J. Water Environ. Nanotechnol., 2(1): 34-38 Winter 2017

ORIGINAL RESEARCH PAPER

Investigation of Conversion CO_2 to Fuel by TiN nanotube-Cu nanoparticle

Leila Mahdavian

Department of Chemistry, Doroud Branch, Islamic Azad University, Doroud, Iran

Received: 2016.08.06 Accepted: 2016.11.26 Published: 2017.01.30

ABSTRACT

The CO and CO_2 effects are global warming, acid rain, limit visibility, decreases UV radiation; yellow/black color over cities and so on. In this study, convention of CO_2 and H_2O to CH_4 and O_2 near TiN- nanotube with Cu-nanoparticle calculated by Density Functional Theory (DFT) methods. We have studied the structural, total energy, thermodynamic properties of these systems at room temperature. All the geometry optimization structures were carried out using GAMESS program package under Linux. DFT optimized their intermediates and transient states. The results have shown a sensitivity enhancement in resistance and capacitance when CO_2 and H_2O are converted to CH_4 and O_2.

TiN-nanotube used photo-catalytic reactivity for the reduction of CO_2 with H_2O to form CH_4 and O_2 at 298K. The calculations are done in state them between of three TiN-nanotubes near Cu-nanoparticle. The calculation shown which heat reaction formation (ΔH) is endothermic for this reaction. This reaction needs to sun, photo active or other energy in the presence of visible light for doing.

Keywords: CO_2 and H_2O, CH_4 and O_2, TiN- nanotube, Waste Pollution, ZINDO/1-DFT.

How to cite this article

Mahdavian L. Investigation of Conversion CO_2 to Fuel by TiN nanotube-Cu nanoparticle. J. Water Environ. Nanotechnol., 2017; 2(1): 34-38. DOI: 10.7508/jwent.2017.01.005

INTRODUCTION

One of the biggest problems of the global environment is an excessive increase of greenhouse gases. Carbon dioxide due to higher shelf life and the most its amount in the atmosphere is the most important greenhouse gas[1, 2]. Carbon dioxide concentration in the pre-industrial era was only 250 ppm, whereas currently it is at 380 ppm[3].

Largest sources and emissions of carbon dioxide are industrial, power plants, fossil fuel (coal), the cars and etc. Preventing the release of greenhouse gases, especially carbon dioxide is the most important problem for industries and societies.

In recent years, many solutions have been proposed to reduce and converted this pollutant[4, 5]. No need to change phase, having the energy needed for regeneration, the small size of the membrane system, the lack of loss stream, the operation is simple, environmentally friendly and low cost investment are caused, the researchers and industry men have led into the potential of membranes, such as membrane polymers, zeolites, carbon nanotubes, metal-organic frameworks (MOFs), Hydrate phase equilibrium and so on[6-8].

Among the various methods that are available for the removal of gaseous pollutants, three main methods are considered for CO_2 removal include chemical reactions, burning and absorption. One of the methods to eliminate carbon dioxide was implemented of gas mixture produced as fuel. Methane and methanol is major product of chemical industry and also a feedstock for many chemicals. However CO_2 conversion to methanol and so on is challenging, there are many methods for it [9-12].

* Corresponding Author Email: mahdavian@iau-doroud.ac.ir

TiN- nanotubes with Cu-nanoparticle have attracted great interest due to their unique electronic properties and nanometer size. Because of these unique properties, they are great potential candidates in many important applications such as nanoscale electronic devices, chemical sensors and field emitters. The effect of gas adsorption on the electrical resistance of a TiN-Cu nanoscale has received great attraction because of fast response, good sensitivity of chemical environment gases and low operating temperature [13].

As shown in Fig. 1, there are four situations in which CO_2 and H_2O can pass between TiNTs-Cu. In this work, the second situations are investigated for them. In Fig. 2, TiN- nanotubes with Cu-nanoparticle simulated by ball-and-stick models, CO_2 and H_2O converted to CH_4 and O_2.

Interactions between CO_2 and H_2O on Cu nanoparticle between TiN-nanotubes are optimized by GAMESS program package and ZINDO/1 method by semi empirical-DFT methods at room temperature was implemented for investigation of thermodynamic properties of considered systems.

THE COMPUTATIONAL METHODS

The computational approach consists of three stages: First, the optimization of geometrical structures is done for the reactions, products and the transition state, in this study theB3LYP/6-31G level of density functional theory (DFT) was used[15, 16]. Then the frequency calculations were performed for each optimized structures to obtain thermo-chemical quantities by ZINDO/1[17, 18] and IR-DFT methods by the GAMESS program package. At the end, the reaction pathway analyzed in order to confirm the obtained structures of the transition state. For removal of pollutants in the environment, we need to new catalysts, are being the most active and selectivity. Basically, the catalytic properties of these compounds are completely determined by their electronic structure. The electronic structure design is important based on

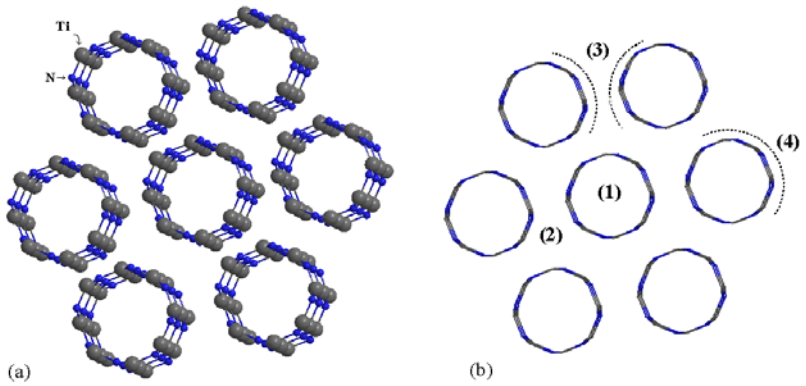

Fig. 1: There are four situations for interaction of CO_2 and H_2O in TiN-nanotube, a) Ball-and-stick, b) stick models Configuration for them.

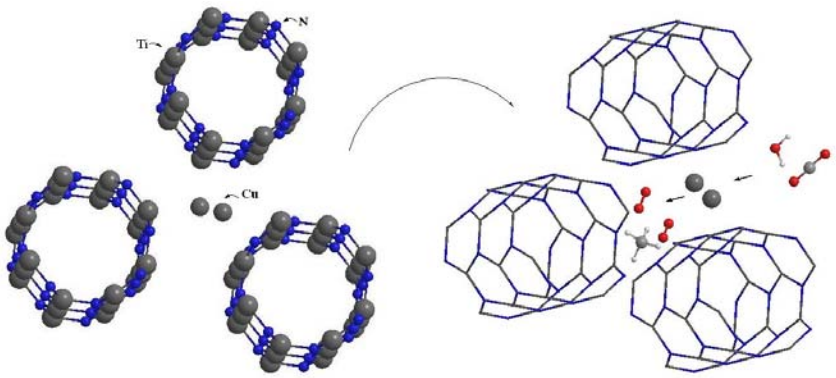

Fig. 2: Ball-and-stick models configuration: Top-view of second situation passing CO_2 and H_2O between TiN-nanotube with Cu- nanoparticle[14] .

changes in the composition and physical structure. For this purpose, the ZINDO/1 calculations enable in complex systems and extended. In this way, we have provided the interaction energies of molecules with sufficient precision to describe the reactivity of transition metal and alloys.

In this study, entry of carbon dioxide and water on Cu nanoparticles between titanium nitride nanotubes have been simulated in three steps (Fig. 2), and then in steps 4 and 5 are transition state conversion of them to CH_4 and O_2. The conversion was completed in 6th step and methane and oxygen are produced, then it is excreted from TiN-NTs in 7th step. The electronic structure and the thermodynamic properties are calculated for all steps by ZINDO/1.

RESULTS AND DISCUSSION

In this research, we have developed a method for converting CO_2 into commodity chemicals, which may reduce the burden on CO_2 storage sites, in addition to providing a means to reduce anthropogenic CO_2 emissions and an inexpensive method for producing useful materials from CO_2. This novel catalytic method for the continuous chemical converting of CO_2 is simulated and thoroughly investigated mechanistically.

The geometry optimizations of TiN nanotube with Cu nanoparticles were performed by B3LYP/6-31G level of theory (Fig. 2). The effects of CO_2 and H_2O have passed between Cu-TiN nanotubes and converted them to CH_4 and O_2 were shown in Table 1 which in this simulation, they are passing in-side to out-side between nanotubes by seven stages. The study includes conformational searches (and further refinement by DFT) and the ab initio calculation of ZINDO/1 methods in semi empirical and the dipole moments for all the steps between nanotubes. The most significant property of ZINDO/1 was finding a good correlation between the ZINDO/1 and the substitution pattern on this conversation.

In Fig. 3, the resistance (Ω) recorded for converted of CO_2 and H_2O to other chemicals on Cu-nanoparticles between TiN nanotubes have shown a sudden decrease. The E_{ele} for them is -51.17 in 5th step (Table 1), and RMS gradient (kcal/mol·Å) is different for the formation of CH_4 and H_2O in this interaction at 298K: $CO_2+2H_2O \rightarrow CH_4+2O_2$

Table 1: The thermodynamic properties of interaction CO_2 and H_2O on Cu-TiN nanotube at 298K.

Steps	E_{total} (MJ/mol)	E_{nuc} (MJ/mol)	Dipol Moment (D)	RMS kcal/mol.°A	E_{bin} (MJ/mol)	H (MJ/mol)	E_{ele} (v)
TiN-Cu	18844.55	39060.15	1.74×10^4	8335	21706.32	21775.13	-49.89
1	20843.06	40819.57	1.73×10^4	8272	23854.13	23924.84	-49.30
2	21057.41	41301.82	1.73×10^4	8317	24068.48	24139.19	-49.96
3	17675.78	41577.29	1.82×10^4	8751	20686.84	20757.56	-58.98
4	14958.85	41733.14	2.16×10^4	1.04×10^4	17969.91	18040.63	-66.07
5	21208.79	41945.84	1.74×10^4	9635	24219.85	24290.57	-51.17
6	17366.76	42840.00	1.97×10^4	1.02×10^4	20424.33	20495.74	-62.61
7	14875.68	41996.33	2.09×10^4	1.05×10^4	17933.24	18004.65	-66.93

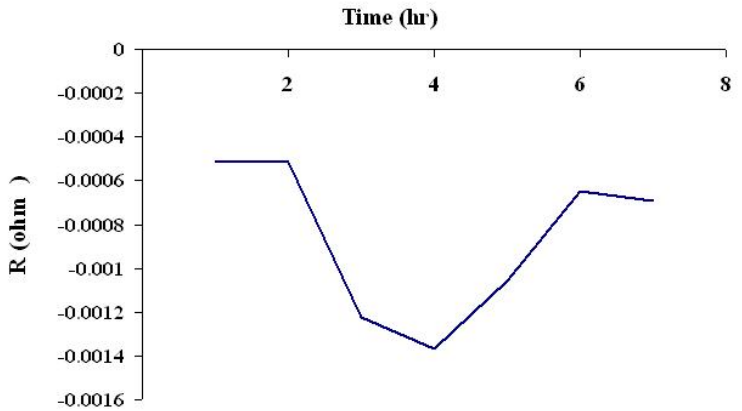

Fig. 3: The resistance (Ω), interaction CO_2 and H_2O on Cu-TiN nanotube at 298K.

Table 2: The thermodynamic properties of CO_2 and H_2O passing through Cu-TiN and convert to CH_4 and O_2.

CO_2 and H_2O passing through Cu-TiN	ΔG_{ele} (MJ/mol)	ΔH_{ele} (MJ/mol)	ΔS_{ele} (MJ/mol)	K
	-6797.78	-5884.21	3.065662	2743725

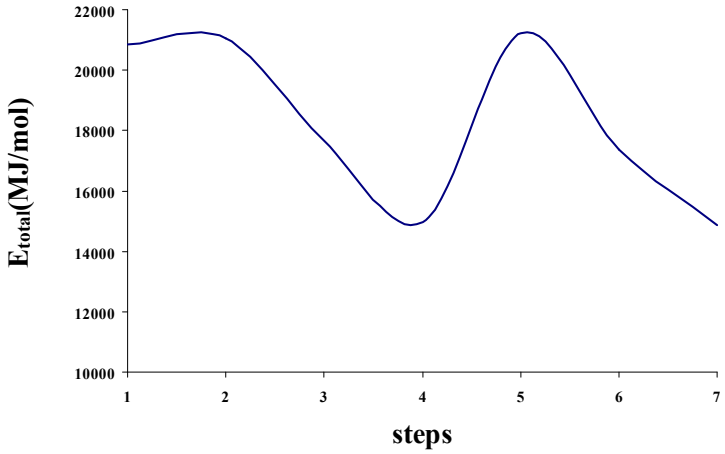

Fig. 4: The total energy (MJ/mol) of converted CO_2 and H_2O to CH_4.

The interaction between them is:

The heat of formation (enthalpy) for their interaction calculated with ZINDO/1 methods by subtracting atomic heats of formation from the binding energy. The heat of formation and binding energy is appropriate for this interaction. The *H* (MJ/mol) for these interactions has a minimum amount in 4th step of TiN-nanotube. The enthalpy of all steps was positive that is shown, this interaction was endothermic. Therefore, this interaction needs to ultraviolet solar radiation. The results show, the dipole moment (D) has the most amounts in the 4th step of this interaction; indicate that location between nanotubes is the perfect place to trapping of CO_2, which can convert it to other products. Table 1 shows the nuclear energy for them, that has an increasing trend.

The least amount of total energy is shown in the middle of nanotube because the field of TiN-nanotube is the largest amount in this place. The total energy for them is shown in Fig. 4. The E_{total} decreases in the middle length between nanotubes, which is a potential for converting CO_2 to CH_4. To determine sensitivity of TiN-nanotube to carbon dioxide, the electrical resistance (Ω) of this interaction is calculated and evaluated, it is shown in Fig. 3. The TiN-NT is an up hole-doped semiconductor, as can be gleaned from the current versus gate voltage curve shown in Fig. 3 (middle curve), where the resistance of them is observed to be decreasing. Band bending induced by charging molecules causes the increase or decrease in surface conductivity responsible for the gas response signal.

Their enthalpy difference was negative; it is an exothermic and spontaneous interaction during which CO_2 is separated from the air in the environment. In Table 2, thermodynamic parameters (ΔG_{ele}, ΔH_{ele}, and ΔS_{ele}) for them between the lengths of the tubes were calculated and the results suggest that the nature of adsorption is exothermic, spontaneous and favorable. This method is best for converting CO_2 in the environment.

CONCLUSION

One of the causes of global warming is due to carbon dioxide emissions from fossil fuel combustion. The new methods have developed for reducing carbon dioxide emissions. For example, removal of carbon dioxide from the flue gases are stating by carbon dioxide-hydrogen-water (Syngas) method [19, 20].

In this study, using filters of titanium nitride nanotubes with copper nanoparticles to convert the pollutants into methane fuel was simulated and calculations were done. We choose armchair TiN-nanotube (4, 4) and it is investigated to know whether CO_2 passes between them. The interaction between them was calculated by ZINDO/1 methods. A change in the potential of all atoms

of inner surface TiN-nanotube was observed in passing and convert of CO_2. According to the results, this nanofilter can be installed in automobile exhaust. Exhaust gas pressure for carbon dioxide gas entry, and convert them between nanotubes on copper nanoparticles is very suitable. Temperatures of automobile exhaust gas are higher than 700 °C, which can provide the energy required to break the double bonds C=O and bonds O-H in carbon dioxide and water on copper nanoparticles. In these calculations, the energy separation of carbon dioxide and water were lower from than the energy of methane and oxygen (Fig. 4), which can improve interaction to remove CO_2.

CONFLICT OF INTEREST

The author declares that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, *et al.*, "Catalysis research of relevance to carbon management: progress, challenges, and opportunities," *Chemical Reviews,* vol. 101, pp. 953-996, 2001.
2. M. Pervaiz and M. M. Sain, "Carbon storage potential in natural fiber composites," *Resources, conservation and Recycling,* vol. 39, pp. 325-340, 2003.
3. F. M. Orr Jr, "CO 2 capture and storage: are we ready?," *Energy and Environmental Science,* vol. 2, pp. 449-458, 2009.
4. P. Styring and K. Armstrong, "Catalytic carbon dioxide," *chimica oggi/Chemistry Today,* vol. 29, 2011.
5. K. M. K. Yu, I. Curcic, J. Gabriel, and S. C. E. Tsang, "Recent advances in CO2 capture and utilization," *ChemSusChem,* vol. 1, pp. 893-899, 2008.
6. O. K. Farha, A. Ö. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, *et al.*, "De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities," *Nature chemistry,* vol. 2, pp. 944-948, 2010.
7. D.-A. Yang, H.-Y. Cho, J. Kim, S.-T. Yang, and W.-S. Ahn, "CO 2 capture and conversion using Mg-MOF-74 prepared by a sonochemical method," *Energy & Environmental Science,* vol. 5, pp. 6465-6473, 2012.
8. J.-W. Du, D.-Q. Liang, X.-X. Dai, D.-L. Li, and X.-J. Li, "Hydrate phase equilibrium for the (hydrogen+ tert-butylamine+ water) system," *The Journal of Chemical Thermodynamics,* vol. 43, pp. 617-621, 2011.
9. Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, and W.-Q. Deng, "Capture and conversion of CO2 at ambient conditions by a conjugated microporous polymer," *Nature communications,* vol. 4, 2013.
10. K. Ikeue, S. Nozaki, M. Ogawa, and M. Anpo, "Characterization of self-standing Ti-containing porous silica thin films and their reactivity for the photocatalytic reduction of CO 2 with H 2 O," *Catalysis Today,* vol. 74, pp. 241-248, 2002.
11. O. K. Varghese, M. Paulose, T. J. LaTempa, and C. A. Grimes, "High-rate solar photocatalytic conversion of CO2 and water vapor to hydrocarbon fuels," *Nano letters,* vol. 9, pp. 731-737, 2009.
12. C. Duke and H. Gibson, "Encyclopedia of chemical technology," ed: Wiley, New York, 1982.
13. N. Yan, G. Li, G. Pan, and X. Gao, "TiN nanotube arrays as electrocatalytic electrode for solar storable rechargeable battery," *Journal of The Electrochemical Society,* vol. 159, pp. A1770-A1774, 2012.
14. L. Mahdavian, "Using of TiN-nanotubes and Cu-nanoparticles for conversion of CO2 to hydrocarbon fuels," *Journal of molecular modeling,* vol. 21, pp. 1-6, 2015.
15. P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Physical review,* vol. 136, p. B864, 1964.
16. J. Huang, C. Liu, Q. Jin, H. Tong, W. Li, and D. Wu, "Density functional theory study on bond dissociation enthalpies for lignin dimer model compounds," *Journal of Renewable and Sustainable Energy,* vol. 6, p. 033116, 2014.
17. M. J. Dewar and M. L. McKee, "Ground states of molecules. 41. MNDO results for molecules containing boron," *Journal of the American Chemical Society,* vol. 99, pp. 5231-5241, 1977.
18. M. J. Dewar and W. Thiel, "Ground states of molecules. 38. The MNDO method. Approximations and parameters," *Journal of the American Chemical Society,* vol. 99, pp. 4899-4907, 1977.
19. S.-P. Kang and H. Lee, "Recovery of CO2 from flue gas using gas hydrate: thermodynamic verification through phase equilibrium measurements," *Environmental science & technology,* vol. 34, pp. 4397-4400, 2000.
20. J. Zhang, P. Yedlapalli, and J. W. Lee, "Thermodynamic analysis of hydrate-based pre-combustion capture of CO2," *Chemical Engineering Science,* vol. 64, pp. 4732-4736, 2009.