



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 acetylacetone 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 acetylacetone. 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.

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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 Brønsted 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 acetylacetone 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 acetylacetone 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 Brønsted 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 Brønsted 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 acetylacetone 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 dm³ 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% H₂O₂, concentrated HNO₃, CH₃COOOH (peroxyacetic acid, PAA, a mixture of acetic acid and hydrogen peroxide [33]) or 2.5 M (NH₄)₂S₂O₈ in 1 M H₂SO₄ (ammonium peroxydisulphate, APS) [34]. In the processes of wet oxidation the sample of 3 g of activated carbon was mixed with 90 cm³ 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 cm³ 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 N₂ amount adsorbed at a relative pressure close to unity. The approximate average pore diameter was calculated using the formula $D_{\text{av}} = 4 V_{\text{tot}}/S_{\text{BET}}$. 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 μ l. 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 acetylacetone 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 cm³ min⁻¹). After reaching a desired temperature, acetylacetone (0.5 cm³) was introduced into the reaction system by an infusion pump at the flow rate of 0.5 cm³ h⁻¹. These conditions correspond to liquid hourly space velocity (LHSV) of about 1.52 h⁻¹ (or 10.0 cm³ 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 acetylacetone 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 μ l 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

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