A TPD-MS study of the adsorption of ethanol/cyclohexane mixture on activated carbons

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Abstract The adsorption of ethanol/cyclohexane binary mixtures on different types of activated carbons was studied in this work by temperature programmed desorption coupled with mass spectroscopy (TPD-MS). The texture, morphology and surface chemistry of the carbons were evaluated by N2 adsorption, scanning electron microscopy (SEM) and TPD-MS techniques. The ethanol and cyclohexane TPD-MS desorption profiles showed that specific interactions between the carbon material and the adsorbate are involved during the adsorption. Most of the activated carbons adsorb strongly ethanol on the surface, leading to desorption temperatures above 100 °C. Only one carbon exhibits an affinity for cyclohexane. These observations were correlated to the different surface chemistry of the materials.

Keywords Activated carbon · Temperature programmed desorption · Ethanol · Cyclohexane

1 Introduction

Brushes and collectors made of Carbon/Carbon composites are widely used in electrical motors to ensure the electrical current to flow from a rotating part to a stationary part (Wilk and Moson 2002; Zhongliang et al. 2008). The wear of these composite materials was studied in the literature and the complex wear mechanism due to the multiples factors such as velocity, atmosphere, pressure, etc. was already underlined (Zhongliang et al. 2008). In applications such as fuel pumps in cars, these motors are in permanent contact with hydrocarbons and an unexpected wear of brushes and collectors is observed in some cases when biofuels are used. The differences between the bio-fuels and classical fuels can be of physical nature (electrical conductivity, density, viscosity, etc.) or chemical nature (presence of alcohols, esters, etc.). There are several different phenomena (electrical, tribological and chemical) (Yoichi et al. 2002; Yasar et al. 2007; Hershberger et al. 2004; McKee et al. 1972) which can play a role in the degradation of the C/C materials. Although there are works about motors working in air (Robert et al. 1995; Hu et al. 2008) the studies concerning motors immersed in organic liquids are almost inexistent (Yamamoto et al. 1995). In the aim of understanding the specific interaction between carbon materials and bio-fuels, the adsorption of oxygenated hydrocarbons (ethanol) from a pure organic mixture on carbon was performed in this work. Since the composition of the C/C composites is quite complex (different type of graphites, binders, lubricants, additives, etc.) (Xia et al. 2009), the adsorption studies were performed on activated carbons with different textural and surface chemistry properties. A model mixture of ethanol (10 % vol.) in cyclohexane was used as considered to be representative for a biofuel. The cyclohexane as organic medium was selected based on the gasoline composition (30–50% saturated hydrocarbons) (Perry and Gee 1995) and for simplicity reasons to avoid studying a complex fuel composition which contains many types of hydrocarbons and additives. Therefore, two types of phenomena should be taken into account: physical adsorption of the alcohol or cyclohexane into the carbon porosity and specific chemical interactions between the surface functional groups and the alcohol or the cyclohexane. In order to study on the specific interactions which may take place between the adsorbates and the carbon materials, temperature programmed desorption coupled with quantitative
analysis by mass spectrometry analysis (TPD-MS) can be used. This method has been successfully used to analyse surface chemistry of carbon materials (Rietsch et al. 2009), but also chemical interactions between carbon materials and organics likes proteins (Munusamy et al. 2010). Therefore, in this work, we have used TPD-MS to study the chemical interactions between carbon materials and ethanol and cyclohexane.

2 Experimental

2.1 Materials

Several types of activated carbons: CGran, CNR115 and R3 extra (Norit, Amersfoort, The Netherlands) were used for the adsorption studies. CGran and CNR115 are activated by chemical activation process with phosphoric acid while the R3 extra is a steam activated carbon. In order to study the effect of surface functional groups in the adsorption process, the CGran carbon surface was oxidised with H2O2 at room temperature (CGran-ox) or reduced under H2 at 600 °C (CGran-red).

2.2 Adsorption measurements

The adsorption of ethanol/cyclohexane mixture (10 %vol. ethanol) onto carbon samples was performed using bath equilibrium technique. The chemicals with high purity (99.8%) were purchased from Sigma-Aldrich. Prior to the adsorption measurements the samples were outgassed under vacuum at 150 °C for 24 h. Typically, 100 mg of activated carbon was placed into glass flasks (25 ml) in which 5 ml of binary liquid mixture of ethanol/cyclohexane were added. The flasks were shaken in a thermostated bath at room-temperature for 2 days with 125 rpm in order to reach the adsorption equilibrium.

2.3 Material characterizations

The textural properties of the materials were investigated with a Micromeritics ASAP 2020 instrument using N2 adsorbate at 77 K. Prior to the analyse the samples were outgassed overnight in vacuum at 300 °C. The BET surface area (S_{BET}) was calculated for the linear plot in the relative pressure range of 0.05–0.15 while the micropore volume (V_{micro}) was estimated by using the αs-plot method. The reference adsorption data employed for the αs analysis for all carbon samples correspond to a nongraphitised carbon black (Cabot BP 280) as reported in (Kruk et al. 1997).

The mesopore volume (V_{meso}) was obtained by subtracting the micropore volume from the total pore volume of N2 adsorbed at relative pressure of 0.95. The pore size distribution was determined using the DFT model on carbon slit pores.

The morphology and composition of the materials were examined by scanning electron microscopy (Philips model FEI model Quanta 400) equipped with an energy dispersive spectrometer.

To evaluate the surface chemistry of the materials and also to study the ethanol and cyclohexane desorption a home-made temperature programmed desorption set-up coupled with a mass spectrometer was used. The samples were placed in a quartz tube in a four and heat-treated with a linear heating rate in vacuum. The material surface chemistry was evaluated in the temperature range 25–950 °C, while for ethanol and cyclohexane desorption measurements were performed in the range 25–450 °C. The heating rate used was 2 °C/min. The gases evolved during the heating process were continuously analysed quantitatively by a mass spectrometer. Before experiments the mass spectrometer was calibrated using N2 (m/z = 28), H2 (m/z = 2), CO (m/z = 28), CO2 (m/z = 44), O2 (m/z = 32), C2H5OH (m/z = 31) and C6H12 (m/z = 56). The total pressure of the gas released during the heat treatment was also measured as a function of the temperature using a Bayard–Alpert gauge. The total gas pressure could then be compared to the one calculated from the sum of the partial pressure of the gas species deduced from the quantitative analysis of the gas phase. From the TPD analysis, the desorption rate of each gas as a function of temperature was determined. The total amount of each gas released was computed by time integration of the TPD curves.

3 Results and discussion

The nitrogen adsorption-desorption isotherms depicted in Fig. 1 show that they are of type I for CNR-115 and R3 extra carbons, hence characteristic of microporous materials. The hysteresis loop (P/P0 = 0.42–1) indicate the presence of mesopores and this is more evident in the case of CGran type carbons which present rather a type IV isotherm. Comparing the carbon textural properties gathered in Table 1, it can be seen that the CNR115 carbon presents the highest surface area and the largest microporous volume. It can be also remarked that the thermal and chemical treatment performed on CGran carbon do not induce significant textural changes (the change in surface area is below 7%). So, it can be assumed that the surface chemistry of these carbons was modified without significant modification of their textural properties. The pore size determined using the DFT model (Fig. 2) is comprised between 0.2 and 5 nm for CNR-115 and R3 extra while for CGran carbons is ranging between 0.5 and 20 nm.