Adsorption (2011) 17: 227–233
DOI 10.1007/s10450-010-9318-y

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

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Received: 15 May 2010 / Accepted: 28 December 2010 / Published online: 13 January 2011

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 N_2 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

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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 H_2O_2 at room temperature (CGran-ox) or reduced under H_2 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 N_2 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 substracting the micropore volume from the total pore volume of N_2 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 N_2 ($m/z = 28$), H_2 ($m/z = 2$), CO ($m/z = 28$), CO_2 ($m/z = 44$), O_2 ($m/z = 32$), C_2H_5OH ($m/z = 31$) and C_6H_{12} ($m/z = 56$). 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 ($P/P_0 = 0.42$–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.

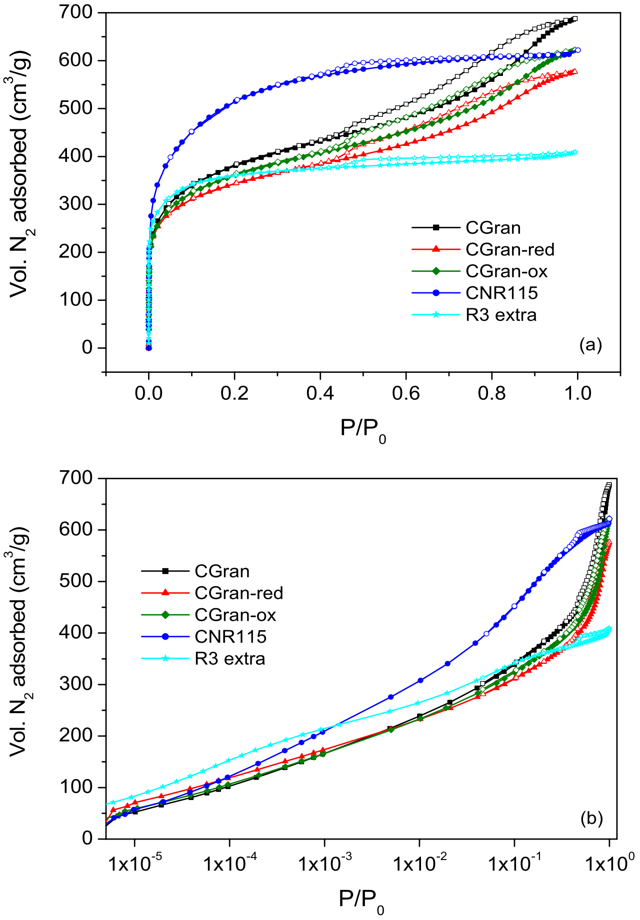

Fig. 1 Nitrogen adsorption/desorption isotherms at 77 K for CGran, CGran-red, CGran-ox, CNR-15 and R3 extra (**a**) linear and (**b**) log P/P_0 plot

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)
CGran	1378	0.37	1.03	0.66
CGran-red	1229	0.35	0.87	0.52
CGran-ox	1314	0.37	0.94	0.57
CNR115	1879	0.83	0.95	0.12
R3 extra	1282	0.54	0.62	0.08

S_{BET}—calculated in the relative pressure region $P/P_0 = 0.05$–0.15

V_{micro} N$_2$—determined using αs-plot method

V_t—total pore volume determined at $P/P_0 = 0.95$

V_{meso} N$_2$—obtained by substracting the micropore volume from the total pore volume (V_t–V_{micro} N$_2$)

The SEM pictures (Fig. 3) show a macroporous morphology for CNR115 and R3 extra while the morphology is significantly smoother for the CGran. These differences can be attributed to the different preparation process (temperature, pressure, precursors, etc.) and it should be mentioned that the CGran is a granular carbon while the other ones are extruded. At the surface of the materials small white particles (1–2 µm) are noticed which can correspond to the inorganic components like P, Ca, Mg as determined by EDX (Table 2) and which are probably due to the activation process. A first estimation of the influence of the chemical treatment performed on CGran carbon can be extracted from Table 2: the oxygen content of CGran was 10.7 %wt. before the treatment, it increases to 11.6 %wt. for CGran-ox and decreases down to 5.1 %wt. for CGran-red. Nevertheless, this global aspect should be refined to analyse the surface groups by TPD-MS.

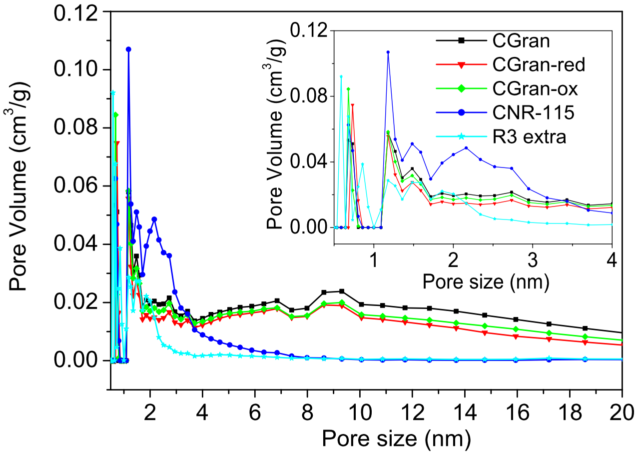

Fig. 2 DFT pore size distribution for CGran, CGran-red, CGran-ox, CNR-15 and R3 extra

In the adsorption process the carbon surface functional groups is of great importance due to their interactions with the molecules to be adsorbed. The type and the quantity of these surface oxygenated groups was determined by temperature programmed desorption. The oxygen surface groups decompose with the evolution of CO and CO_2 gases and their type and release temperature gives indication of their nature. It has been shown (Figueiredo et al. 1999) that the CO_2 arises from groups like carboxylic acids, anhydrides and lactones while the CO derives from groups like phenol, carbonyl or quinone. The desorption profiles and quantities of CO, CO_2, H_2 and H_2O are shown in Fig. 4 and Fig. 5 respectively. The H_2O profile exhibits two peaks corresponding to chemisorbed water and to dehydration reactions of neighbour hydroxyl groups. This last process leads to the formation of anhydrides and lactones which decomposes at higher temperature to CO and CO_2. The water and CO_2 profiles show that these functions are removed by the H_2 treatment on CGran-red carbon, together with the carboxyl groups. Only functions with a high thermal stability are kept on CGran-red: that are ethers or quinones which decompose to CO above 600 °C. For the oxidation process, the CGran-ox desorption profile remains unchanged suggesting no modification of the surface groups nature but only an in-

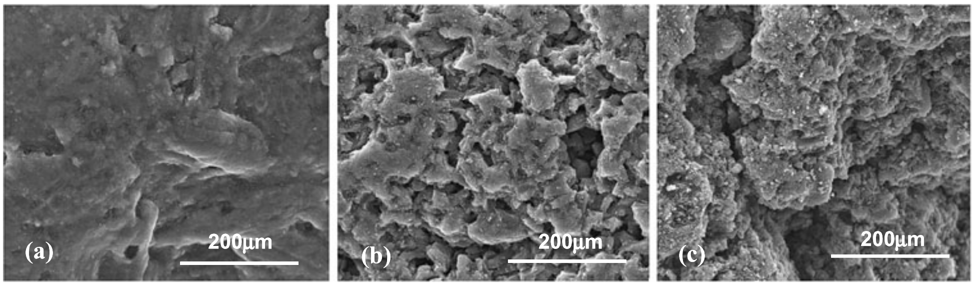

Fig. 3 SEM pictures of (**a**) CGran, (**b**) CNR115 and (**c**) R3 extra

Table 2 Carbon composition determined by EDX

wt%	CGran	CGran-red	CGran-ox	CNR-115	R3 extra
C	88.7	94.5	89	78.9	83.4
O	10.7	5.1	11.6	17.4	9.6
P	0.7	0.7	0.4	1.4	–
Ca, Mg	–	–	–	–	1.6

crease in their amount. The CNR-115 present similar desorption profiles as CGran for all gases, excepted the presence of a second well defined peak in the high temperature region on the CO_2 at CO profiles. This indicates the presence of very stable basic groups such as ethers or quinones. Contrary to these activated carbons, the R3 extra is characterized by a very low concentration of oxygenated groups on its surface, hence suggesting a hydrophobic surface. Two well defined CO_2 peaks are found before and after 600 °C, they correspond to calcium or magnesium carbonates decomposition (see the elemental analysis in Table 2) and not to surface groups.

To study the specific interactions of ethanol and cyclohexane with the surface of carbon materials, the desorption studies were performed in the range 25–450 °C using the TPD-MS method. Prior to the analysis the carbon materials were extracted from the solution and further outgassed at room temperature and 10^{-6} mbar. Consequently, the molecules which are simply physisorbed evaporate and only the strongly adsorbed molecules are kept on the surface of the material. The TPD-MS profiles of adsorbates for ethanol/cyclohexane mixtures are presented in Fig. 6. A significant amount of ethanol is released above 100 °C indicating that it was strongly adsorbed on the carbon surface. The desorption rate profile, 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. The TPD-MS analysis shows also that not only ethanol is adsorbed on the carbon surface but also cyclohexane (see Fig. 6b). For the desorption of ethanol, two contributions to the overall desorption profile are observed. The first peak between 25 and 100 °C is similar to the one of cyclohexane desorption. It can be assigned to the desorption of molecules which are adsorbed on the surface through hydrophobic interactions or trapped in the microporosity of the activated carbons. The second peak is located above 100 °C, it corresponds to stronger interactions which are specific of oxygenated molecules, that is interactions between –OH groups and surface functions like carbolylic acids. The ethanol desorption profile of CNR115 is quite different than the other carbons, with the first peak presenting a very high intensity reported to the second one. Taking into account that the surface chemistry of this carbon is very similar to that of CGran carbon, except the second CO_2 and CO peak in the high temperature region (around 800 °C), we can assumed that these supplementary oxygenated groups (ethers…) can provide supplementary site of adsorption. Hence, the strong chemical interaction of the alcohol group with the carbon surface in the detriment of the hydrocarbon group is highlighted for all carbons except R3 extra. This carbon present a strong affinity to cyclohexane, with a desorption profile (Fig. 6b) very well defined with higher temperature region and with higher amounts desorbed than the other carbons. This behaviour can be due the hydrophobic nature of this carbon as showed in Fig. 4. It should be mentioned that in the case of the carbon which have the oxygenate functional groups reduced by hydrogen thermal treatment (CGran-red), the quantity of adsorbed cyclohexane is three times higher than the pristine carbon (CGran).

Therefore, the TPD-MS results show that the adsorption of ethanol and cyclohexane depends mainly on the surface chemistry of the carbon, so on their hydrophilic/hydrophobic nature. In this case the adsorption is performed from a binary mixture of ethanol/cyclohexane and it should be take into account that these liquids are characterized by different polarity and a certain competition of the two molecules for the carbon adsorption sites can be developed during the adsorption process. In other words, one of the two components can be preferentially adsorbed on the carbon surface depending mainly on the surface chemistry of the carbon and on the fraction of each component in the mixture. Therefore it is of great interest to study also the adsorption of single components on the activated carbons. In Fig. 8 the TPD profiles of ethanol and cyclohexane desorbed from the CGran carbon surface in the case of mono-component and bi-component systems are shown. For ethanol desorption, it

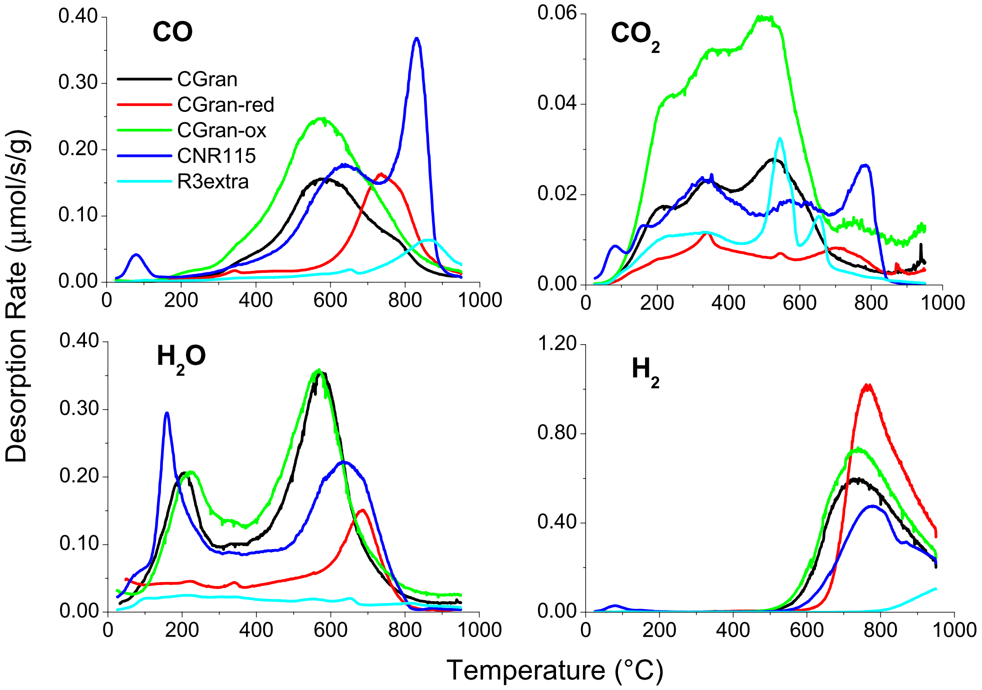

Fig. 4 TPD desorption profiles for CGran, CGran-red, CGran-ox, CNR-115 and R3 extra

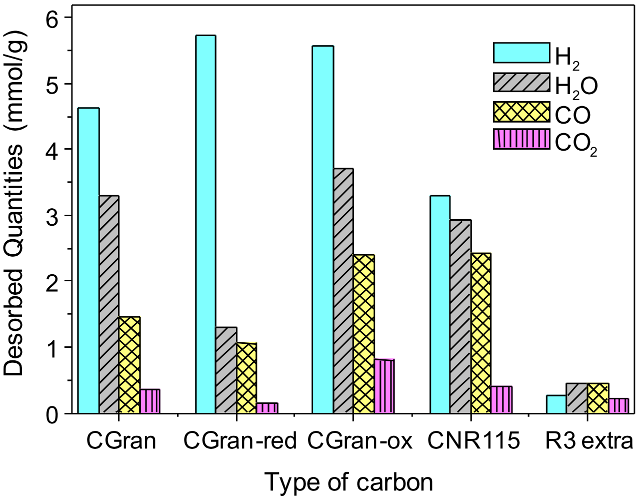

Fig. 5 Amounts of H_2, H_2O, CO and CO_2 released, obtained by integration of the carbon TPD-MS peaks

can be noticed a modification in the TPD profile, i.e., strong increase of the first desorption peak, when pure ethanol is adsorbed compared with ethanol adsorbed from binary mixture with cyclohexane. It can be assumed that in the case of binary mixture some carbon hydrophobic sites are occupied by cyclohexane and when the adsorption is made with pure ethanol these sites are available for the adsorption of the hydrophobic part of the ethanol (CH_3–CH_2–). Another possible explanation for this behaviour is that the presence of cyclohexane in the adsorbed layer could prevent the cooperative adsorption of alcohols by preventing the formation of hydrogen bond between ethanol molecules. Still some questions can arise from the fact that the quantity of desorbed cyclohexane is several times smaller than ethanol for most of the carbons except R3 extra which shows an opposite behaviour (Fig. 7), hence, the active sites occupied by cyclohexane are maybe not sufficient to explain the modification of ethanol profile. For this reason, the influence of the carbon porosity on the adsorption process should be investigated. In this case the size of the molecules compared to the pore size become important. The ethanol has a size of 0.45 nm (Furukawa et al. 2004) while cyclohexane has a size of 0.6 nm (Magalhaes et al. 1998), hence, they can be both accommodated in most of the carbon pores, except evidently the ultramicropores (<0.5 nm). Between the carbons, the R3 extra presents the smallest pores (Fig. 3) and porous volume (Table 1) and actually it desorbs the highest quantity of cyclohexane, so, there is not a direct correlation between the adsorption capacity and the pore size or molecule size. This result it is not surprising if we take into consideration that by TPD technique we studied only the chemisorbed molecules, the physisorbed ones being removed by vacuum before the analysis. Hence in conclusions, we can say that the carbon surface chemistry is the key parameter which controls the chemical adsorption of the molecules, i.e., the carbons reach in surface groups adsorb preferentially the ethanol while the carbon with poor surface chemistry adsorb preferentially the cyclohexane. This can also be sustained by the results reported by Kanyo et al. who showed using surface excess isotherms for the adsorption of ethanol/cyclohexane mixtures on carbon nanotubes that the carbon with a very hydrophilic surface adsorb preferentially ethanol from almost any ethanol/cyclohexane mixture while

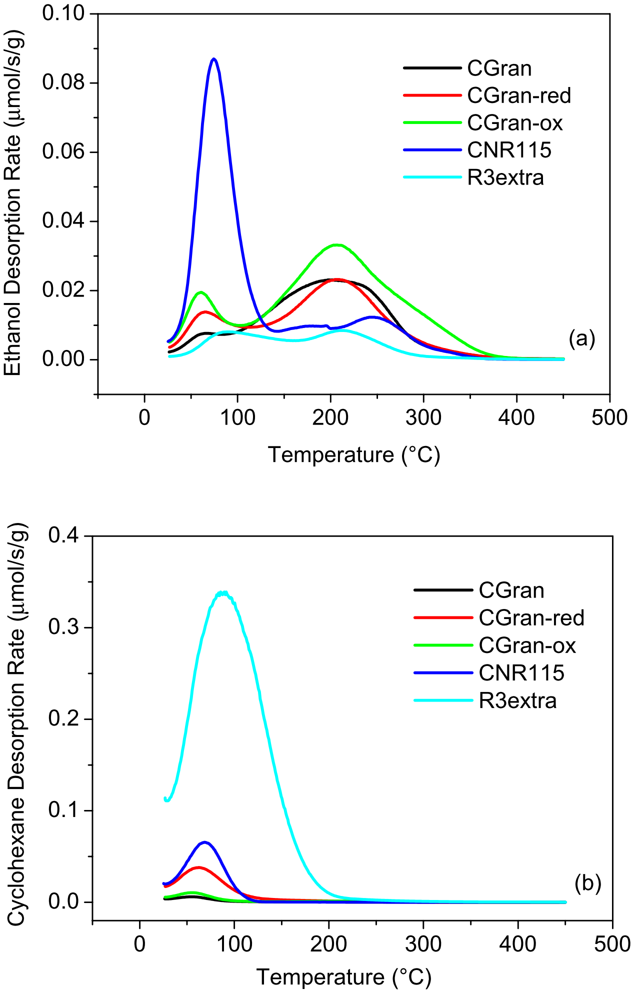

Fig. 6 TPD desorption profile of (**a**) ethanol and (**b**) cyclohexane adsorbed on carbon surface from a mixture containing 10 %vol. ethanol in cyclohexane

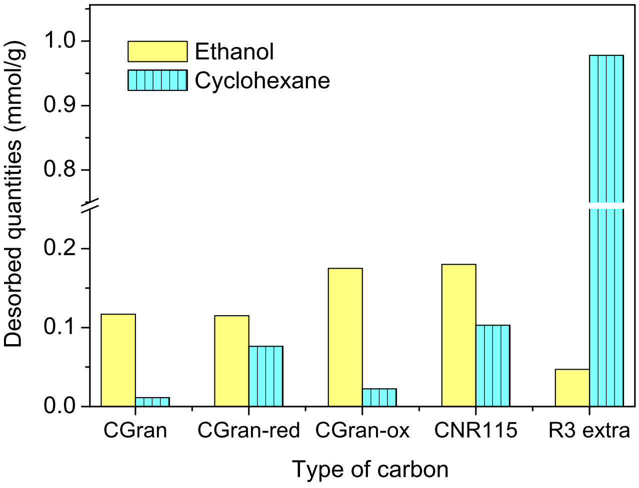

Fig. 7 Amounts of ethanol and cyclohexane released determined by the integration of the TPD area peaks

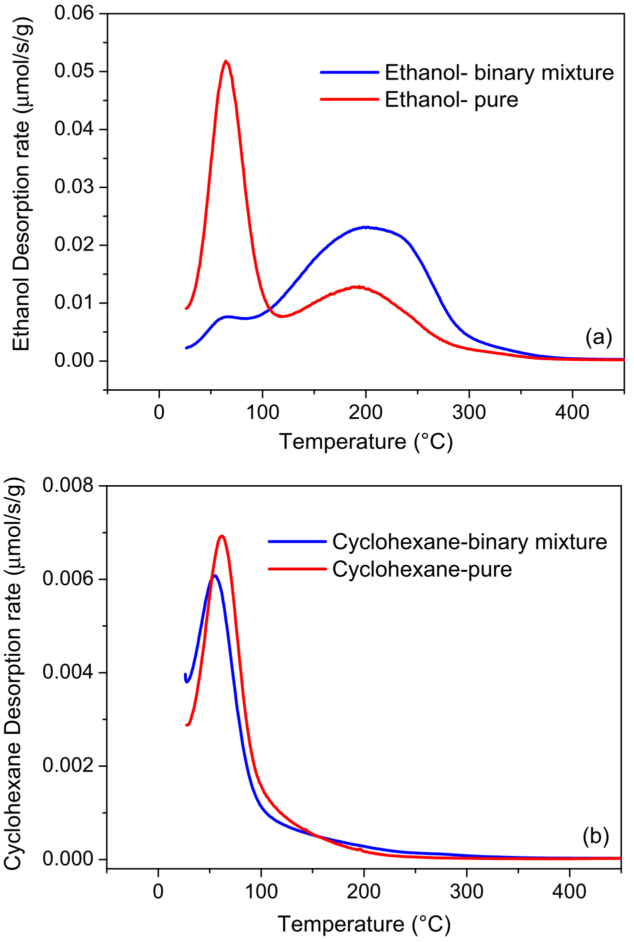

Fig. 8 TPD desorption profile of (**a**) ethanol and (**b**) cyclohexane adsorbed on carbon surface from a mixture containing 10% ethanol in cyclohexane and from pure ethanol or cyclohexane

the carbons with hydrophobic surface adsorb preferentially the cyclohexane (Kanyo et al. 2004).

Concerning the desorption of the cyclohexane from pure and binary mixtures, no significant modifications in the TPD profiles are noticed. This was expected since in the mixture with ethanol the cyclohexane has already a very high concentration (90 %vol.). The desorbed quantities of ethanol and cyclohexane in the both cases are not very different, only a slight increase of the desorbed quantities from pure components being observed. Similar experiments were conducted on the most hydrophobic carbon used in this study (R3 extra) and the same behaviour as CGran was seen.

4 Conclusion

This study shows that the Temperature Programmed Desorption with quantitative analysis by Mass Spectrometry is a powerful technique to study the interactions between carbon materials and adsorbates. In this work, it was applied to ethanol/cyclohexane mixtures on five activated carbons. A preliminary TPD-MS analysis of the carbon materials showed that they exhibit different surface chemistries. Then the influence of the presence or absence of oxygenated surface groups on the adsorption process could be demonstrated: ethanol can lead to strong interactions with carbon surface through different ways: with acid groups in hydrophilic materials, but also with thermally stable groups like ethers or quinones. Strong interactions of cyclohexane were also seen for the most hydrophobic carbon. Therefore, during adsorption from a pure organic mixture, the carbon/adsorbate interactions are therefore strongly governed by the carbon surface hydrophilic/hydrophobic character.

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

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