

CATALYTIC DEHYDROHALOGENATION OF ALKYL HALIDES OVER ACTIVATED CARBONS. THE EFFECT OF SURFACE FUNCTIONAL GROUPS ON CARBON CATALYTIC ACTIVITY

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Introduction

The contamination of the environment with chlorinated organic pollutants is of 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-bromopropane.

Experimental

Commercial granulated activated carbon D43/1, obtained from Carbo-Tech GmbH (Essen, Germany), was used in the present investigations. The deashed (with conc. HF and HCl) commercial activated carbon (D-NM) was divided into three portions. The first one was annealed under vacuum (10^{-2} Pa) at 1000 K for 3 hours (D-HT), the second was oxidised with conc. nitric acid at 353 K for 3 hours (D-Ox). Subsequently, the two portions (D-HT, D-Ox) were annealed in a stream of gaseous ammonia for 2 hours at 1170 K and 1070 K, respectively, and then cooled in this stream (D-HT-N, D-Ox-N). Afterwards, the ammonia treated carbons were desorbed in vacuum (10^{-2} Pa) at 400 K for 3 hours. All the prepared samples were handled in ambient air. BET surface area from the N_2 adsorption at 77 K was determined. The acid-base properties of the modified carbon surface were estimated by neutralisation 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 dehydrohalogenation of 2-bromopropane was investigated in a fixed bed flow-type microreactor by micropulse technique. The product analysis was performed by on-line gas-chromatography. The catalytic tests were conducted in the temperature range of 423 -523 K.

Results and Discussion

The surface modification procedures applied to the studied deashed carbon change its surface area only slightly (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 [2].

The catalytic tests indicate that the carbons exhibit high catalytic activity in decomposition of 2-bromopropane in the investigated range of temperature (Fig. 1). The chemical modification leads to considerable changes in catalytic activity of the commercial carbon (D-NM). The most active are carbons heated in ammonia (D-HT-N, D-Ox-N) or in vacuum (D-HT), while the oxidation with conc. nitric acid diminishes the catalytic activity. The shape of the conversion curves indicates that the reaction mechanism or the number of active sites change with an increase in the reaction temperature.

The comparison of the catalytic activity at different temperatures, determined for various volumes of 2-bromopropane pulses, suggests the chemisorption of the reagents (Fig. 2). For small pulses of 2-bromopropane (0.5 μ l), there is no substrate as well as products in an effluent gas below 453 K. The presence of propene in this region of temperature for higher volumes of pulses indicates that chemisorption of 2-bromopropane as well as propene occurs. Probably, the desorption of propene is the rate determining step of the reaction.

Above 493 K, a proportionality between the carbon catalytic activity and its surface basicity is observed (Table 1, Fig. 3), for small pulses of 2-bromopropane (0.5 μ l). This relationship indicates that dehydrohalogenation of 2-bromopropane occurs with the participation of basic sites. However, the shape of the curve of catalytic activity plotted against the ratio of surface acidity to surface basicity (C_a/C_b) indicates that

Table 1. Physicochemical properties of carbon samples

Modified Carbon	S_{BET} (m^2/g)	pH	Neutralization capacity (mmole/g)	
			NaOH	HCl
D-NM	1131	6.8	0.37	0.30
D-HT	1133	10.7	0.13	0.42
D-HT-N	1178	10.4	0.10	0.63
D-Ox	1071	3.1	1.66	0.13
D-Ox-N	1153	10.2	0.14	0.72

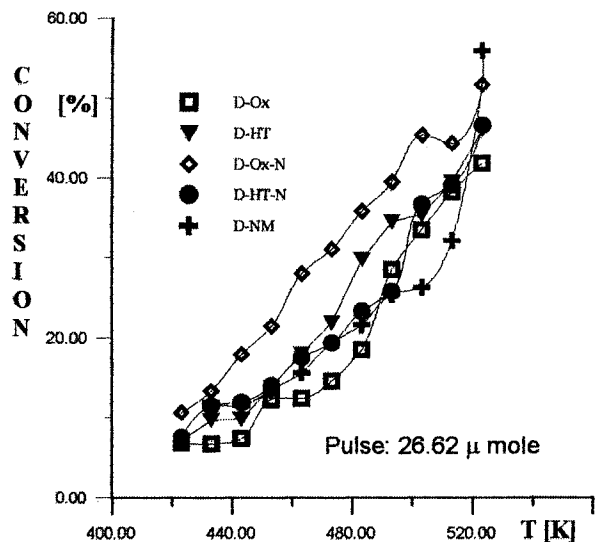


Figure 1. Catalytic activity of the investigated carbons

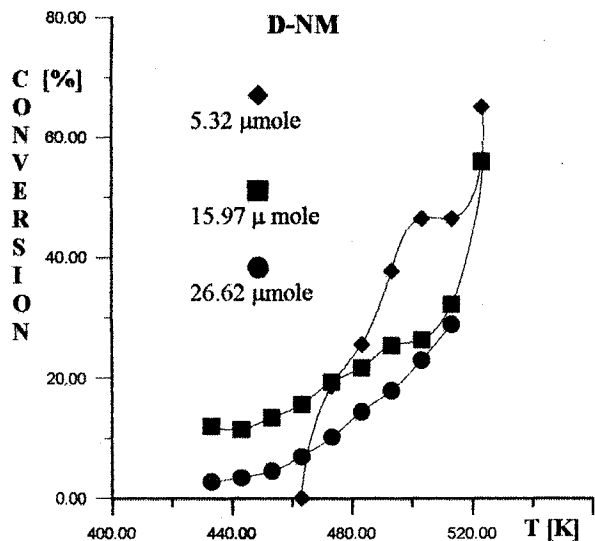


Figure 2. Effect of injected 2-bromopropane amount on the catalytic activity of the D-NM carbon

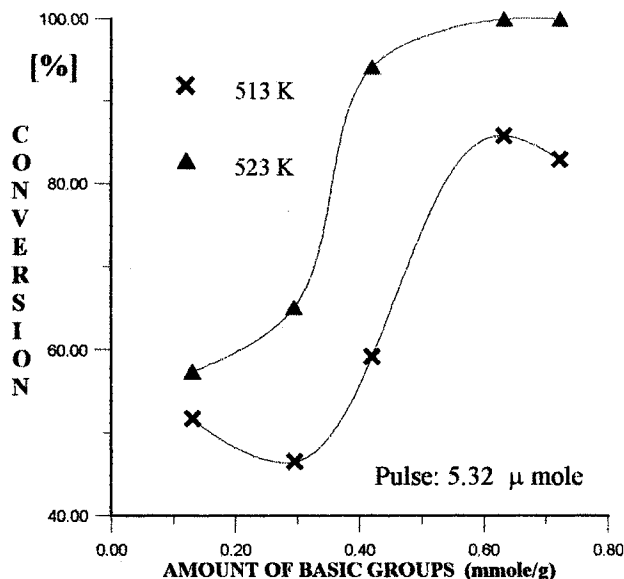


Figure 3. Effect of surface basicity on carbon catalytic activity

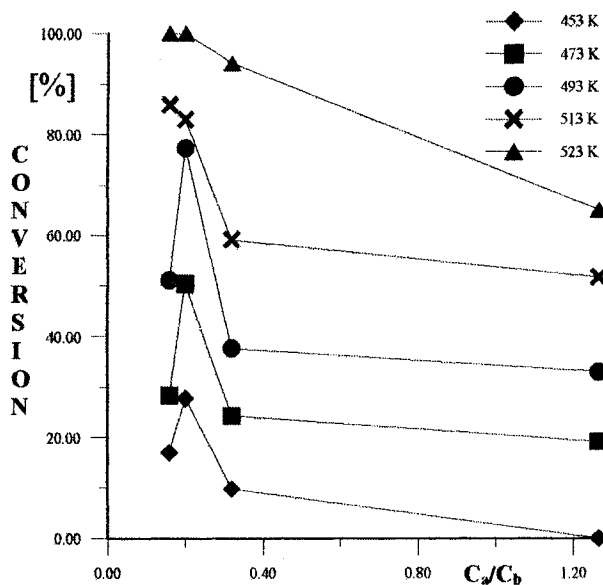


Figure 4. Effect of Ca/C_b ratio on carbon catalytic activity

acidic groups may be also involved in this process.

An increase in basity after annealing in ammonia results from the formation of pyridine-like species [2]. Thus, these groups act as additional active centers.

References

- [1] Petrosius S., Drago R., Young V. and Grunewald G. C., *J. Am. Chem. Soc.*, 1993, 115, p. 6131.
- [2] Biniak, S., Szymanski, G., Siedlewski, J. and Swiatkowski, A., *Carbon* (in press)