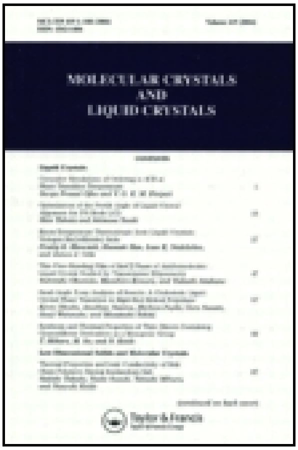

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Studies of the Surface of Fluorinated Carbon in the Aspect of its Catalytic Properties

Piotr Fiedorow [a] , Alina Krawczyk [a] , Ryszard Fiedorow [a] & Karl T. Chuang [b]

[a] Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland

[b] Department of Chemical and Materials Engineering, Edmonton, Canada

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Studies of the Surface of Fluorinated Carbon in the Aspect of its Catalytic Properties

PIOTR FIEDOROW[a], ALINA KRAWCZYK[a], RYSZARD FIEDOROW[a]
and KARL T. CHUANG[b]

[a]*Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland and*
[b]*Department of Chemical and Materials Engineering, Edmonton, Canada*

Surface properties of fluorinated carbon were characterised from the point of view of its use as a material for catalytic purposes. Samples with different fluorine content (from 10 to 65 wt.%) were tested for their catalytic activity for a number of reactions of acid-base catalysis involving residual hydroxyl groups as active centres. It was found that they were capable of catalysing only such a reaction proceeding through the formation of carbenium ion for which the presence of very weak acid centres is sufficient. The generation of only weak acidity as a result of fluorination was unexpected, therefore calculations were performed using AM1 method to explain this fact. A simple molecule used as a model of fluorinated carbon surface enabled to predict acidity of residual OH groups which was in agreement with experimental findings.

Keywords: fluorinated carbon; computational surface model; surface acidity; catalytic activity

INTRODUCTION

Although fluorinated carbon was first synthesised in 1934, only recently it found an application to catalysis. It is also used as a cathode material for lithium cells, a lubricant and modifier of filled plastics. Fluorinated carbon can be prepared from different carbon feedstocks such as active carbon obtained from various natural and synthetic starting materials, as well as from graphite, carbon black and fullerenes by subjecting them to the action of elemental fluorine. Fluorinated carbon is a highly hydrophobic substance characterised by high thermal stability and these properties make it an excellent material for support of catalysts for a number of reactions, e.g. hydrogen peroxide synthesis from hydrogen and oxygen[1], selective reduction of NO_x with hydrogen[2], airborne tritium cleanup [3], low-temperature deep oxidation of volatile organic compounds[4], isotopic hydrogen-deuterium exchange between hydrogen gas and liquid water[5-9]. Studies carried out hitherto were focused on catalytic role played by platinum group metal and hydrophobicity of fluorinated carbon support in the reactions investigated. No attention was paid, however, to the properties of catalytically active centres on the surface of fluorinated carbon itself, although their presence could affect catalyst selectivity. Our study was aimed at characterising acid properties of hydroxyl groups, small number of which remained on the surface after fluorination of carbon black as evidenced by diffuse reflectance FTIR spectroscopy.

RESULTS AND DISCUSSION

Experimental results

Three samples of fluorinated carbon of different fluorine content (10, 28 and 65 wt.% F, designated as FC 2010, FC 2028 and FC 2065, respectively) were tested for their activity in such reactions of acid-base catalysis as alcohol dehydration, hydrocarbon cracking and olefin double-bond isomerisation. Reactants used in this study were 2-propanol, cumene and 1-butene, respectively. Catalytic activity for the first of the mentioned reactions was investigated at 250°C using a pulsed microreactor connected to a gas chromatograph which made possible to analyse reaction products leaving the microreactor in the stream of helium carrier gas[10, 11]. Fluorinated carbon loading into the microreactor was 0.1 g and volume of 2-propanol injected in each pulse was 0.2 μl. The same technique of catalytic activity measurements was used in the case of hydrocarbon conversions, but reaction temperatures were 300 and 200°C when performing cumene and 1-butene reactions, respectively. Alcohol dehydration can proceed even in the presence of very weak acid centres[10] yielding olefin and water, i.e. in the case of 2-propanol dehydration - propylene and water. Data on catalytic activity in the above reaction are presented in Fig. 1 which shows that acid centres capable of catalysing alcohol dehydration are present on surfaces of FC 2010 and FC 2028 samples. In addition to them, a small number of surface sites active for the alcohol dehydrogenation to acetone were detected as well. High selectivity to propylene (about 88%) indicates, however, that the reaction pathway leading to acetone is of minor importance to overall conversion of 2-propanol.

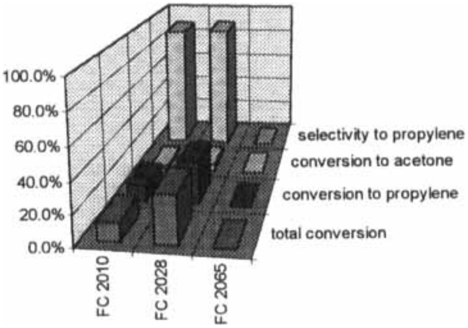


FIGURE 1 Catalytic activity and selectivity of fluorinated carbon samples in 2-propanol decomposition

The increase in the extent of fluorination to 65 wt.% results in the absence of catalytic activity in FC 2065 sample, most likely due to the substitution of all hydroxyl groups with fluorine. Somewhat unexpected is, however, the lack of parallelism between catalytic activity and fluorine content in the case of the samples FC 2010 and FC 2028. A possible explanation of this fact can be a difference in the initial concentration of OH groups in the starting material subject to fluorination.

No activity was detected for cracking of cumene to benzene and propylene, which requires the presence of strong Broensted acid centres, and for isomerisation of 1-butene, which can proceed on acid centres of moderate strength. This observation points to the absence of strong proton acidity on fluorinated carbon surfaces investigated, contrary to the effect of fluorine on oxide surfaces, such as alumina, where OH groups become stronger acid sites due to the effect of very electronegative fluorine[12]. In the case of cumene, only non-acidic pathway of its decomposition was observed on fluorinated carbon, namely its dehydrogenation to α-methylstyrene (Table 1) which proceeds according to free-radical mechanism. Possible source of the latter activity can be paramagnetic centres resulting from the rupture of carbon-carbon bonds. The presence of such centres was established in our recent ESR study of the same fluorinated carbon samples as those investigated in this work. It was found that their concentration was drastically reduced when fluorine content reached 65 wt.%, most likely due to saturation of broken C-C bonds with fluorine[13]. It is worth to add that the change in catalytic activity for cumene conversion to α-methylstyrene exactly follows that observed for unpaired electron concentration in the mentioned ESR study.

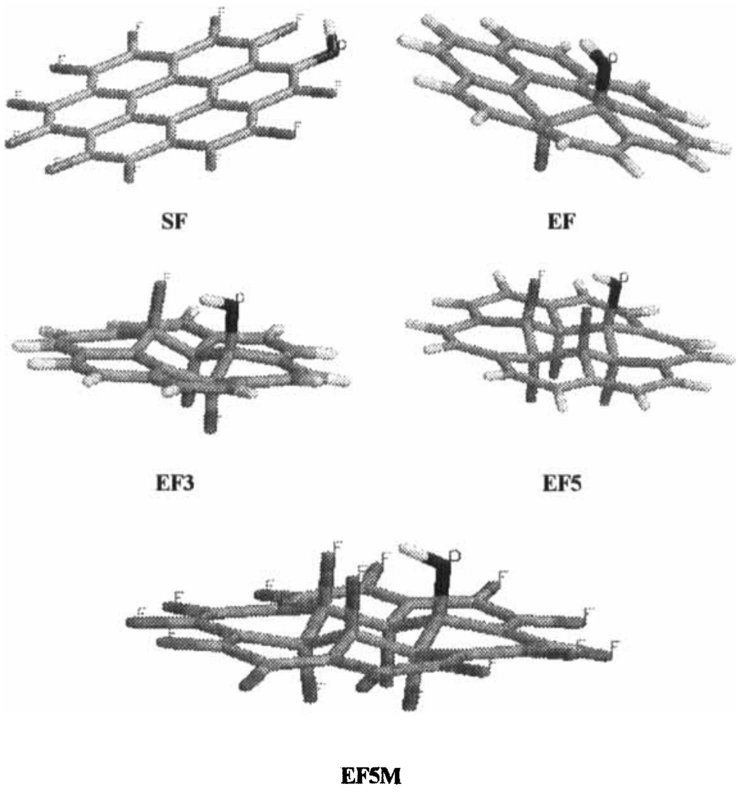
TABLE I Cumene conversion on fluorinated carbon

Catalyst	conversion to α-methylstyrene, %	
	at 350°C	at 400°C
FC 2010	24.4	32.1
FC 2028	26.1	30.8
FC 2065	0.0	0.0

Computational model

An attempt was made at applying a computational model to explain why hydroxyl groups on fluorinated carbon surface are so weak Broensted acid sites. Relatively simple molecules consisting of condensed aromatic rings, shown in Fig. 1, were used in the model applied and the effect of fluorine atom presence on the energy of proton detachment was investigated. The calculations were performed by means of MOPAC 6.0 program package using semiempirical Hamiltonian AM1. Geometries of model molecules were optimised. Proton detachment energies were determined by adding heats of anion formation to those of single proton formation and subtracting heat of formation of initial molecule from the above sum. The obtained values were compared with those calculated for a number typical Hammett indicators for which pK_a values were found in the literature[14]. The pK_a values of the model molecules were determined by means of linear regression (Fig. 3).

Model molecules can have two kinds of OH groups: rim ones (phenol-type hydroxyls - Fig. 2 SF, and its non-fluorinated analogue SH) and those formed as a



SF

EF

EF3

EF5

EF5M

FIGURE 2 Selected model molecules

TABLE II Results of calculations by AM1 method, obtained for models of fluorinated carbon surface and for Hammett indicators

Molecule	Heat of formation of molecule, kcal/mol	Heat of formation of anion, kcal/mol	Sum of heats of formation of anion and H^+, kcal/mol	Proton detachment energy, kcal/mol
SH	54.11	15.40	330.31	276.20
EH	86.46	86.41	401.32	314.86
EH3	96.28	95.13	410.04	313.76
EH5	96.50	93.98	408.89	312.40
SF	-397.48	-464.48	-149.57	247.91
EF	56.34	51.84	366.75	310.41
EF3	7.52	0.53	315.44	307.92
EF5	-53.38	-62.22	252.69	306.07
EF5M	-550.48	-594.12	-279.21	271.27
TNA	34.77	-22.51	292.40	257.63
DNA	25.47	-15.80	299.11	273.64
NA	21.61	-7.22	307.69	286.07
ClA	7.58	4.60	319.51	311.93

TNA - 2,4,6-trinitroaniline (pK_a=12.2), DNA - 2,4-dinitroaniline (pK_a=15.0), NA - 4-nitroaniline (pK_a=18.4), ClA - 4-chloroaniline (pK_a=26.5), SH (pK_a=16.2) - model molecule with OH group situated on the rim, SF (pK_a=8.9) - perfluorinated SH, EF (pK_a=25.0) - model molecule with OH group situated perpendicularly to the ring plane, EF3 (pK_a=24.4), EF5 (pK_a=23.9), EF5M (pK_a=15.0) - similar model molecules with higher number of fluorine atoms, EH (pK_a=26.2), EH3 (pK_a=25.9), EH5 (pK_a=25.6) - non-fluorinated analogues of EF, EF3, EF5.

result of the disappearance of double bonds (alcohol-type hydroxyls - Fig. 2 EF, EF3, EF5, EF5M, and their non-fluorinated analogues). It results from Table II that energy of proton detachment decreases with increasing fluorine content, i.e. in both cases the presence of fluorine atoms at neighbouring carbon atoms enhances acidity, but the enhancement is small and does not result in the formation of strong acid sites even in the case of phenol-type hydroxyl groups. The lowest pK_a value calculated for phenolic OH groups is 8.9 (Fig. 3) and weakly acidic OH groups of similar strength (pK_a of about 9-10) are present e.g. on silica surface[15]. This conclusion is in good agreement with

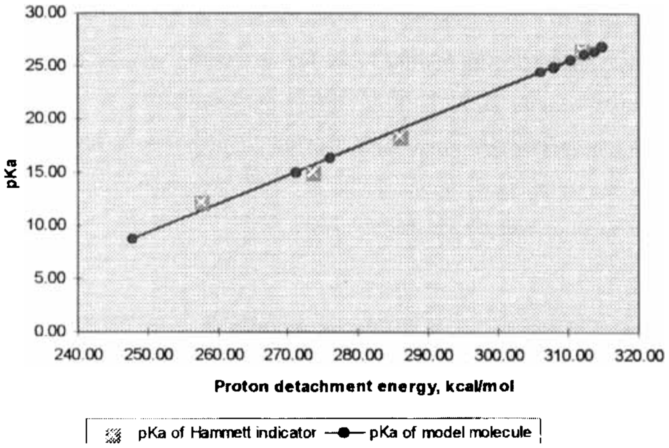


FIGURE 3 pK_a values of Hammett indicators and those calculated by linear regression for model molecules

results of catalytic activity measurements and shows that the simple model used in our study can serve for predicting some properties of fluorinated carbon in a satisfactory way.

CONCLUSIONS

- Fluorination increases acid strength of residual hydroxyl groups on carbon black surface, but the increase is insufficient to create acid centres capable of catalysing reactions proceeding on active sites of low H_0 values, such as cumene cracking or isomerisation of olefin double bond. However, weak acid sites active for alcohol dehydration are present on the surface of fluorinated carbon samples.
- Higher level of fluorination results in a rise in the acid strength of OH groups, but surface of the sample with the highest fluorine content (65

wt.%) seems to be non-acidic at all, because all of its hydroxyl groups are probably substituted with fluorine. Therefore it makes a very good material for an inert hydrophobic support for catalytic purposes.

- Calculations performed using AM1 method to determine geometry and energy of a simple model molecule can serve for predicting acid properties of fluorinated carbon in a satisfactory way.

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