Int. J. Bio-Inorg. Hybr. Nanomater., 4(3): 161-167, Autumn 2015

Theoretical study of reduced benzopyran to CO_2 by rTiO$_2$-NP

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Received: 17 June 2015; Accepted: 20 August 2015

ABSTRACT: In this study, catalyst of rutile titanium dioxide nanoparticles (rTiO$_2$-NP) has been investigated for the removal and reduction of unburned hydrocarbons as benzopyran. To evaluate and calculate the thermodynamic properties of this aim, pollutants are closed to the nanoparticles and converted them into other products and the carbon dioxide molecules are simulated in the 12th steps. The geometrical structure of all stages is optimized by Density Functional Theory (DFT) method based on B3LYP/6-31G. The structure of rutile titanium dioxide nanoparticles, there are several different locations on it as the cross bridge Ti-O and Ti-Ti, the thermodynamic properties of these conversions and locations are calculated by a semi empirical method (ZINDO/S). The results shown these interactions are exothermic and spontaneous. The total energy (kcal/mol) for conversion benzopyran on Ti-O bond is lower than Ti-Ti bond. Therefore the probability of interaction with Ti-O is more. This phenomenon dramatically increases the electrical conductivity of the nano-particles, suggesting that the rTiO$_2$-NP may be potential sensor for benzopyran gaseous molecule detection.

Keywords: *Benzopyran; Density Functional Theory (DFT); Empirical method (ZINDO/S); Rutile titanium dioxide nanoparticles; Unburned hydrocarbons*

INTRODUCTION

The unburned hydrocarbons are toxic and carcinogenic to humans and can react with components of air (NO_x, O_2 and H_2O) and can create ozone in these reactions with presence of sunlight in the troposphere (Chmielarz, *et al.*, 2011, Kwon and Min 2010 and Bhandarkar 2013). Ways and methods have been developed to eliminate and reduce them; the catalyst is neutralized to 90% of toxic gases and unburned hydrocarbons emitted from the engine to convert carbon dioxide and water (farayedhi 2002 and Kirkpatrick, *et al.*, 2011).

Gasoline consumption in Iran has a high percentage of unburned hydrocarbons, which have caused the pollution of the air and the environment (Shamekhi, *et al*., 2008). The use of a catalytic converter to reduce pollutants at source shall be considered an essential requirement.

In this study, reduced of benzopyran (is an unburned hydrocarbon) by rTiO$_2$-NP is simulated and calculated. The rTiO$_2$-NP size range between clusters and colloids, powders and single crystals of large are an ideal photo catalyst. The nano scale titanium dioxide is one of the most widely used industrial materials in the production of cosmetics, laboratory photosynthesis, refining of water and air, is a synthesis of pigments and so on (Diebold 2003, Leavy, *et al*., 2006 and Xia, *et al*.,

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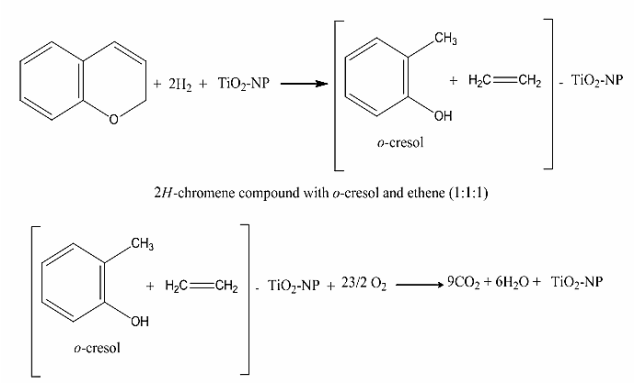

Scheme 1: Oxidation of benzopyran into carbon dioxide and water

2007). Titanium dioxide (titania) can be appeared in three crystalline form, rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic) and so on (Dhage and Ravi 2004, Torres, *et al.,* 2007, Jones, *et al*., 2007 and Yang and Parr 1988). The structure of the rutile is the most common form of titania, that system is the most resistant phase thermodynamically.

COMPUTATIONAL METHODS

Chemical computations involving different mathematical methods are divided into two groups: 1- Molecular mechanics, 2- Quantum mechanics.

In this research, the simulation of nano-surfaces reaction of titanium dioxide and benzopyran are done Gauss View 5.0 software and its geometrical shape and structure is improved by GAMESS-US program package (Becke 1993, Caricato, *et al*., 2006 and Ridley and Zerner 1973), and changing benzopyran into less dangerous products on the connection of different *r*TiO_2 nanoparticles in different states is studied and calculated. Fig. 1 shows the ball and stick model of a rutile TiO_2-NP, shown all probability of the pollutants approaching. In this research, the pollutants approaching to Ti-O connection, the first and second probability (there are two connections for Ti-O) and Ti-Ti connection, the third probability (Fig. 1) were calculated and studied. After all geometrical structures are optimized by B3LYP/6-31G. Their thermodynamic properties were assessed by the ZINDO/S in semi-empirical method. ZINDO/S method is extensively used to compute heat formation, geometric form of the molecule, ionization energy, electron adherence, and other features (Zerner 1991).

RESULTS AND DISCUSSION

In this study, the interaction of benzopyran on *r*TiO_2 nanoparticles have been simulated in twelve steps (Fig. 2), from 1st until 2nd steps entry benzopyran on *r*TiO_2-NPs then in 3th and 4th steps are transition state conversion of them to o-cresol and ethylene and in 5th step, product generated from the surface is removed. In 6th step, o-cresol is closed on surface and from 8th step is transiting state conversion of them to propanol and butane in 9th steps. Then new produces are adsorbed on the surface and 10th step is its transition state. The conversion was completed in 11th step and CO_2 molecules are produced, then it is excretion from *r*TiO_2-NPs in 12th step. The electronic structure and the thermodynamic properties are calculated for all steps by ZINDO/S-DFT.

ZINDO/S has been widely used to calculate the heat of formation, molecular geometry, dipole moment,

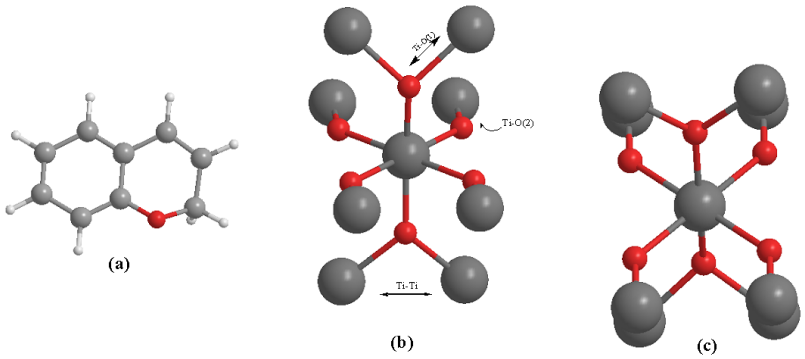

Fig. 1: The ball and stick model of a) benzopyran and rutile TiO_2-NP, b) front view and c) top view.

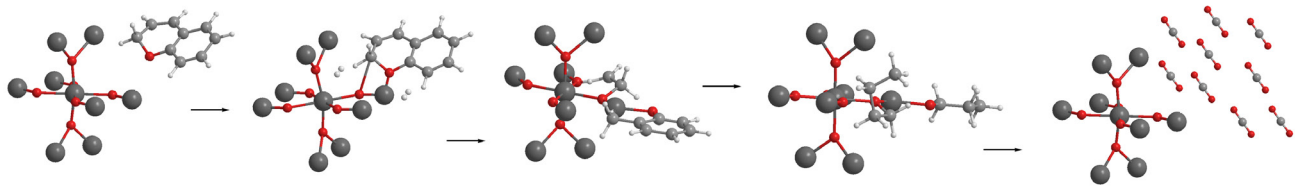

Fig. 2: Ball-and-stick models configuration of benzopyran interaction on cross bridge of Ti-O in rutile TiO_2 nanoparticle.

Table 1: The thermodynamic properties of adsorption benzopyran on Ti-O (1) bridge cross of $rTiO_2$ nanoparticle and converted to CO_2 at 298K (ZINDO/s)

The benzopyran converted to CO_2 on Ti-O(1)								
Steps	E_{total} (kcal/mol)	Dipol Moment (D)	RMS kcal/mol.°A	E_{bin} (kcal/mol)	H (kcal/mol)	G_{ele} (kcal /mol)	E_{nuc} (kcal/mol)	E_{elec} (V)
$rTiO_2$-NP	-67934.53	3.81	415.1	-12183.09	-10815.04	-237906.98	169972.45	10354.50
Benzopyran	-42736.33	2.00	190.8	-7866.31	-5851.92	-153227.46	110491.13	6668.97
Steps	ΔE_{total} (kcal/mol)	Dipol Moment (D)	RMS kcal/mol.°A	ΔE_{bin} (kcal/mol)	ΔH (kcal/mol)	ΔG_{ele} (kcal/mol)	ΔE_{nuc} (kcal/mol)	ΔE_{elec} (V)
1	-1730.78	4.43	311.5	-1730.79	-1730.79	-154822.85	153092.07	6738.40
2	-2694.03	10.21	313.4	-2694.04	-2694.03	-183210.49	180516.47	7973.93
3	-3189.59	28.99	321.5	-3189.59	-3189.60	-190346.32	187156.74	4142.25
4	-3292.95	5.64	323.5	-3292.96	-3292.97	-190010.41	186717.46	4134.94
5	-4179.13	20.01	319.8	-3576.79	-3472.59	-202479.79	198300.65	8812.59
6	-3664.55	6.69	306.0	-2459.85	-2251.45	-167947.62	164283.07	3654.82
7	9844.98	9.69	335.3	768.95	152.08	-63225.54	73070.51	1375.89
8	9803.6	11.16	333.2	727.57	110.70	-64163.04	73956.64	2792.59
9	8255.61	17.31	336.6	-820.41	-1437.28	-90893.11	99148.72	3955.97
10	5507.25	20.45	323.7	-2364.06	-2772.53	-123820.35	129327.61	5389.07
11	5626.31	12.20	321.8	-1642.65	-1946.91	-117004.07	122630.09	5092.41
12	-70462.81	5.03	460.0	-3910.02	-4184.36	-511283.58	440820.77	22252.76

ionization energy, electron affinity, and other properties. The corresponding calculated thermodynamic data (ΔE_{total}, ΔH_{ele}, ΔS_{ele}, and ΔG_{ele}) were determined. After simulation and writing files, for the perform of calculation, their Z- matrix files, send on the site: High performance computing research center (http://hpcrc.aut.ac.ir) by using special software file (Open VPN, VNC Viewer and …). This institute has computers 48 cores and GAMESS-US program package for Linux.

All thermodynamic properties shown in the Tables 1-3 except the dipole moment and RMS gradient are obtained by the following:

$$E_{T_{initial}} = E_{T_{(clean\ surface)}} + E_{T_{(molecule)}}$$
$$E_{T_{final}} = E_{T_{(surface\ with\ molecule)}}$$
$$E_{ads} = \Delta E_T = E_{T_{final}} - E_{T_{initial}} \quad (1)$$

The thermodynamic properties of these interactions on Ti-O (2 locations) and Ti-Ti cross bridges are shown

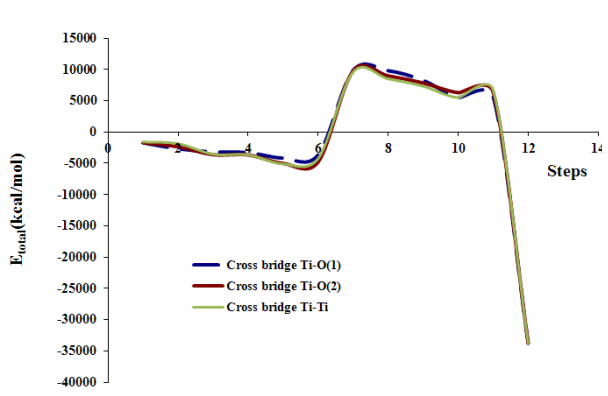

Fig. 3: The total energy of benzopyran interaction on $rTiO_2$-NP by ZINDO/S method.

Table 2: The thermodynamic properties of adsorption benzopyran on Ti-O(2) bridge cross of $rTiO_2$ nanoparticle and converted to CO_2 at 298K (ZINDO/S).

The benzopyran converted to CO_2 on Ti-O(2)								
Steps	E_{total} (kcal/mol)	Dipol Moment (D)	RMS kcal/mol.°A	E_{bin} (kcal/mol)	H (kcal/mol)	G_{ele} (kcal/mol)	E_{nuc} (kcal/mol)	E_{elec} (V)
$rTiO_2$-NP	-67934.53	3.81	415.1	-12183.09	-10815.04	-237906.98	169972.45	10354.50
Benzopyran	-42736.33	2.00	190.8	-7866.31	-5851.92	-153227.46	110491.13	6668.97
Steps	ΔE_{total} (kcal/mol)	Dipol Moment (D)	RMS kcal/mol.°A	ΔE_{bin} (kcal/mol)	ΔH (kcal/mol)	ΔG_{ele} (kcal/mol)	ΔE_{nuc} (kcal/mol)	ΔE_{elec} (V)
1	-1730.78	4.43	311.5	-1730.79	-1730.79	-154822.85	153092.07	6738.40
2	-2368.58	14.69	310.9	-2368.59	-2368.59	-174859.15	172490.57	7610.45
3	-3624.51	14.15	328.9	-3624.52	-3624.52	-194604.90	190980.39	8469.85
4	-3664.54	7.83	341.0	-3664.55	-3664.56	-194874.88	191210.34	8481.60
5	-5021.39	12.16	341.2	-4419.05	-4314.84	-213623.17	208601.78	9297.59
6	-4799.58	16.26	304.0	-3594.88	-3386.48	-209434.96	204635.38	9115.30
7	9779.46	4.69	337.4	703.44	86.56	-64972.05	74751.51	2827.80
8	8981.34	12.87	343.2	-94.68	-711.56	-80746.30	89727.65	3514.35
9	7836.38	19.41	341.9	-637.29	-1149.97	-95319.52	103155.89	4148.62
10	6280.35	9.84	314.0	-988.61	-1292.88	-114418.43	120698.78	4979.87
11	6350.61	21.81	318.7	-918.36	-1222.62	-96478.53	102829.14	4199.07
12	-70462.81	5.03	460.0	-3910.02	-4184.36	-511283.58	440820.77	22252.76

in Tables 1-3. The E_{ads} (kcal/mole) is shown in Fig. 3, that change the total energy of this interaction on all locations of rTiO$_2$-NP can be observed and compared. The E_{ads} of this interaction for all locations of rTiO$_2$-NP is same. Only minor changes are observed in the transition states (3rd, 8th and 10th steps). The most changing of E_{ads} is for across bridge of Ti-O (1), which is related spatial structure of this location on rTiO$_2$-NP.

Dipole moment for all steps are calculated and are shown in Tables 1-3, which its most changes are in the transition state of intermediates and maximum moment of it is 28.99D for 3rd in across the bridge of Ti-O(1).

As the results show, compared of data in Tables 1-3, the probability of pollutant interaction on cross bridge of Ti-Ti is more than other locations. The bond distance between Ti-Ti, Ti-O (1) and Ti-O (2) are 2.95, 2.02 and 1.62 oA respectively. Therefore distance, the location and spatial structure of titanium, titanium bond is more suitable for close pollutants.

In order to access to the electrical properties these interactions by using the electrical energy and the following equation (Lee 2005):

$$E_{elec} \quad RI \tag{2}$$

where R is the electrical resistance and I is the current intensity per (A), that I can be found from I=q/t the

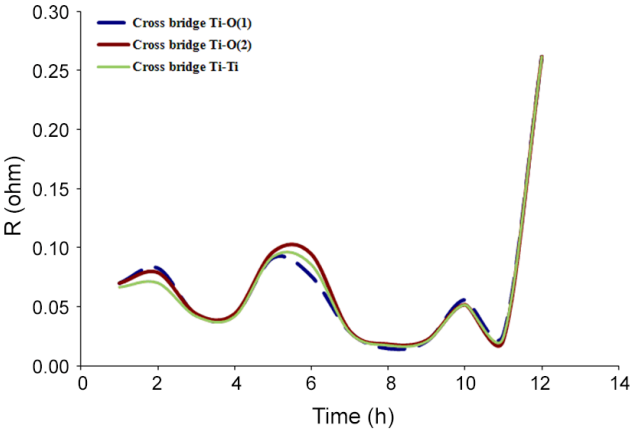

Fig. 4: The electrical resistance of benzopyran interaction on aTiO_2-NP by ZINDO/S method.

Table 3: The thermodynamic properties of adsorption benzopyran on Ti-Ti bridge cross of $rTiO_2$ nanoparticle and converted to CO_2 at 298K (ZINDO/s).

The benzopyran converted to CO_2 on Ti-Ti								
Steps	E_{total} (kcal /mol)	Dipol Moment (D)	RMS kcal/mol.°A	E_{bin} (kcal /mol)	H (kcal /mol)	G_{ele} (kcal /mol)	E_{nuc} (kcal/mol)	E_{elec} (V)
$rTiO_2$-NP	-67934.53	3.81	415.1	-12183.09	-10815.04	-237906.98	169972.45	10354.50
Benzopyran	-42736.33	2.00	190.8	-7866.31	-5851.92	-153227.46	110491.13	6668.97
Steps	ΔE_{total} (kcal /mol)	Dipol Moment (D)	RMS kcal/mol.°A	ΔE_{bin} (kcal /mol)	ΔH (kcal /mol)	ΔG_{ele} (kcal/mol)	ΔE_{nuc} (kcal/mol)	ΔE_{elec} (V)
1	-1594.49	4.19	311.2	-1594.49	-1594.50	-147313.24	145718.75	6411.56
2	-1869.53	8.90	372.3	-1869.54	-1869.53	-155320.09	153450.56	6760.04
3	-3553.68	12.67	323.0	43652.49	-3553.70	-185463.87	181910.18	4036.00
4	-3658.12	6.32	323.3	-3658.14	-3658.13	-184843.73	181185.60	4022.51
5	-5099.25	9.07	316.5	-4496.91	-4392.70	-204822.13	199722.88	8914.54
6	-4257.8	7.52	306.7	-3053.11	-2844.70	-189596.47	185338.66	8251.87
7	9594.48	8.75	328.7	518.45	-98.42	-62074.47	71668.95	2701.69
8	8496.39	5.77	345.8	-579.63	-1196.5	-76377.83	84874.22	1662.11
9	7316.12	18.48	342.5	-1157.55	-1670.22	-90868.57	98184.69	1977.45
10	5508.97	12.86	315.1	-1759.99	-2064.25	-114269.07	119778.04	4973.37
11	6663.07	4.77	320.6	-605.89	-910.16	-107249.62	113912.69	2333.93
12	-70462.81	5.03	460.0	-3910.02	-4184.36	-511283.58	440820.77	22252.76

equation so:

$$R = \frac{E_{elec} t}{nF} \quad (3)$$

The electrical resistance of all steps and conversions are computed based on electrical data, (2) and (3) equations, as can be seen in Fig. 4.

The electrical resistances of all steps for different locations $r$$TiO_2$-NP are same, except for 2nd and 5th steps. In 2nd step, electrical resistance converted pollutant to CO_2 on Ti-Ti is lower than in other locations and in 5th step, Ti-O (1) is lower than.

Equation constant and other thermodynamic parameters such as Gibbs free energy, enthalpy and entropy of the whole reactions were computed through the following equation:

$$K = \exp\left(-\frac{\Delta G_{ele}}{Rt}\right) \quad (4)$$

That T is the reaction temperature that in these computation is considered 298K. In order to compute the entropy reactions:

$$\Delta S_{ele} = \frac{\Delta H_{ele}}{T} \quad (5)$$

The Gibbs free energies (ΔG_{ele}) for Ti-Ti location in this interaction is negative than in other locations for all Intermediates (Table 4). The function mechanism for this conversion on $r$$TiO_2$-NT can be as follows:

$TiO_2 + h\nu \rightarrow TiO_2 (e_{cb}^- + hole_{vb}^+)$

$H_2O \rightarrow OH^- + H^+$

Oxidative reaction:

$^{\bullet}OH + benzopyran + 3/2H_2 \rightarrow C_7H_8O + C_2H_2$

$^{\bullet}OH + C_7H_8O + C_2H_2 + 23/2O_2 \rightarrow 9CO_2 + 6H_2O$

Titanium dioxin molecules on the metal surface activate by ultraviolet radiation and during some chemical processes make bacteria, algae and fungi disappeared (Varghese, *et al.*, 2009). When ultraviolet ray radiates

Table 4: The thermodynamic properties of adsorption benzopyran on $rTiO_2$ nanoparticle and converted to CO_2 at 298K (ZINDO/S).

		ΔG_{ele} kcal/mol	ΔH_{ele} kcal/mol	ΔS_{ele} kcal/K.mol	lnK
Cross bridge of Ti-O(1)	Benzopyran to o-cresol & ethylene	-35187.56	-1562.18	112.84	14202437
	o-cresol to butane & propanol	-27667.57	-1589.36	87.51	11167211
	Butane & propanol to CO_2	-6697.52	825.62	25.25	2703259
Cross bridge of Ti-O(2)	Benzopyran to o-cresol & ethylene	-40052.03	-1933.76	127.91	16165839
	o-cresol to butane & propanol	-15774.25	-798.12	50.26	6366818
	Butane & propanol to CO_2	-1159.01	-72.65	3.65	467801
Cross bridge of Ti-Ti	Benzopyran to o-cresol & ethylene	-37530.49	-2063.63	119.02	15148093
	o-cresol to butane & propanol	-28794.10	-473.72	95.03	11621902
	Butane & propanol to CO_2	-7019.45	-1154.09	19.68	2833197

to titanium dioxide, and electrochemical reactions happen and it frees the radical, free radicals confront to pollutants and destroy them. After attracting the sun's ultraviolet by *r*TiO_2-NP the electrons of capacity balances displace to guide band balance, and an empty hole appears in capacity balance.

CONCLUSIONS

Air pollution is 11 times more than water pollution and food contamination are 16 times more dangerous for human. 92% of respiratory diseases and 20% of cardiovascular diseases caused by air pollution. 3 million people worldwide each year lose their lives due to air pollution. Thus reducing pollution induced fossil fuels by car shall be considered a necessity.

The aim of this study was to find a way to eliminate and reduce unburned hydrocarbons (butadiene, formaldehyde, etc.) and source control before entering the environment is by TiO_2 nanoparticles. TiO_2-NP is a strong photocatalytic which caused the loss of pollutants and a substance into low-risk (that is environmental friendly). These particles have high potential for detoxification and elimination of industrial pollutants. In this study, benzopyran after absorption on *r*TiO_2 NPs is converted to o-cresol & ethylene and they are reduced to butane & propanol, then are decreased into the water and carbon dioxide.

Locations on the surface of *r*TiO_2 nanoparticles to absorb pollutants are investigated such as cross bridges Ti-O (1), Ti-O (2) and Ti-Ti pollutants close to the locations. After being optimized interaction structures, the thermodynamic properties are calculated ZINDO/S. The results showed that these interactions and conversions are endothermic, and needs to solar or other energy. According to the exhaust gas high temperature of car may be used for this conversion. The results show that the energy of approaching to Ti-Ti cross bridge is the lease other locations on *r*TiO_2-NP. This means that the chance of close pollution to the cross bridge of Ti-Ti is greater because it is more symmetric and electron bond polarity.

ACKNOWLEDGEMENT

I would like to thank from Doroud branch of Islamic Azad University, for providing me with all the necessary facilities for the research.

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