

CATALYTIC DEHYDROHALOGENATION OF 1,2-DICHLOROETHANE OVER ACTIVATED CARBONS. THE EFFECT OF SURFACE CHEMICAL NATURE ON CARBON CATALYTIC ACTIVITY

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Introduction

It has been reported that various activated carbons and fibres effectively catalyze the dehydrohalogenation of 1,2-dichloroethane (1,2-DCE) to vinyl chloride (VC) at relatively low temperatures. The most active are polyacrylonitrile-based active carbon fibres (PAN ACF) [1]. The active sites is believed to be nitrogen species.

In the present study, the catalytic performances of modified activated carbons were studied to clarify the correlation between their catalytic activity and surface properties.

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) activated carbon (D) was divided into several portions which were then modified in a different way. The details of modification are given in Table 1. All the prepared samples were handled in ambient air. BET surface area from the N₂ adsorption at 77 K was determined. Surface chemistry of the modified carbons was studied by FTIR spectroscopy using KBr pellet technique. Additionally, the acidities (pHs) of carbon slurries in 0.1 M. NaCl were determined. The dehydrohalogenation of 1,2-DCE 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 573 -623 K.

Results and Discussion

The modification of activated carbons slightly changes their surface area) but strongly influences their surface chemical nature (Table 1). The alkaline pH of suspension of virgin carbon (D43/1) indicates the basic character of the inorganic impurities. After deashing the carbon D possesses some acidic character. Subsequent oxidation with conc. nitric acid leads to formation of many different acidic surface structures whereas annealing, especially in ammonia, enhances basicity of the carbons.

For all FTIR spectra recorded in the 2000-700 cm⁻¹ range

(Fig.1), the presence of absorption bands of C=O (1750-1350 cm⁻¹) and C-O (1300-950 cm⁻¹) moieties can be observed. The oxidation with nitric acid increases the band at 1720 cm⁻¹ characteristic for carboxylic structures, whereas the annealing in hydrogen or in ammonia enhances the band at 800-900 cm⁻¹ typical for ring C-H deformation vibrations in polyaromatic or pyridine-like structures. This supports our previous XPS findings about formation pyridine-like structures during the ammonia treatment [2]. Thus, it seems that the incorporated pyridinic nitrogen is responsible for the observed high surface basicity (strong alkaline pH of carbon suspension).

The catalytic tests indicate that the virgin carbon (D43/1) exhibits some catalytic activity for the selective dehydrohalogenation of 1,2-DCE into vinyl chloride in the temperature range of 573-623 K (Fig. 2). The deashing of the D43/1 carbon increases its catalytic activity due to removing of basic inorganic impurities which may chemisorb hydrogen chloride. Subsequent chemical modification of the deashed carbon (D) leads to considerable changes in the catalytic activity. The most active catalytically are the carbons heated in ammonia (DN) or in hydrogen (DH), while the oxidation with conc. nitric acid (DOx) diminishes the catalytic activity (Fig.2). The amoxidation (DNO) enhances the catalytic activity only slightly. The conversion curves for the carbons heated in ammonia indicate that the most efficient and selective catalysts among them are the carbons annealed at 1023-1123 K for 3 to 6 hours. However, dehydrohalogenation of 1,2-dichloroethane over these catalysts at 613 K and above results in partial oligomerization of the formed vinyl chloride.

The observed correlation between the carbon catalytic activity and its surface basicity (pH of suspension) (Fig. 5) indicates that the dehydrohalogenation of 1,2-DCE occurs on basic sites through carboanion mechanism. It is believed that the high catalytic activity of the ammonia treated carbons results from the presence of pyridinic nitrogen.

References

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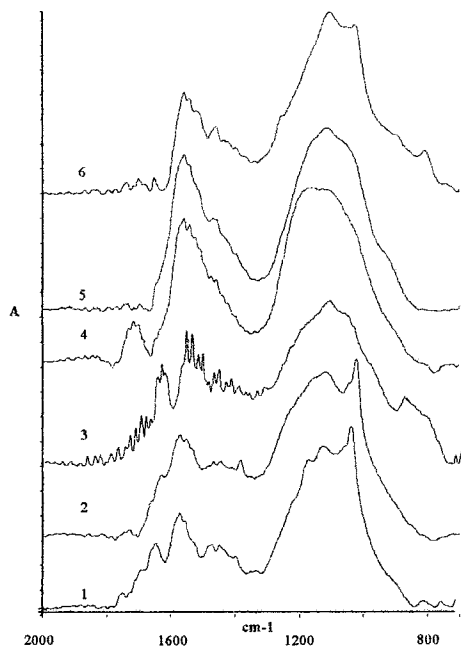


Fig. 1. Transmission FTIR spectra of the modified carbons: 1-D43/1; 2-D; 3-DH; 4-Dox; 5-DNO673; 6-DN1023.

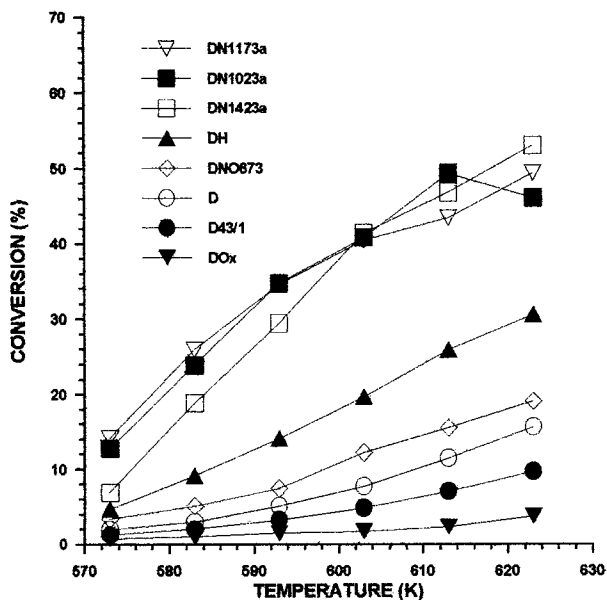


Fig. 2. Catalytic activity of the modified carbons.

Table 1. Physicochemical properties of the modified carbons

Modified Carbon	Conditions of Modification	S _{BET} (m ² /g)	pH
D43/1	Virgin	1001	9.44
D	Deashed (HCl, HF)	990	5.10
DH	H ₂ (1173 K, 3 h), He	-	10.38
Dox	HNO ₃ (353 K, 3 h), He (573 K, 3 h)	929	3.78
DN1023a	NH ₃ (1023 K, 3 h), He	980	10.57
DN1023b	NH ₃ (1023 K, 6 h), He	1006	10.57
DN1023c	NH ₃ (1023 K, 9 h), He	-	10.19
DN1173a	NH ₃ (1173 K, 3 h), He	-	10.47
DN1173b	NH ₃ (1173 K, 6 h), He	-	10.41
DN1423a	NH ₃ (1423 K, 3 h), He	-	10.89
DN1423b	NH ₃ (1423 K, 6 h), He	-	10.76
DNO673	NH ₃ +Air (2:5, 673 K, 6 h), NH ₃ (673 K, 1 h)	-	9.82

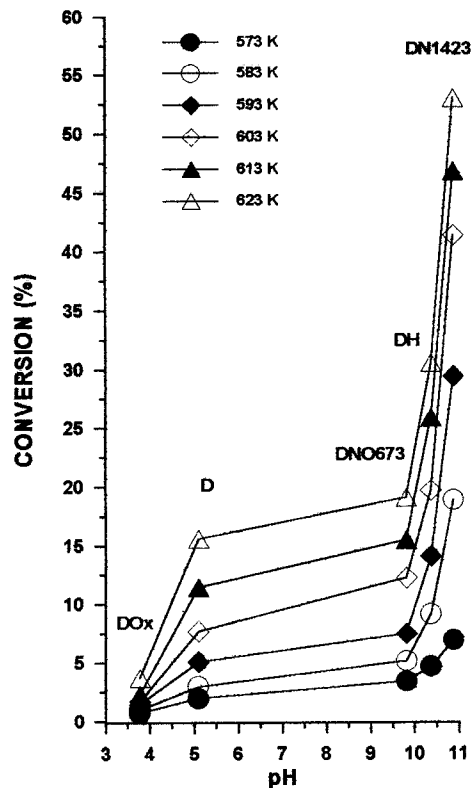


Fig. 3. Effect of surface basicity on carbon catalytic activity.