Design of Novel Catalysts Based on Acridine Derivatives Immobilized on Carbon Materials for Molecular Hydrogen Production

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Abstract—Immobilization of acridine and its derivatives (9-phenylacridine and *N*-methyl-9-phenylacridinium iodide) has been studied and quantitative data on physical adsorption have been obtained. The adsorption equilibrium constants *K*, the parameters A_{∞} and ΔG_{ads} have been calculated from the Langmuir adsorption isotherms. The electrochemical properties of organic compounds immobilized on a carbon material surface have been studied by means of cyclic voltammetry.

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Despite significant progress achieved recently in the field of hydrogen energetics, practical application of the developed technologies has remained extremely limited due to low efficiency of synthetic catalysts [1, 2]. Unique properties of the carbon-based materials make them promising for hydrogen energetics [3–9]. It has been recently shown that metal-free catalysts based on carbon structures exhibit high catalytic activity towards the reaction of molecular hydrogen production [10–19]. It has been shown that electrocatalysts based on metal complexes containing polyaromatic groups can be efficiently immobilized on the surface of the working glassy-carbon electrode [19]. Heterogeneous catalysts obtained via this method are of new promising class of heterogeneous catalysts for molecular hydrogen production.

It has been shown earlier that electrocatalytic system based on acridine, 9-phenyl-*N*-phenylacridinium iodide (PhAcrI), can efficiently catalyze the process of molecular hydrogen production using aprotic solvents in the presence of chloric acid, as well as using water with different pH [20, 21]. Hence, it can be assumed that the immobilization of acridine and its derivatives (Scheme 1) on the surface of carbon materials will afford highly efficient heterogeneous catalytic systems for molecular hydrogen electrochemical production.

This report contains the data on acridine and its derivatives adsorption on carbon materials as well as electrochemical properties of the obtained systems. The main goal of this study was determination of optimal conditions for the process of organic compounds adsorption on carbon supports with the aim to obtain innovative types of catalytic materials based on organic molecules immobilized on a surface via strong physical adsorption (π - π -stacking of aromatic rings with regions of sp^2 -hybridized carbon at the surface). Carbon paper (Sigraset GD39), activated carbon (VulcanXC-72, VU), and glassy-carbon were used as carbon materials. Acridine 1, 9-phenylacridine 2, and *N*-methyl-9-phenyl-acridine 3 (Scheme 1) were chosen for the investigation of the features of organic compounds adsorption at the carbon materials.



Elucidation of the major factors affecting adsorption of model compounds should allow the control of the adsorption of more complex compounds of the same series and perform targeted modification of the surface to impart desired properties.

The presence of extended conjugated regions in the structure of compounds 1-3 makes their immobilization possible due to strong physical adsorption on the surface of carbon support via π - π -stacking. However, carbon paper and glassy-carbon were not found to be suitable for the investigation of adsorption processes. Adsorption of the test organic compounds on them did not occur even at high concentrations of adsorbate in the solution. That was the reason why further investigations were conducted using VulcanXC-72 material which showed excellent adsorption properties. The investigation of adsorption rate of compounds 1-3 in the presence of VulcanXC-72 was performed via conventional methods.

The time to attain equilibrium sorption changed in the following order: 1 > 2 > 3. Compound 1 possessed planar structure which should be ideal for the adsorption on the carbon support surface via π - π -stacking. Probably, its high sorption rate was due to the same reason, since compound 2 had a substituent at position 9, which, according to quantum-mechanical simulation, was orthogonal to the π -system of acridine scaffold. Such molecule geometry would be less favorable for immobilization on the support surface. The structure of molecule 3 was more distorted in comparison with compounds 1 and 2. In order to confirm the obtained results, we performed quantummechanical simulation to model the process of adsorption of compounds 1-3 on graphene support, the graphite-like regions were simulated using the DFT method with the B3LYP/6-31+G basis; the obtained vibrational frequencies confirmed that those structures corresponded to the energy minimums (Fig. 1). A model of graphene surface consisting of 28 conjugated cycles was used in the simulation. Free valences of the terminal carbon atoms of graphene surface were saturated with hydrogen atoms.

Weak interactions between the molecules and the surface with parallel face-to-face orientation and distance between planes of the interacting fragments close to 3 Å were found in those three cases. The obtained values coincided with the X-ray crystallography data for the systems known to exhibit π - π stacking (3 to 3.5 Å). The calculated adsorption

Fig. 1. Equilibrium states for adsorption of compounds (a) 1, (b) 2 and (c) 3 on graphene surfaces obtained via B3LIP/6-311+G(2d,p) simulation.

energies were low and close to each other [ΔE_{ads} = -2.1603 (1), -0.28 (2), and -1.30 kJ/mol (3)]. Since the energy of stacking-interaction strongly depends on the degree of overlapping, it could be assumed that the orbitals of interacting fragments were marginally overlapping. The reason for such weak interaction was a prominent difference between the energies of the boundary orbitals of graphene surface and of compounds 1-3, meaning that strong difference in energy did not lead to stabilization of a system during adsorption. As can be seen from the simulation results, planar molecule of acridine had the highest ΔE_{ads} value, the HOMO-LUMO values and the distance between interacting fragments of compound 1 and 2 being close. Hence, the orbitals of polyaromatic planar systems could overlap better than those of nonplanar ones.



Parameter	Acridine	9-Phenylacridine	9-Phenyl-10-methylacridinium iodide
A_{∞} , mol/kg	0.143	0.125	0.08
tanα	0.0014	0.0018	0.0006
K, m ³ /kmol	4995	4444	20833
$\Delta G^{\circ}_{ m ads}, { m kJ/mol}$	-21.1	-20.8	-24.6

Calculated parameters of acridine and its derivatives adsorption on carbon-containing sorbent VulcanXC-72

To investigate the adsorption process in more detail, we plotted the Langmuir isotherms were plotted and determined adsorption constant (*K*), limiting adsorption value (A_{∞}) , and free energy of adsorption process (ΔG_{ads}°) . The sorption isotherms of the investigated organic compounds on carbon-containing sorbent corresponded to Langmuir monomolecular adsorption and showed convex shape. That equilibrium could be described by Langmuir equation (1):

$$A = A_{\infty} \frac{Kc}{1 + Kc}.$$
 (1)

Here A being the adsorption value, mol/kg; A_{∞} being the limiting monomolecular adsorption (capacity of monolayer); K being the adsorption equilibrium constant, m³/kmol (ratio of adsorption and desorption rate constants characterizing the energy of adsorbateadsorbent interaction); c being concentration of adsorbate in the solution, kmol/m³.

The experimental adsorption data were processed using the Langmiur equation in linearized form (2).

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K} \cdot \frac{1}{C}$$
 (2)

The plotted dependences 1/A = f(1/C) should be linear with the intercept being the reciprocal of monolayer capacity $(1/A_{\infty})$ and the slope being $1/(A_{\infty}K)$ which gave the equilibrium adsorption constant *K*.

The experimental isotherms were transformed in the linear form, and tg α , *K* (adsorption equilibrium constant), and ΔG°_{ads} (change of Gibbs adsorption energy) were calculated using equations (3)–(5).

$$\tan \alpha = \frac{1}{A_{\infty}K} , \qquad (3)$$

$$K = \frac{1}{A_{\infty} \text{tg}\alpha} , \qquad (4)$$

$$\Delta G_{\rm ads}^{\rm o} = -RT \ln K. \tag{5}$$

The calculated sorption parameters are given in the table. As it can be seen, the A_{∞} , parameter

reflecting the process efficiency was higher for compound 1, than for compound 2, being significantly lower for compound 3. The increase in the size the molecule volume of compound 3 led to almost twofold decrease in the maximal adsorption (A_{∞}) in comparison with compound 1. The obtained data coincided with the conclusion that adsorption of compounds 1-3 was a structure-dependent process, strongly affected by the presence and the size of the substituents in acridine core. It is interesting to notice that the introduction of phenyl substituent (2) at position 9 of the parent acridine 1 led to minor decrease in parameter A_{∞} , while the introduction of methyl group at the nitrogen atom led to the decrease in parameter A_{∞} by almost 1.5 times in comparison with compound 2. Such unusual behavior could not be explained solely by steric factors. Also it is worth notice that the A_{∞} value being the lowest (for compound 3), the K value was almost 5 times higher than that for compounds 1 and 2, and the $\Delta G_{\rm ads}^{\circ}$ values for compounds 1 and 2 were therefore significantly higher. In our opinion, high value of the constant for compound 3 was related to its positive charge allowing the interaction and stabilization at the surface of carbon support bearing different functional groups (COOH, COH, OH). The presence of functional groups at the surface was confirmed by the data of IR spectroscopy for that carbon support. Its IR spectrum contained characteristic signals of carboxyl, carbonyl, and hydroxyl groups. The obtained data coincided with the reference ones [22] where the presence of organic functional groups at the surface of VulcanXC-72 was evidenced by means of X-ray photoelectron spectroscopy (XPS) analysis. Hence, compound 3 adsorbed on the surface of the support was stabilized by coulomb interaction with the surface groups and formed the surface layer partially blocking channels and pores of carbon support, thus reducing the efficiency of sorption process in terms of maximal adsorption. That assumption was in line with the significant decrease in the A_{∞} parameter for compound 3 in comparison with compound 2, their structures

being very similar. Besides that, the ΔG_{ads}° values were significantly higher than the theoretically obtained values of ΔE_{ads} . Similar values of ΔG_{ads}° were obtained in the study of adsorption of clathrate-chelate cobalt complexes containing polyaromatic groups in apical position on mesoporous carbon materials [21]. It has been suggested by the authors that the sorption process has occurred in the sorbent pores. Taking that fact in the account, we concluded that the structure-dependent adsorption of compounds 1-3, strongly affected by the structure of adsorbate (the amount and type of substituents in acridine molecule) also occurred as physical adsorption in material pores rather than π - π -stacking.

The determinative parameter affecting the adsorption of polyaromatic compounds via π - π -stacking mechanism is the compatibility of HOMO and LUMO energies of the adsorbate and surface; therefore, to make adsorption via π - π -stacking mechanism more efficient, it is necessary to control the energies of frontier orbitals of the interacting fragments, which can be achieved via chemical modification of the surface or adsorbate structure. In this study, the decrease in the energy of LUMO of the adsorbate was achieved by the introduction of electron-acceptor substituents in the structure of compound **1**, which allowed to significantly enhance ΔE_{ads} value.

Hence, one can conclude that nonpolar molecules of **1** and **2** compounds were adsorbed in the carbon support pores via physical interactions rather than via π - π -stacking mechanism. The mechanism of sorption of compound **3** was complicated and could involve physical adsorption as well as chemical one.

Electrochemical properties of the adsorbed compounds were studied via cyclic voltammetry method. CVAs of compounds 1-3 immobilized on carbon material VulcanXC-72 showed a single one-electron wave in at cathodic potentials close to those of the compounds in the solution (Fig. 2). It is important to notice that during cycling of compounds 1 and 2 between 0 to -1.8 V and compound 3 (50 cycles) between 0 to -0.8 V, the peak current of compounds 1 and 2 was not decreased, while for compound 3 the peak current was decreased. That could correspond to partial washing out to the solution of the molecules adsorbed on the surface via coulomb stabilization by surface functional groups. The constant peak current values for compounds 1 and 2 evidenced the electrode stability during electrochemical reactions and no desorption from the electrode surface. It is worth notice that the electron transfer from electrode to

100 Ι, μΑ 0 -100-200-300-0.80.0 0.2 -ĭ.0 -0.6-0.4-0.2E, V(b) 50 0 Ι, μΑ -50-100-150-200-1800-1400-1000-600-200*E*, V (c) 50 -50Ι, μΑ -150-250 -350-1.4-1.8-1.2-1.0-0.8-1.6-0.6E, V

(a)

Fig. 2. CVA curve for compounds (a) 1, (b) 2 and (c) 3 immobilized on carbon support Vulcan 72. Conditions: methylene chloride, V = 20 mV/s, Ag/AgCl/KCl.

catalytic centers at the electrode surface should be fast and not limited by the rate of electron transfer between redox sites to obtain an efficient electrocatalytic system. The linear log $I_{pvs}/log v$ dependence with the slope close to unity was found for the immobilized compounds, which is common of the systems where electron transfer from electrode surface to catalyst is

300

200

the limiting stage rather than charge transfer between redox sites. Hence, electrochemical data showed that compounds 1-3 immobilized on carbon support could be used as heterogeneous catalytic systems for molecular hydrogen production.

In summary, the process of organic heterocyclic compounds (acridine, 9-phenylacridine, and N-methyl-9-phenylacridinium iodide) adsorption of carbon material Vulcan XC-72 (VU) was comprehensively studied. The adsorption of acridine and 9-phenylacridine was a structure-dependent process affected by the presence of functional substituents in the molecule. while the mechanism of N-methyl-9-phenylacridinium iodide adsorption has complicated and partially occurred as the compound stabilization on the support surface due to the presence of functional groups. Quantum-chemical simulation showed that adsorption of the studied compounds on graphite-like regions via π - π -stacking mechanism did not take place due to energy inconsistence between frontier orbitals of the adsorbates and the adsorbent. Electrochemical characteristics of organic compounds immobilized on carbon material were elucidated by cyclic voltammetry. Further plans include the investigation of electrocatalytic properties of the obtained heterogeneous systems.

EXPERIMENTAL

Graphitized carbon black Vulcan XC 72 (Cabot Corporation) and graphite paper SigrasetGD39 (Fuel Cell Store) were used as carbon materials.

9-Phenyl-10-methylacridinium iodide (PhAcrI) was obtained via quaternization of 9-phenylacridinium with methyl iodide in a sealed test tube during 10 h as described elsewhere [19]. The compound purity according to NMR data was 99.6%. ¹H NMR spectrum (CD₃CN), δ , ppm: 8.69 d (2H, H⁴, J = 9.2 Hz), 8.42 d. d (2H, H³, J = 9.2, 6.8 Hz), 8.04 d (2H, H¹, J = 8.5 Hz), 7.88 d. d (2H, H², J = 8.5 Hz), 7.83–7.73 m (3H, *m,p*-Ph), 7.56 d (2H, *o*-Ph, J = 7.2 Hz), 4.90 s (3H, Me). ¹³C NMR spectrum (CD₃CN), δ_{C} , ppm: 161.65 (C⁹), 141.70 (C¹²), 138.74 (C³), 133.32 (*ipso*-Ph), 130.25 (*p*-Ph), 130.18 (C¹), 129.92 (*o*-Ph), 128.89 (*m*-Ph), 127.82 (C²), 126.21 (C¹¹), 118.68 (C⁴), 39.15 (Me).

Electrochemical data were obtained via cyclic voltammetry method (CVA) in acetonitrile solution [0.1 M. of background electrolyte $(n-C_4H_9)_4NBF_4$] in a 10 mL electrochemical cell using a Gamry Instruments Reference 3000 potentiostat. The modified carbon electrode was used as the working electrode

with the active surface area 0.125 cm². Scanning rate was 20 mV/s. Platinum electrode was used as the counter electrode, standard silver-chloride electrode ($E^0 = 0.41$ V in CH₃CN, vsFc/Fc⁺) was used as the reference electrode. The solutions were deaerated with argon.

CONFLICT OF INTEREST

No conflict of interest was declared by authors.

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