characterised on the basis of nitrogen adsorption isotherms measured at 77 K. The use of KOH in the chemical activation process permitted obtaining the initial activated carbon of specific surface area close to 2800 $m^2 g^{-1}$ (Table 1). This carbon had a distinct microporous structure as follows from the calculated ratio of micropore area to the total surface area and the contribution of the volume of micropores in the total pore volume. Activated carbon modifications with different chemical agents did not cause essential changes in the carbon porous structure; however its exposure to concentrated nitric acid led to considerable destruction of the carbon surface, which is surely related to a very strong oxidising effect of this acid.

3.2. Catalytic activity of carbons in decomposition of ethanol

According to the literature, ethanol decomposition leads not only to ethylene, diethyl ether and acetic aldehyde, but also produces ethyl acetate and 1,1-dietoxyethane [23-25]. The two latter compounds are produced in the secondary reactions between acetic aldehyde and ethanol. The reaction of dehydrogenation takes place in a simultaneous presence of Lewis base and acid centres, while that of dehydration involves only acid centres [23]. Results of the catalytic tests performed in this study proved that all activated carbon samples that were studied acted as catalysts of ethanol decomposition, but to a different degree. The main products of decomposition are ethylene and acetic aldehyde. Diethyl ether is formed in trace amounts (and that is why its presence is not shown in the plots), whereas formation of 1,1-dioxyethane and ethyl acetate is not detected. Catalytic activity of the activated carbon samples was evaluated on the basis of the temperature dependencies of alcohol conversion (Figs. 1-7). As follows from the results, for the initial sample and for the majority of the modified activated carbons , the decomposition of ethanol proceeds mainly by dehydrogenation (which is in contrast to the decomposition of isopropanol [28]). The exceptions are the carbon samples oxidised with concentrated HNO_3 (Fig. 2), whose use as a catalyst leads mainly to the formation of ethylene (by dehydration). The latter observation confirms the literature reports which state that oxidation with nitric acid increases the activity of carbon catalysts and their selectivity towards dehydration of lower alcohols [23]. These samples also yielded the highest amount of ethylene (about 35-50%). The reaction of ethanol dehydration over activated carbons oxidised with concentrated nitric acid (Fig. 2) demonstrated a clear maximum of activity at 600 K, followed by a decrease in activity probably caused by the decomposition of certain acidic active centres, i.e. carboxyl groups located on the catalyst's surface. This observation is in agreement with the results published by Szymański *et al.* [37], who reported that carboxylic groups decompose to CO_2 at 373-673 K. A time extension

Table 1. Characteristics of activated carbons investigated.

Sample	Ash (dry basis)	Atomic ratio O/C	Atomic ratio N/C	Atomic ratio Cl/C	S_{BET} (m^2 g^{-1})	S_{micro}/S_{BET}	V_{micro}/V_{tot}
Activated carbon (K)	3.3	0.014	0.001	-	2802	0.954	0.894
K/HNO$_3$/8 h/353 K	1.1	0.367	0.012	-	415	0.978	0.905
K/HNO$_3$/16 h/353 K	1.0	0.461	0.013	-	3	-	-
K/H$_2$SO$_4$/8 h/523 K	1.5	0.042	0.002	-	2369	0.954	0.879
K/H$_2$SO$_4$/16 h/523 K	0.3	0.108	0.003	-	1952	0.968	0.900
K/PAA/6 h/313 K	1.5	0.069	0.004	-	2746	0.961	0.901
K/PAA/6 h/333 K	3.3	0.072	0.003	-	2457	0.959	0.901
K/AIR/4 h/673 K	2.4	0.056	0.006	-	2826	0.958	0.897
K/AIR/8 h/673 K	5.1	0.065	0.003	-	2639	0.960	0.899
K/Cl$_2$/4 h/723 K	1.9	0.047	0.004	0.032	2374	0.966	0.913
K/Cl$_2$/4 h/923 K	5.9	0.005	0.002	0.028	2498	0.968	0.923
K/NH$_3$/2 h/1073 K	3.5	0.000	0.009	-	2986	0.947	0.878
K/NH$_3$/2 h/1223 K	2.7	0.000	0.007	-	2967	0.916	0.816

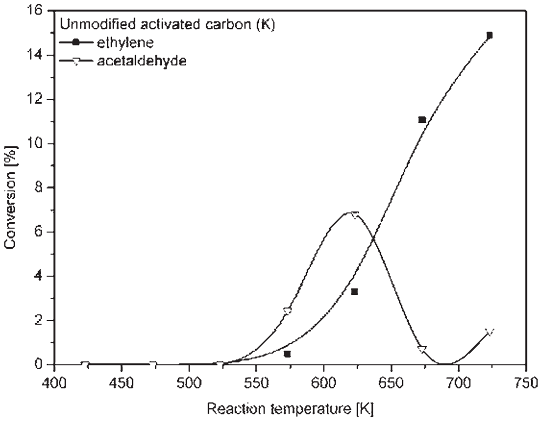

Figure 1. Catalytic activity of unmodified activated carbon in the decomposition of ethanol.

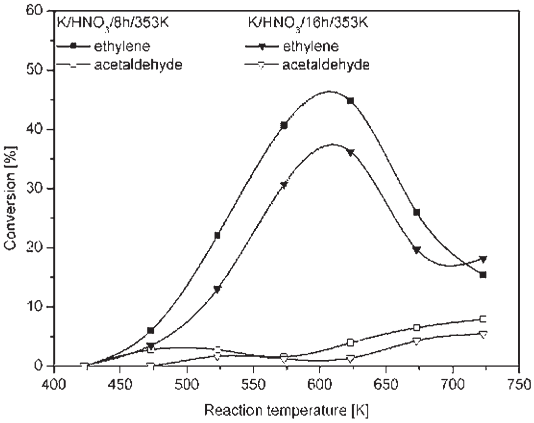

Figure 2. Conversion of ethanol for samples modified with nitric acid.

from 8 to 16 hours for carbon oxidation with nitric acid increased the content of oxygen (Table 1), but decreased the catalytic activity both towards ethylene and acetic aldehyde (Fig. 2). This decrease was a consequence of a drastic decrease in the surface area caused by rapid oxidation. The other oxidised samples (Figs. 3-5) were considerably less active and showed higher selectivity towards dehydrogenation, which could be explained by a lower content of acidic oxygen groups. The influence of modification temperature on the catalytic activity of the sample treated with peroxyacetic acid was small and related to small differences in the content of oxygen functional groups. Slightly greater differences in the catalytic activity were noted for the samples oxidised with sulphuric acid or air.

When the reaction was performed over chlorinated carbon catalysts (Fig. 6) the domination of the process of dehydrogenation over dehydration was greater than for oxidised carbon samples (Figs. 3-5). Pérez-Cadenas *et al*. [38] claimed that chlorination leads to increased acidity of the Lewis acid centres on the activated carbon but, on the other hand, to reduced acidity of the Brönsted

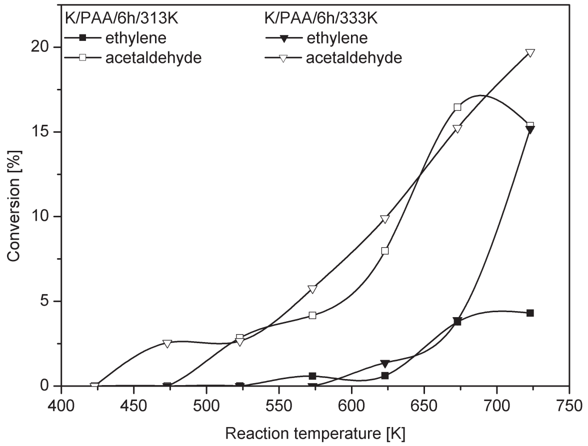

Figure 3. Conversion of ethanol for samples modified with peroxyacetic acid.

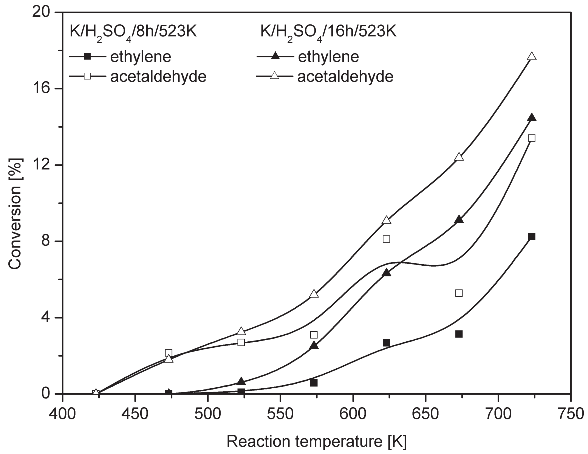

Figure 4. Conversion of ethanol for samples modified with sulfuric acid.

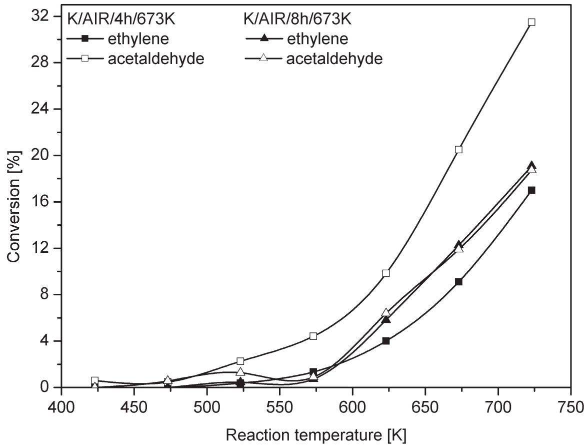

Figure 5. Conversion of ethanol for samples modified by contact with air.

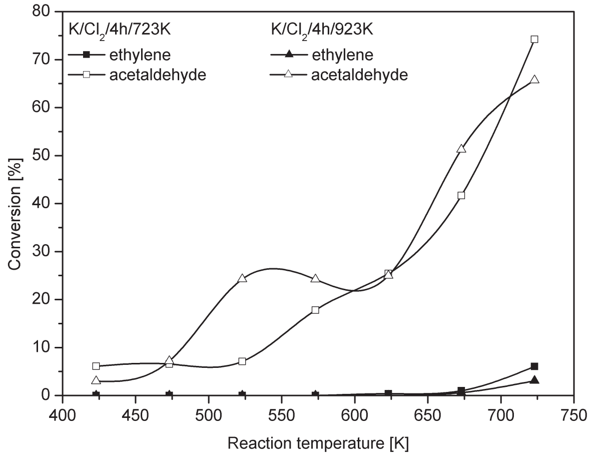

Figure 6. Conversion of ethanol for samples modified by contact with chlorine.

centres in the surface oxygen complexes, which well explains the relations noted. A clear domination of dehydrogenation over dehydration can be also noted for the samples of activated carbon modified with ammonia (Fig. 7). Moreover, these samples showed the lowest catalytic activity from among all samples studied, which is most probably a consequence of almost total absence of the oxygen groups in the structure of these carbons (Table 1). It is worth noting that for the majority of the samples studied (exceptions are those modified with nitric acid), its catalytic activity increases with increasing temperature of the process, similarly as for the decomposition of isopropanol [28].

3.3. Catalytic activity of carbons in decomposition of methanol

Decomposition of methanol over the activated carbon catalysts was much less effective than that of ethanol or earlier studied isopropanol [28], which suggests that this reaction needs stronger catalytic centres. As follows from our results, methanol decomposition takes place by its dehydration, and the only product is dimethyl ether. No other possible products of methanol decomposition (such as formaldehyde) were detected. Only a few activated carbon samples proved to be catalytically active (K/H$_2$SO$_4$/16 h/523 K, K/HNO$_3$/16 h/353 K, K/AIR/4 h/673 K, K/AIR/8 h/673 K), while the others were almost totally inert. Thus, the results indicated that only the oxidised carbon samples were active as catalysts in methanol decomposition, which is in agreement with the results reported by Zawadzki *et al*. [22]. From among the above mentioned catalytically active samples, the highest activity towards dimethyl ether formation was observed for the sample oxidised with concentrated nitric acid for 16 h (Fig. 8). The activated carbon samples oxidised with air or sulphuric acid were characterised by a much lower degree of methanol conversion to dimethyl ether. The catalytic activity of the oxidised carbon samples was also found to increase with increasing temperature. A comparison of the catalytic data (Figs. 1-8) with

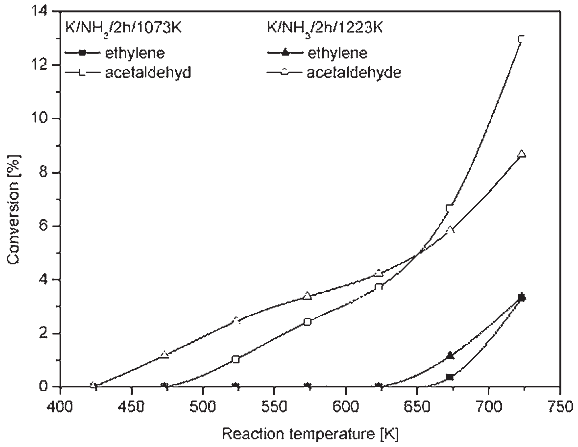

Figure 7. Conversion of ethanol for samples modified by contact with ammonia.

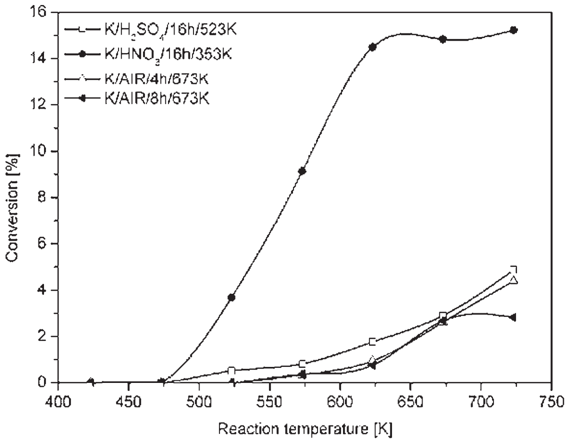

Figure 8. Conversion of methanol.

textural properties of individual samples (Table 1) leads to a conclusion that a specific surface area does not directly determine the catalytic activity of the activated carbons.

4. Conclusions

Results of the above described catalytic tests have proved that all activated carbon samples, modified with different chemical agents, catalyse the decomposition of alcohols, however, to a different degree. No correlation between the specific surface area of the activated carbons and their catalytic activity in alcohol decomposition confirmed our earlier observations. The majority of tested catalysts showed activity towards acetic aldehyde, except for the activated carbon oxidised with concentrated nitric acid which showed the highest content of oxygen in the carbon structure. This sample proved the most effective in the ethanol decomposition towards ethylene (dehydration process). On the other hand, chlorinated activated carbon was highly effective in the ethanol decomposition towards acetic aldehyde.

Only a few of the activated carbon samples were found catalytically active in the methanol decomposition; these were the activated carbon samples oxidised with nitric acid, sulphuric acid and air. The conversion of methanol to dimethyl ether was only observed over these catalysts (dehydration process), while no even trace amounts of formaldehyde – a product of dehydrogenation – were detected.

As follows from the results obtained for the decomposition of ethanol, methanol and isopropanol [28] over the activated carbon catalysts, in the same conditions of the reactions the processes of decomposition of different alcohols take place with different yields. The highest degree of conversion was obtained for isopropanol, then ethanol and next for methanol.

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