NEW INSIGHTS ON THE ADSORPTION OF ORGANIC BINARY MIXTURES ON CARBON USING TPD AND XPS TECHNIQUES

Camelia Matei Ghimbeu[1], Roger Gadiou[1], Joseph Dentzer[1], Patrice Brender[1], Philippe Fioux[1], Christine Liétard[2], Cathie Vix-Guterl[1]

[1] Institut de Science des Matériaux de Mulhouse, CNRS LRC 7228, 15 rue Jean Starcky, 68057 Mulhouse-France
[2] AVO CARBON, 9 rue des imprimeurs, 86000 Poitiers-France

Introduction

Carbon/Carbon composites are widely used in brushes and collectors for electrical motors. In applications such as fuel pumps in cars, these motors are in permanent contact with hydrocarbons and an unexpected wear is observed in some cases when using bio-fuels. The differences between the bio-fuels and classical fuels can be of physical nature (electrical conductivity, density, etc.) or chemical nature (presence of alcohols, esters, etc.). Different phenomena (electrical, tribological and chemical) can play a role in the degradation of the C/C materials, but the literature on the evolution of carbon material properties in organic liquids is very scarce. In the aim of understanding the specific interaction between carbon materials and bio-fuels, the adsorption of oxygenated hydrocarbons (ethanol and methyl acetate) on activated carbons with modified surface chemistry was performed in this work. The total quantity of ethanol (methyl acetate) adsorbed was determined by gas chromatography (GC) using the adsorption isotherms while the chemical interaction were studied through TPD-MS and XPS analysis.

Experimental

Activated carbon CGran provided by Norit was used for the adsorption studies. In order to study the effect of carbon surface chemistry on the adsorption process, the carbon surface was oxidised with H_2O_2 (CGranox) or reduced in H_2 atmosphere (CGranred) at 600°C. The adsorption of ethanol (methyl acetate) /cyclohexane mixture onto carbon samples was performed using bath equilibrium technique. The activated carbon was placed into glass flasks with a known volume of binary liquid mixture of ethanol in cyclohexane (or methyl acetate in cyclohexane) with concentrations (0.1-15% vol.). The flasks were shaken in a thermo-stated bath at room-temperature for 2 days in order to reach the adsorption equilibrium. The ethanol (or methyl acetate) concentration at equilibrium was measured by gas chromatography while the adsorption capacity has been calculated according to the equation: $q_e = V (C_0-C_e)/m$, where: V is the volume of the solution, C_0 and C_e are the initial and the equilibrium concentration and m is the weight of absorbent. The chemical interactions between carbon and adsorbed molecules were studied by XPS and TPD-MS (temperature programmed desorption coupled with mass spectrometry). The carbon textural properties were determined by nitrogen adsorption at 77K and CO_2 adsorption at 298K.

Results and Discussion

The isotherms of the carbons (not shown) suggest that they are of type I, characteristic for microporous materials. The presence of the hysteresis loop (P/P_0 = 0.4-1) indicates the presence of mesopores. Comparing the carbon textural properties gathered in Table 1, it can be shown that the CGran and CGranox samples have very similar textural properties. For CGranred a decrease of the specific surface area can be noticed while the microporous volume is kept constant for all samples.

Table 1. Textural properties of carbon materials.

Material	S_{BET} (m^2/g)	V_{micro} N_2 (cm^3/g)	V_t (cm^3/g)	V_{meso} N_2 (cm^3/g)	V_{micro} CO_2 (cm^3/g)
CGran	1462	0.55	1.18	0.63	0.24
CGranred	1378	0.52	1.12	0.60	0.25
CGranox	1481	0.55	1.23	0.68	0.24

The surface chemistry of the materials was studies with TPD-MS and XPS and it was showed that the chemical and thermal treatments were efficient to modify the surface chemistry, i.e., to increase and decrease the surface oxygenated groups, respectively.

The total quantity of ethanol (methyl acetate) adsorbed onto the surface of the carbons from their binary mixture with cyclohexane was determined by GC. CGranox exhibits the highest ethanol (methyl acetate) adsorption capacity while the the smallest adsorption capacity is observed for CGranred sample. The carbon surface chemistry influences the adsorption capacity, i.e., the higher the amount of surface oxygenated groups the higher the adsorption capacity is. The adsorption capacity is also influenced by the type of adsorbent molecule. The adsorption capacity for ethanol is higher than for methyl acetate. This behaviour can be attributed to the adsorbent functional group (alcohol, ester) interactions with the carbon surface or due to the size of the adsorbed molecules.

To further elucidate the specific interactions of the ethanol and methyl acetate with the carbon surface, desorption studies were performed using the TPD method (Fig. 1). The desorption rate profiles, the maximum temperature of desorption and the amount of ethanol desorbed depend on the type of carbon, suggesting that the adsorption sites do not have the same interaction energy. In the case of ethanol desorption (Fig. 1a), two contributions to the overall desorption profile are observed. The first peak (between 25-100°C) can be assigned to the desorption of alkyl group and is similar with that of methyl acetate or cyclohexane desorption (Fig. 1b)

while the second peak (between 100-400°C) corresponds the oxygenated –OH group desorption. Hence, the strong chemical interaction of the alcohol group with the carbon surface in the detriment of the hydrocarbon group is highlighted. The highest quantity of ethanol desorbed is observed for CGran while for methyl acetate or cyclohexane the CGranred presents the highest adsorption capacity (Fig. 2b). The quantities of ethanol adsorbed are higher than of methyl acetate or cyclohexane.

The quantities of ethanol determined by TPD are significantly lower than those evaluated using the GC adsorption isotherms. This is related to two types of phenomena: (a) specific chemical interactions between the surface functional groups and the alcohol and (b) physical adsorption of the alcohol into the carbon porosity.

It obvious that the surface chemistry of the carbon significaly influences the adsorption process as also confirmed by XPS (not shown here).

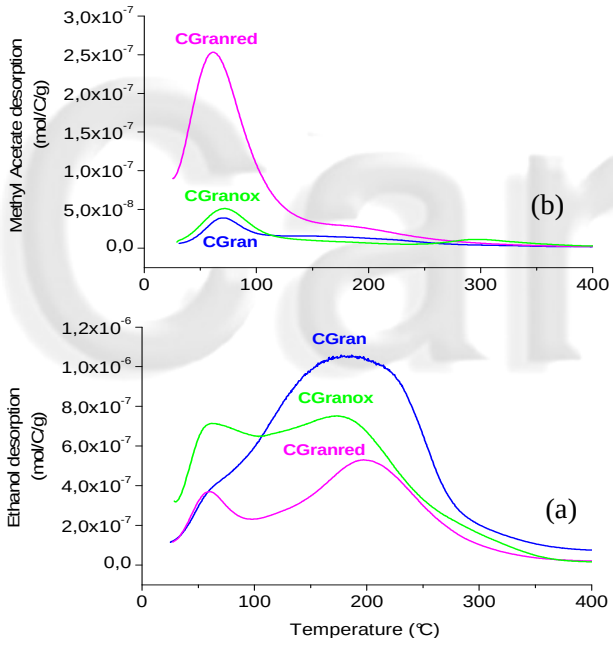

Fig. 1 TPD desorption profile of (a) ethanol and (b) methyl acetate adsorbed on carbon surface from their mixture with cyclohexane.

As it was mentioned before, the size of the molecule may play an important role in the adsorption mechanism. To get more information about this aspect the adsorption of a shorter (methanol) and longer chain (1-butanol and 2-butanol) alcohol with linear chain (1-butanol) and ramified chain (2-butanol) was performed on CGranred. We observe in Fig. 2 that the intensity of the first desorption peak is increasing with the length of the alcohol so, we can confirm the above mentioned hypothesis that this peak is related to the alkyl chain length. The ramification of the hydrocarbon chain plays also an important role, the 2-butanol which has a ramified chain being less adsorbed than 1-butanol which presents a linear chain.

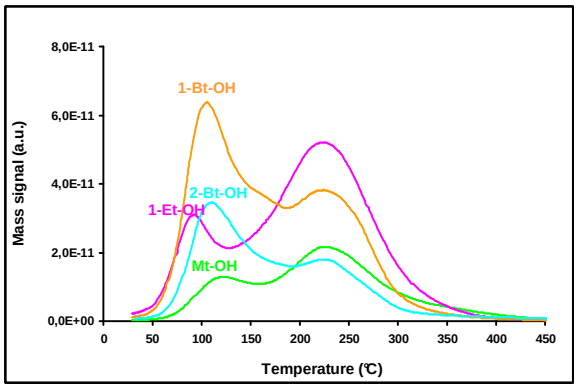

Fig. 2 TPD desorption profile for different type of alcohols (a) methanol (b) ethanol (c) 1-butanol and (b) 2-butanol adsorbed on carbon surface from their mixture with cyclohexane.

The variation of the heating rate used for TPD-MS experiments allowed to determine the activation energy of the adsorbed molecules, which is higher for ethanol than for methyl acetate and cyclohexane and depends mainly on the carbon surface chemistry (Table2).

Table 2: Activation energy determined using the highest temperature maximum of the TPD curves.

Carbon Type	Ethanol /Cyclohexane mixture		Methyl Acetate /cyclohexane mixture	
	Ea ET (kJ/mol)	Ea CH (kJ/mol)	Ea MA (kJ/mol)	Ea CH (kJ/mol)
CGran	64.1	33.1	40.9	39.6
CGranred	104.4	32.6	31.4	29.5
CGranox	52.8	35.7	25.9	26.9

Conclusions

The adsorption of organic binary mixtures onto activated carbons with modified surface chemistry was studied in this work. The gas chromatography and thermal programmed desorption measurements allowed to determine the total quantity of adsorbed molecules and the irreversible adsorbed molecules respectively. Strong interactions of ethanol with carbon surface were observed with TPD and XPS techniques. In addition, using different length chain alcohols the hydrophilic/hydrophobic interactions between carbon surface and these molecules were highlighted. The carbon surface chemistry significantly influences the adsorption process.

Acknowledgment: The French National Research Agency (ANR) is acknowledged for financial support of this project (ANR Matériaux et Procédés, MATETPRO06).