CATALYTIC DEHYDROCHLORINATION OF 2-CHLOROPROPANE OVER ACTIVATED CARBONS. THE EFFECT OF CHEMICAL NATURE OF SURFACE ON CATALYTIC ACTIVITY OF CARBON

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Introduction

The environment contamination with chlorinated organic pollutants is of a major ecological importance, as illustrated by recent restrictions passed by the Environmental Protection Agency [1]. The responsibility for solving this problem will rest upon chemical manufacturers and processors, making them to limit the emission of these pollutants and restore ecosystems damaged already by contamination. The present technology for disposal of chlorinated organics involves combustion at extremely high temperatures (>1000 K) in order to obtain complete oxidation of the pollutant. The large energy input and expensive materials required for thermal combustion makes it impractical for large-scale use [1]. Therefore, the development of catalytic decomposition systems utilizing less extreme conditions is of vital importance.
The purpose of this study is to examine porous carbon materials as catalysts for the catalytic decomposition of 2-chloropropane.

Experimental

Commercial granulated activated carbon D43/1, obtained from Carbo-Tech GmbH (Essen, Germany), was used. The deashed (with conc. HF and HCl) commercial activated carbon (D) was divided into three portions. The first one was annealed under vacuum (10^{-2} Pa) at 1000 K for 3 hours (DH), the second was oxidised with conc. nitric acid at 353 K for 3 hours (DO). Subsequently, the two portions (DH and DO) were annealed in a stream of gaseous ammonia for 2 hours at 1170 and 1070 K, respectively, and then cooled in this stream (DHN and DON). Afterwards, the ammonia-treated carbons were desorbed in vacuum (10^{-2} Pa) at 400 K for 3 hours. The oxidized carbon DO was stabilized by annealing in vacuum at 573 K for 2 hours (DO573). All the prepared samples were handled in ambient air. Surface characteristics from the N_2 adsorption at 77 K were determined by the DFT method. The acid-base properties of the modified carbon surface were estimated by neutralization with NaOH and HCl (both of 0.1 M). Additionally, the acidities (pHs) of carbon slurries in 0.1 M NaCl were determined. The more detailed carbon characteristics are given elsewhere [2].
The dehydrochlorination of 2-chloropropane was investigated in a fixed bed flow-type microreactor by the micropulse technique. The product analysis was performed by on-line gas-chromatography. Prior to the catalytic tests, the samples placed in the microreactor were conditioned in helium stream at 473 K for 2 hours. The catalytic tests were conducted in the temperature range of 553-673 K at every 10 degrees. When the tests at the highest temperature were performed, they were repeated by lowering the temperature at every 10 degrees.

Results and Discussion

The surface modification procedures applied to the studied deashed carbon change its surface area slightly only (Table 1). However, oxidation with conc. nitric acid leads to formation of many different acidic surface structures whereas annealing, especially in ammonia, enhances basicity of the carbons. There is correlation between the HCl uptake and the nitrogen content (Table 1). An increase in basicity after annealing in ammonia results from the formation of pyridine-like species [2].

Table 1. Physicochemical properties of carbon samples

Carbon	S_{DFT} (m^2/g)	V_{DFT}^{mic} (cm^3/g)	N Content [%]	pH	Capacity (mmole/g)	
					NaOH	HCl
D	850	0.367	-	6.8	0.37	0.30
DH	897	0.356	0.2	10.1	0.13	0.42
DHN	883	0.346	1.9	10.4	0.10	0.63
DO573	804	0.358	0.6	4.0	1.28	0.23
DON	924	0.360	2.8	10.2	0.14	0.72

The catalytic tests indicate that the commercial carbon (D) exhibits high catalytic activity in decomposition of 2-chloropropane over the investigated range of temperature

(Fig. 1). The chemical modification of this carbon leads to considerable changes in its catalytic activity. The most active are carbons heated in ammonia (DHN and DON) while the heating in vacuum (DH) and the oxidation with conc. nitric acid (DO573) diminishes the catalytic activity. The activity of the oxidized carbon is lower than that of the D carbon at temperatures below 600 K. Above 600 K the activities of both carbons are close to each other.

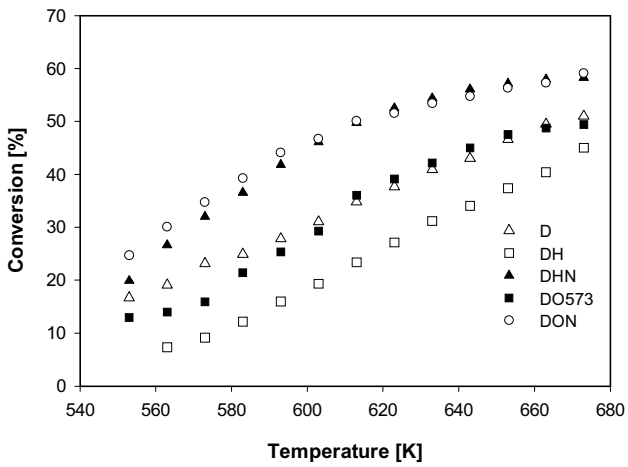

Figure 1. The catalytic activity of the modified carbons.

For all the catalysts, the observed lower conversions in catalytic tests performed in a falling temperature mode (Figs.2-3) indicate that chemisorption of the reagents plays an important role in dehydrochlorination of 2-chloropropane over the investigated carbon catalysts. This is agrees with previous findings for 2-bromopropane decomposition [3]. It was found that for small pulses of 2-bromopropane (0.5 μl), there is no substrate as well as no products in an effluent gas below 453 K. The presence of

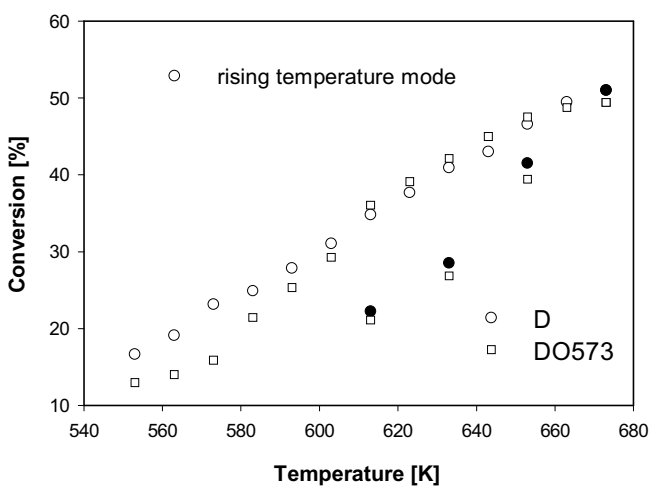

Figure 2. The effect of the temperature changes mode on the catalytic activity of the D and DO573 carbons.

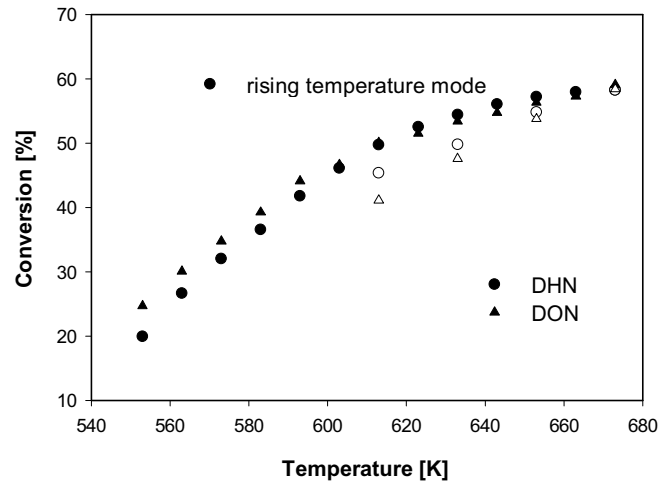

Figure 3. The effect of the temperature changes mode on the catalytic activity of the DHN and DON carbons.

propene in this range of temperatures for larger pulses indicates that chemisorption of 2-bromopropane as well as of propene occurs. Probably, the desorption of propene is the rate determining step of the reaction.

When some quantities of reactants are retained after injection into the catalyst bed, the subsequent increase in temperature may remove them. Whereas, the decreasing of temperature to the required for the next test accumulate them and as a consequence the conversion decreases. This effect is especially clear for the samples containing polar surface groups like the virgin carbon D and its oxidized form (DO573) (Fig.2). In addition, this may explain the lower activity of the DO573 carbon than that of the D carbon in the region of low reaction temperatures. The presence of many surface oxides may inhibit the reaction due to strong chemisorption of the reagents on these functional groups. When the reaction temperature is higher than the temperature of the carbon stabilization, less thermally stable, surface oxides can be destroyed. Therefore, the observed similar activity of both carbons at higher temperatures (above 573 K) results probably from decomposition of such inhibiting surface oxides. Both carbons indicate nearly the same catalytic activity at higher temperature of the reaction in the rising as well as in the falling temperature mode.

The lowest activity of the D carbon heated under vacuum (DH) indicates that annealing may deactivate the surface due to destruction of part of catalytically active sites. However, creation of new sites with high ability to strongly chemisorb some of the reactants cannot be excluded. It is known that the destruction of surface species during the heat treatment in an inert gas or in vacuum leads to the increase in concentration of the delocalized basal-plane π electrons [4]. Such delocalized π electrons act as Lewis bases that interact with protons in an aqueous solution [4]

(Table 1). The basal planes with such delocalized π electrons may also interact with the double bond of propene (the Lewis acid).
On the contrary, the heat treatment of the DH carbon as well as of the oxidized D carbon (DO) in ammonia at a high temperature leads to obtaining the catalysts with the highest catalytic activity. There is correlation between the nitrogen content and the catalytic activity (Fig.4).

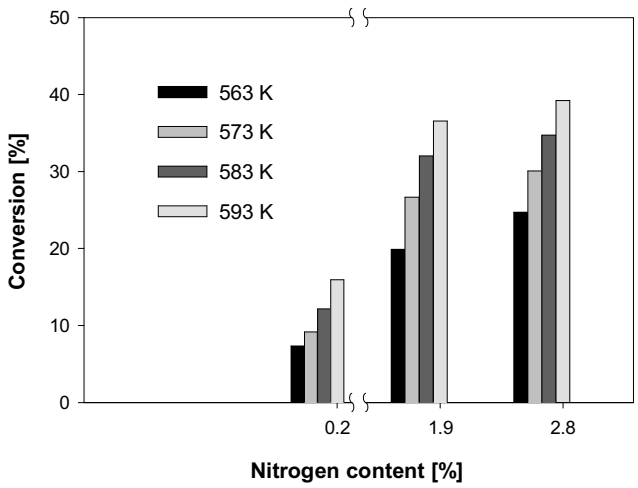

Figure 4. The effect of nitrogen content on the catalytic activity

At a high rection temperatures at which the effect of the reactant chemisorption can be neglected, a proportionality between the carbon catalytic activity and its surface basicity is observed (Table 1, Fig. 1) This relationship indicates that dehydrohalogenation of 2-chloropropane occurs with the participation of basic sites.
The highest activity of the ammonia-treated carbons results from the presence of pyridine-like species that play the role of additional basic groups [2].

References

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