



Nitrogen-doped pyrene as a catalyst for fuel cells

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ABSTRACT

Density functional theory (DFT) was applied to study nitrogen-doped pyrene as an oxygen reduction reaction (ORR) cathode catalyst for fuel cells. Transition states and energy barriers were calculated to predict the catalytic properties of this substance.

Keywords: fuel cells, oxygen reduction reaction, DFT

1. INTRODUCTION

A fuel cell is a device that converts chemical energy from a fuel into electricity through a chemical reaction. Fuel cells are different from electrochemical cells in that they require a continuous source of fuel and pure oxygen or oxygen from air to sustain the chemical reaction, whereas in an electrochemical cell the chemicals placed beforehand react with each other to generate an electromotive force [1]. Fuel cells have many advantages: high conversion efficiency, high power density, quiet operation and no pollution [2].

In fuel cells, the most common fuel is hydrogen, which must be supplied to the anode; oxygen is the oxidant supplied to the cathode. There is a membrane between the electrodes. The membrane is semi-permeable, which means it passes only protons. At the anode hydrogen is broken into protons and electrons. The membrane is impermeable to electrons; they flow to the cathode via the external conductor, thus generating electricity. The protons, electrons and oxygen molecules combine at the cathode to give water and heat [3]. This step

is slow and requires a catalyst. For many years, platinum and its alloys were the most efficient catalysts. Platinum is both highly selective and active but, on the other hand, it is expensive, easily undergoes inactivation (e.g. by CO₂) and its catalytic properties relatively quickly deteriorate [4].

Therefore, the search for new metal-free [5] catalysts of high activity and practical durability has received a great deal of interest. These include honeycomb systems (such as graphene), often contain a heteroatom in their structure [6] and can be obtained via chemical vapour deposition [7]. In this work we have carried out a computational study of a catalyst based on pyrene, wherein one carbon atom is replaced with nitrogen – see Figure 1.

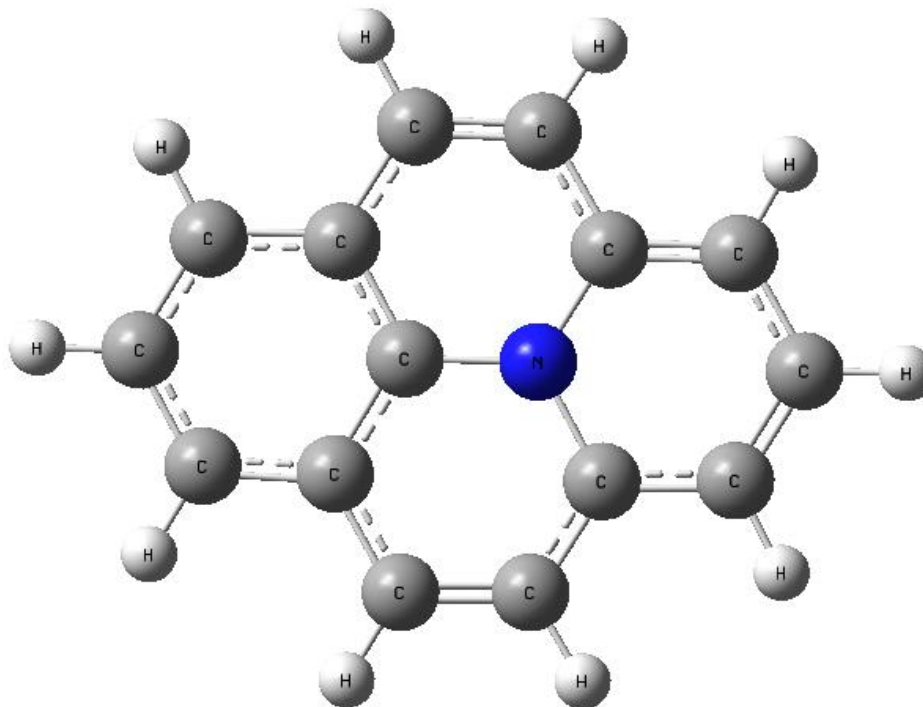


Figure 1. The studied catalyst

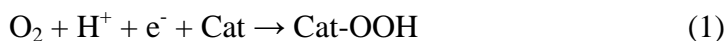
2. RESULT

2. 1. Computational details

Geometry optimization was performed by means of the density functional theory (DFT) methods [8], utilizing the Becke's three-parameter functional [9] with the Vosko et al. local correlation part [10] and the Lee et al. nonlocal part [11] (B3LYP). The standard cc-pVDZ basis set [12] was applied. The calculations were performed using the Gaussian 09 program [13]. The pictures were prepared with the Gaussview 5 visualizer [14].

2. 2. Determination of the reaction site

The ORR begins with the following one step, where *Cat* denotes a catalyst:



The number of possible reaction sites involving a catalyst is determined by its structure and symmetry elements; thus for the catalyst depicted in Figure 1, the reaction (1) can take place at ten different atoms (see Figure 2).

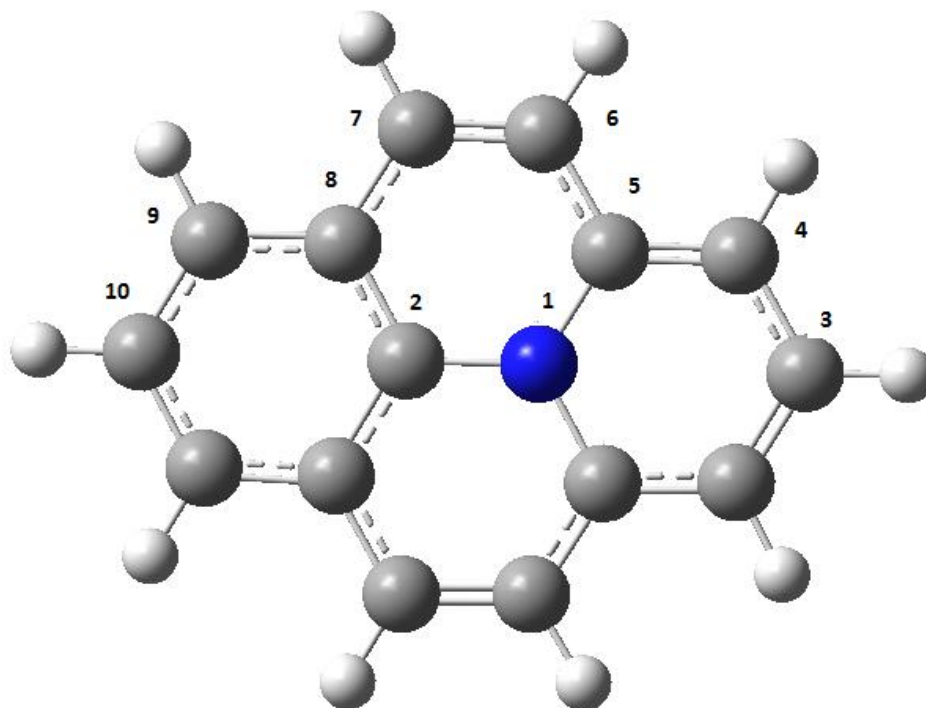


Figure 2. Ten possible reaction sites

The relative stabilities of the possible products are presented in Table 1.

Table 1. Energy and relative stability of the reaction (1) products.

Reaction site	Energy (kcal/mol)	E _{rel} (kcal/mol)
1	---	---
2	-491548,4	9,1
3	-491551,9	5,6
4	-491552,3	5,2
5	-491555,8	1,7
6	-491543,5	14,0
7	-491557,5	0,0

8	-491532,0	25,5
9	-491549,2	8,3
10	-491536,7	20,8

In this table no value is shown for a system where the connection takes place on a heteroatom. It is associated with filling orbitals: nitrogen does not have a free orbitals, which could be filled to create a bond with OOH. The most stable product forms at the carbon atom No. 7, therefore we will focus on it in our further calculations.

2. 3. ORR mechanism

The overall ORR reaction can follow according to two distinct pathways. The first mechanism involves a two-electron transfer according to the following reaction equation:



The proton and electron react with the Cat-OOH molecule produced in reaction (2), yielding hydrogen peroxide and the restored catalyst (see the energy diagram shown in Figure 3):

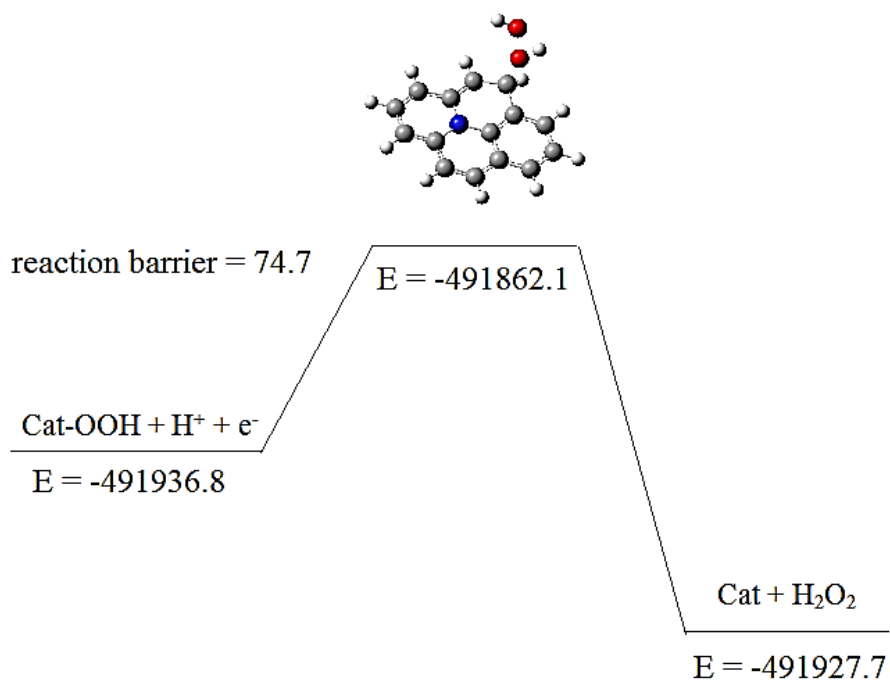
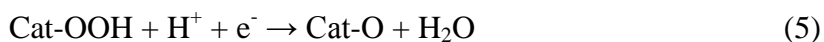


Figure 3. Calculated energy diagram of reaction (3)

The second ORR mechanism is a four-electron transfer pathway according to the following reaction equation:



The catalyzed reaction is a multi-stage process. After reaction (2), water molecule is generated (see the energy diagram shown in Figure 4):



Another proton and electron react with the oxygen atom adsorbed on a catalyst, forming the Cat-OH species (see the energy diagram shown in Figure 5):



During the last step, a second water molecule is being produced and the catalyst is finally restored (see the energy diagram shown in Figure 6):

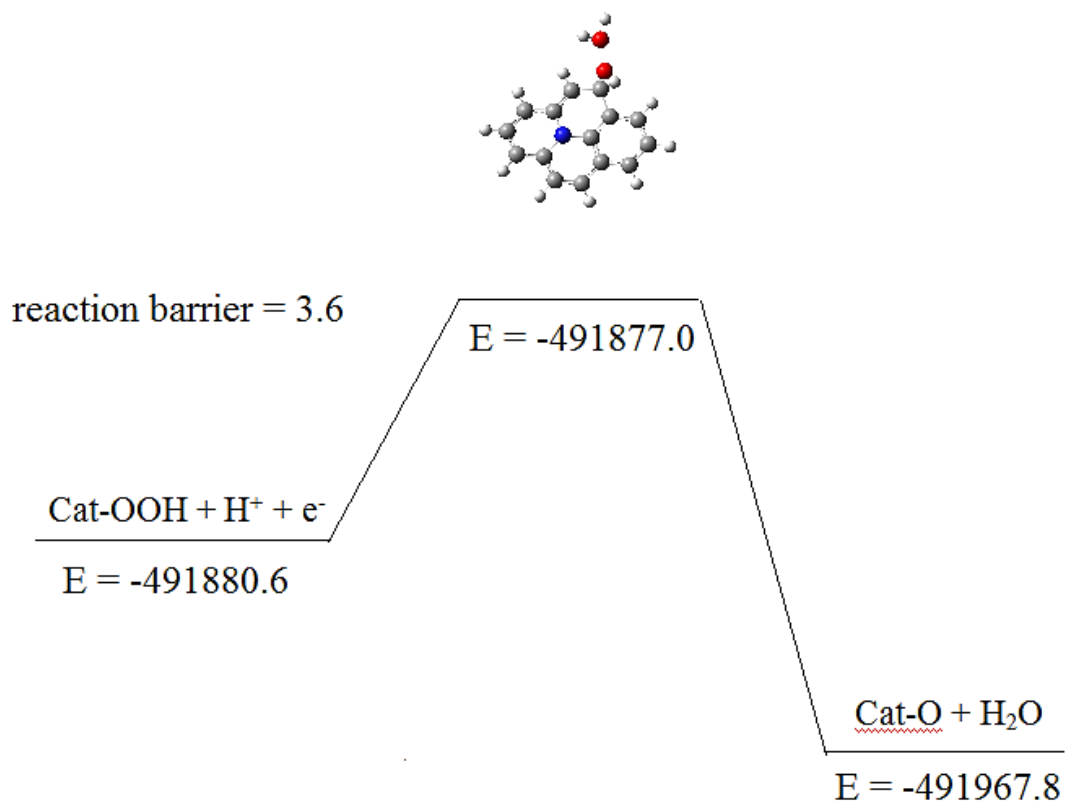
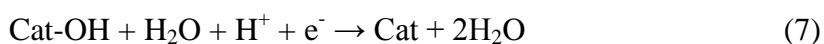


Figure 4. Calculated energy diagram of reaction (5)

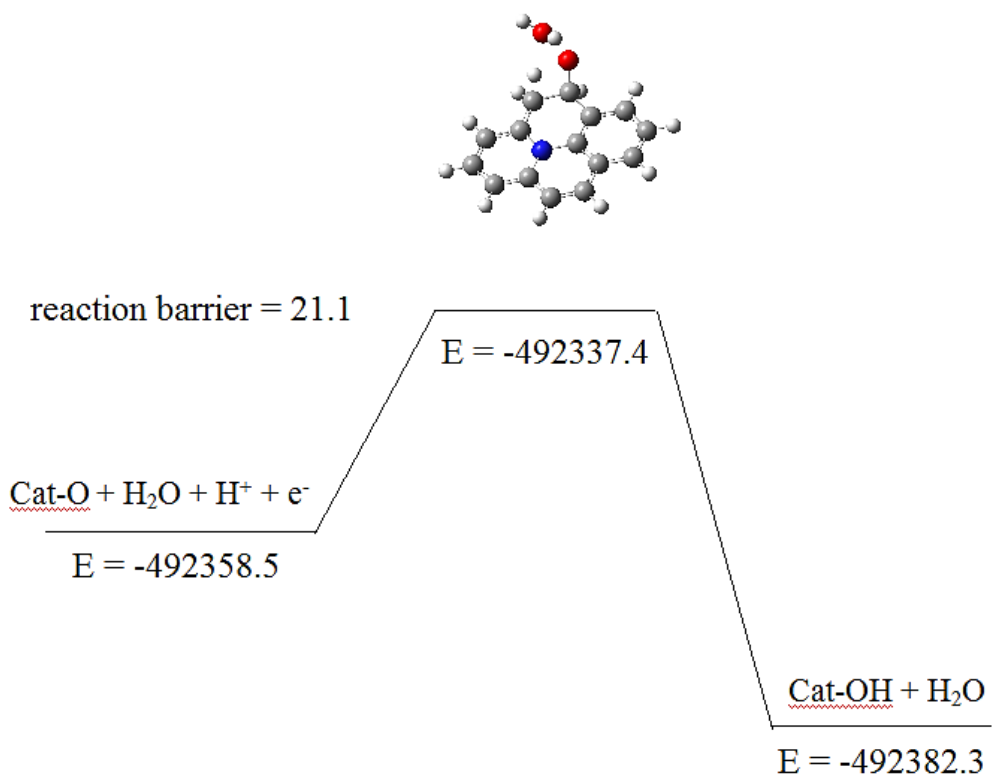


Figure 5. Calculated energy diagram of reaction (6)

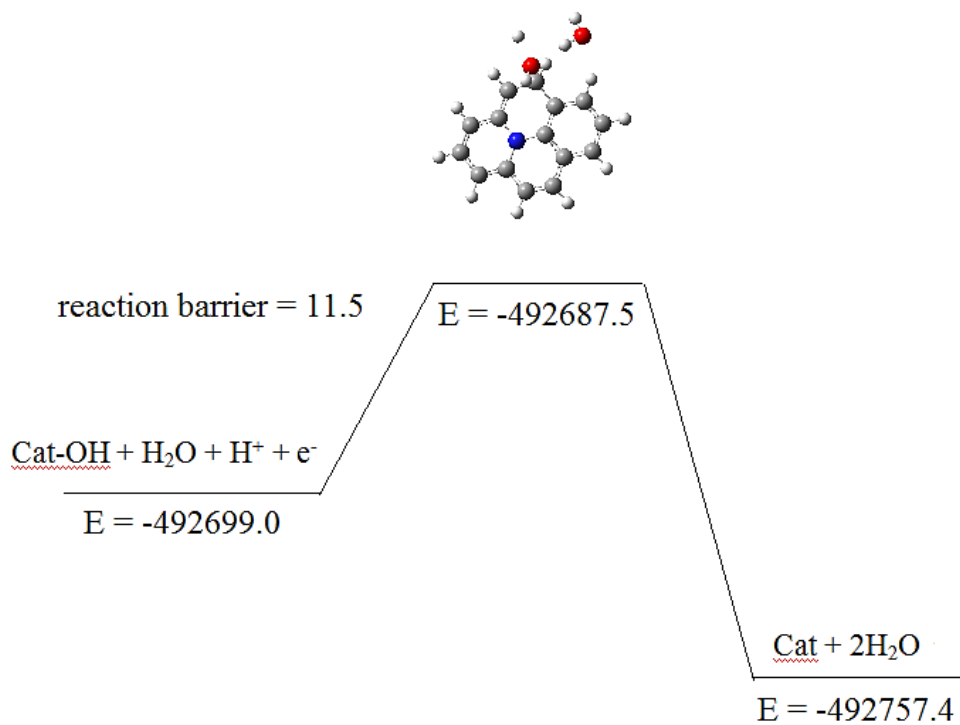


Figure 6. Calculated energy diagram of reaction (7)

3. SUMMARY AND CONCLUSIONS

Studies have shown that the four-electron transfer pathway has lower energy barriers than the two-electron pathway [15]. This is also the case in our present work – see Table 2. Therefore a way to search for a new efficient catalytic system is to determine whether it facilitates the four-electron pathway.

Table 2. Reaction barriers within two ORR mechanisms.

Mechanism	Reaction No.	Reaction barrier (kcal/mol)
Two-electron transfer pathway	(3)	74.7
Four-electron transfer pathway	(5)	3.6
	(6)	21.1
	(7)	11.5

Acknowledgement

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