Ab initio studies of Magnesium Hydroxide Nanoparticles as potential catalysts for thermal decomposition of Acetic Acid

Duwage C. Perera[1], Jinasena W. Hewage[2], Jayendran C. Rasaiah[1]

[1] Department of Chemistry, University of Maine, [2] Department of Chemistry, University of Ruhuna, Sri Lanka

Abstract

We use MP2 and DFT calculations to investigate the thermal decomposition of acetic acid to carbon dioxide and methane $CH_3COOH \rightarrow CO_2 + CH_4$ in the presence of magnesium hydroxide nanoparticles which act as a catalyst for the reaction which is of interest in reducing the odor of sweat. Catalysis is enhanced in the nanophase. Health benefits dictated the use of magnesium hydroxide instead of Magnesium oxide used previously as a catalyst for the same reaction [1]

We investigated the adsorption and decomposition of acetic acid on the surfaces built of $[Mg(OH)_2]_n$ clusters for n=1,2,….,12 and observed the equilibrium structures and calculated their energies. The total cluster energy and the binding energy of acetic acid molecule were calculated for each cluster. The adsorption of acetic acid on $[Mg(OH)_2]n$ clusters were carried out at the same level of theory, keeping the cluster frozen.

Decarboxylation of acetic acid ($CH_3COOH \rightarrow CO_2 + CH_4$) on the cluster surface was investigated by calculating IRC while locating the transition state.

Simulation Method

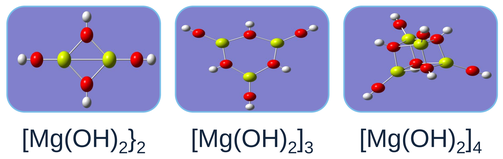
- Level of theory : MP2/6-31G(d,p)
- Software : Gaussian 09
- Visualizing tool : Gausseview 05

Optimization of acetic acid and $[(Mg(OH)_2]_4$

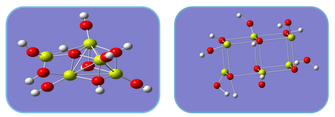
Determination of the transition state by QST3

AIM analysis and ChelpG calculation

Results



$[Mg(OH)_2\}_2$ $[Mg(OH)_2]_3$ $[Mg(OH)_2]_4$



$[Mg(OH)_2]_5$ $[Mg(OH)_2]_6$

Figure1: Optimized structures of $[Mg(OH)_2]_n$
Mg atom = yellow O atom = red H atom = ash

Table1: Adsorption energies of acetic acid molecule (AA) on $[Mg(OH)_2]_n$ surface obtained using at the MP2/6-31G(d,p) level of theory

System	Adsorption energy (kJ mol^{-1})
$[Mg(OH)_2]_2$	-102.415
$[Mg(OH)_2]_3$	-149.684
$[Mg(OH)_2]_4$	-199.576
$[Mg(OH)_2]_5$	-118.172
$[Mg(OH)_2]_6$	-795.693

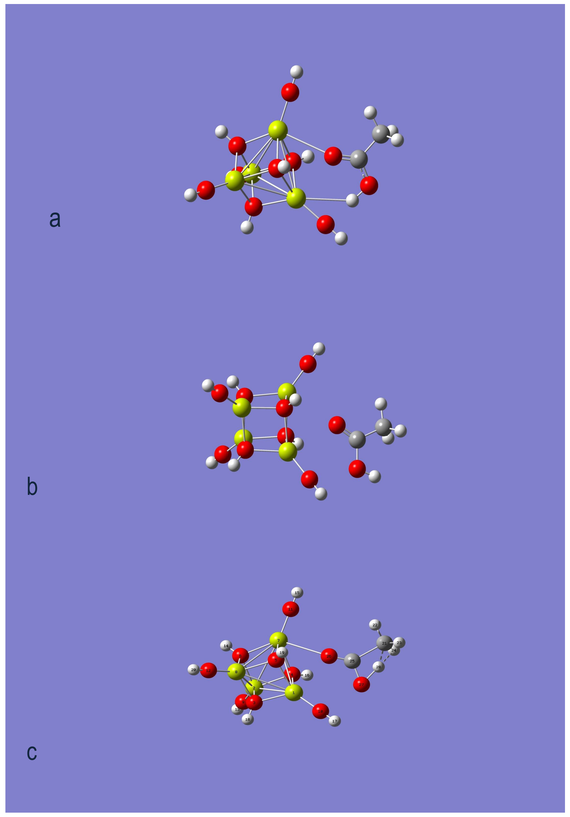


Figure2: Equilibrium structures of acetic acid decomposition on $[Mg(OH)_2]_4$ surface at the MP2/6-31G(d,p) level of theory: (a) lower energy $[Mg(OH)_2]_4$ –AA complex(isomer1), (b) high energy intermediate $[Mg(OH)_2]_4$ – AA complex (isomer2), and (c) transition state, $\{[Mg(OH)_2]_4$ -AA$\}^{\#}$ between isomer2 and the products of the decarboxylation

Table2: Electronic density ρ (a.u.), Laplacian of electron density $\nabla^2\rho$ (a.u.) values and bond distances D ($\dot{A}$) from AIM calculations for isomer-1 and for isolated acetic acid in parenthesis at the MP2/6-31G(d,p) level of theory.

Bond/ Characteristic	ρ (a.u)	$\nabla^2\rho$ (a.u)	D ($\dot{A}$)
25C – 21C	0.3(0.3)	-0.7(-1.0)	1.50(1.51)
25C – 27O	0.3(0.3)	-0.4(0.2)	1.33(1.37)
25C – 26O	0.4(0.4)	0.0(0.2)	1.24(1.21)
27O – 28H	0.3(0.4)	-1.7(-0.2)	1.01(0.97)
26O – 7Mg	-	-	2.83
28H – 5O	-	-	4.00
28H – 21C	-	-	3.22

Table3: ChelpG atomic charges of isomer-1 and isolated acetic acid obtained using the MP2/6-31G(d,p) level of theory.

Atom/ Characteristic	isomer-1	AA
21C	-0.4	-0.5
25C	0.8	0.8
22H	0.2	0.2
23H	0.2	0.2
24H	0.2	0.2
28H	0.4	0.4
26O	-0.6	-0.5
27O	-0.7	-0.6

Table 4: Electronic density ρ (a.u.), Laplacian of electron density $\nabla^2\rho$ (a.u.) values and bond distances D ($\dot{A}$) from AIM calculations for transition state and isomer-2 in parenthesis at the MP2/6-31G(d,p) level of theory

Bond/ Characteristic	ρ (a.u)	$\nabla^2\rho$ (a.u)	D ($\dot{A}$)
25C – 21C	0.1(0.3)	0.0(0.0)	1.89(1.50)
25C – 27O	0.3(0.3)	-0.7(-0.6)	1.33(1.35)
25C – 26O	0.4(0.4)	0.6(0.6)	1.19(1.22)
27O – 28H	0.2(0.0)	-0.5(-0.4)	1.29(0.97)
26O – 7Mg	-	-	2.83(2.95)
28H – 5O	-	-	5.18(5.60)
28H – 21C	0.1	-0.1	1.30(2.34)

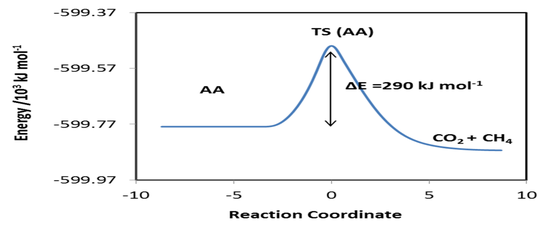


Figure 3: Intrinsic reaction coordinate diagram for the gas phase decomposition of acetic acid molecule (AA = Acetic acid)

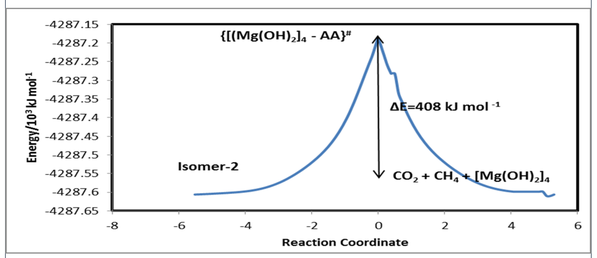


Figure 4: Intrinsic reaction coordinate diagram for the decomposition of acetic acid molecule adsorbed on $[Mg(OH)_2]_4$ surface

Conclusion

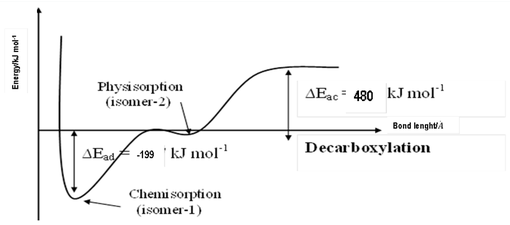


Figure 5: Schematic representation of potential energy surface for adsorption and decomposition of acetic acid on $[Mg(OH)_2]_4$ surface: ΔE_{ac} is the activation energy for the decarboxylation and ΔE_{ad} is the adsorption energy of acetic acid on to the surface.

Future work

Modify the experiment to compare the decomposition behavior on a graphene sheet and cellulose and polymer.

References

1. Perera, D. C.; Hewage, J. W.; de Silva, N. Computational and theoretical Chemistry. 2015,1064,1-6.
2. Nguyen, M. T.; Sengupta, D.; Raspoet, G.; Vanquickenborne, L. G. J. Phys. Chem. 1995, 99, 11883-11888

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Contact Information

Email: charitha.perera@maine.edu
Mobile: +1 207 889 2030