Journal of Engineering and Applied Sciences 12 (17): 4431-4436, 2017
ISSN: 1816-949X

A DFT Study of Hydrogen Adsorption Kinetics and Thermodynamics on Mixed Oxides of $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$

M. Abdus Salam and Suriati Sufian
Department of Chemical Engineering, Universiti Teknologi Petronas,
32610 Bandar Seri Iskandar, Perak, Malaysia

Abstract: Hydrogen sorption mechanism, kinetics and thermodynamics of hydrotalcite derived mixed oxides of $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$ have been studied using the density functional theory. Hydrotalcite based magnesium and nickel and aluminum containing mixed oxides showed significant hydrogen sorption kinetics and thermodynamics. Reduced mixed oxides or active metals of Magnesium (Mg) and Nickel (Ni) converted to hydrides of MgH_2 and Mg_2NiH_4. The study indicated the favorable hydrides formation which is due to the electrostatic interaction and strong hydrogen bonding type interaction between them. The materials itself facilitate to diffuse hydrogen molecules to different layers of the materials and enhances the sorption kinetics. Hydrogen adsorption and desorption energy of MgH_2 and Mg_2NiH_4 are 60.13, 64.31, 40.22 and 45.72 kJ/mol, respectively. Model predicted values of hydrogen adsorption enthalpy and entropy changes of MgH_2 and Mg_2NiH_4 are -48.18 Kj/mol, -135j/mol.K, -55.10 Kj/mol and -155 J/mol.K, respectively. The rate constant of adsorption are 6.0×10^{12} and 1.3×10^{13} sec^{-1} for MgH_2 and Mg_2NiH_4 those are indicating physical and chemical adsorption of hydrogen.

Key words: Hydrogen, adsorption, thermodynamics, kinetic, DFT, indicating

INTRODUCTION

Chemical hydrides show high hydrogen adsorption capacities though discharging all of the hydrogen from the material at moderate temperatures is impossible. Light metal hydrides do not adsorb hydrogen at room temperature and ambient pressure. Many investigations have been focused to overcome the crucial shortcomings of the hydride materials such as stability of metal hydride, formation of surface oxides, slow dissociation of hydrogen on adsorbent surface and slow diffusion of hydrogen to bulk metals surfaces. Different hydride formation methods, doping catalytic elements have been investigated to develop better hydride materials. None of them meets the DOE benchmarks and overcome the limitations. De hydrogenation or decomposition of MgH_2 is not possible at ambient conditions due to strong binding energy between magnesium and hydrogen. Another limitation is metal doping as additives with MgH_2 and surface oxidation reduces the hydrogen adsorption capacity. Despite the tremendous research effort in the last few decades no promising hydride material with favorable thermodynamics and kinetics has been found to store higher than 2 wt.% reversible hydrogen below at 100°C and pressure 1 bar (Li *et al*., 2012). Magnesium (Mg) based hydride materials can be tuned or modified by applying few techniques to minimize the limitation of hydrogen sorption capacity of materials.

Hydrogen gas can bonded chemically with the active site of the reduced metals. Mixed oxides are able to store high quantities of catalytic hydrogen (Johansson *et al*., 2006). Hydrogen physisorption isinfluenced by textural properties of materials and surface energies. Different cations are dispersed homogeneously in mixed oxides thus showed Kubas interaction with hydrogen (Hanada *et al*., 2005). After H_2 reduction of mixed oxides, anion vacancies are generated due to the devolution of water. These anion vacancies of metals generate deficiencies of electron to capture hydrogen as hydride form. The anionic vacancies are necessary to get the catalytic activity and the diffusion phenomena of the molecular hydrogen. Siegel showed that the number of coordinating instauration positions on a site and set of elementary reaction are connected (Berlouis *et al*., 2007). The entire coordinative unsaturated site will receive hydrogen species. Existence of different kinds of active site in reduced mixed oxides allows formation of the hydride and increases the ability of the solid solution of adsorbents (Kim *et al*., 2010).

Corresponding Author: M. Abdus Salam, Department of Chemical Engineering, Universiti Teknologi Petronas, 32610 Bandar Seri Iskandar, Perak, Malaysia

The oxides-hydrogen interactions can have a double in nature. More hydrogen enter into the bulk oxide layer to occupy the active vacant site of metals due to significan telectrostatic interaction. Secondly, hydrogen-oxides interaction involves defects (in the case of MgO) on lattice surface. The nature of MgO is quite ambiguous. According to, the literature, MgO blocks hydrogen diffusion inside the materials. Low oxygen content (below 150 ng/cm^2) enhances the rate of hydrogen uptake but decreases of total hydrogen uptake. At low oxygen concentration, the surface is patchy and MgO creates a nucleation site for hydride phase, depleting the adjacent metallic phase. In such way, the area at the interface between Ni and Mg is depleted and kinetics is increased. Hydrogenation reactions occurred due to the presence of hydride ion in oxygen vacancies. A fundamental rule is that the negative charge of the hydride ion must be compensated by the electrostatic interaction with a positive charge center. A reversible interaction between oxygen and hydrogen follow three steps: hydrogen insertion (or hydrogen release), hydrogen migration in suitable conditions and hydrogen stabilization inside the oxide lattice. Hydrogen can be formed in three oxidation states. Possible forms of oxidation states are H^+, H^0 and H^{-1}. Hydrogen is always associated with other atoms because of its high reactivity in all these three oxidation states. The best oxidation state for molecular hydrogen is thought to be H^- (hydride) (Salam *et al*., 2013a-d).

Hydrogen sorption mechanism of $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$ and its kinetics and thermodynamics have not yet been studied in details. The objective of the study is to explore hydrogen sorption mechanism of $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$ and its kinetics and thermodynamics using the DFT study.

MATERIALS AND METHODS

Material preparation and characterization: Appropriate amount of magnesium (Mg), Nickel (Ni) and Aluminum (Al) nitrate precursor's solution have been used to synthesize layered structured of hydrotalcite (Mg:Ni:Al = 2:1:1) using coprecipitaion method as developed else where (Salam *et al*., 2013 a-d). The fresh dried material was calcined in air at the temperature of 650°C for 12 h together with 2 h holding time with a ramp of 2°C/min and allowed to cool down to room temperature. Water, hydroxyl groups and interlayer carbonates have been eliminated at this calcination temperature and formed well crystalline spinel phases of $M^{II}O$ and $M^{II}M^{III}{}_2O_4$ (Wiitala *et al*., 2006).

Elemental composition of mixed oxides of $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$ was confirmed using ICP-MS analysis (Agilent 7500 series). A 0.1 gm of powder sample (mixed oxides) had been converted to diluted liquid solution before ICP-MS analysis using ETHOS EZ closed vessel microwave digestor from milestone scientific.

Computational methods: Geometry optimization of hydrides and calculation of its electronic energy, vibrational frequencies and related descriptors for the system have been carried out using the hybrid meta exchange-correlation functional, M05-2X (Hehre, 1986) in combination with the 6-311+G (d, p) basis set (10/140). To obtain a stable wave function and to recover a larger fraction of the exchange-correlation energy, multiple function; 6-311+G (d, p) had been used. The M05-2X functional was more precise for calculation of the thermochemistry and non-covalent interaction especially weak interaction, hydrogen bonding and interaction energies of nucleo-bases. Geometry optimization of the hydrides and its frequency calculation (using the functional, M05-2X) was carried out to ensure the minima on Potential Energy Surface (PES) and generated acceptable values of global descriptors which were consistent with the experimental results. All calculations had been performed by using the GAUSSIAN 09W program package (Frisch *et al*., 2009). The second derivative calculation had been done at the optimized geometries to check the minima on the potential energy surface (real frequencies). Geometries of the optimized N-electron systems or hydrides at the M05-2X/6-311+G (d, p) level of the theory had been used to determine the energies of the N±1 electron system by single point energy calculations. IP = E (N±1)-E (N) and EA = E (N)-E (N±1)values had been calculated using DFT energy calculations from the bottom of the potential well of the neutral. Electronegativity (Sen and Jorgenson, 1987; Pearson, 1997) hardness (Ochterski, 2000) and electrophilicity (Parr and pearson, 1983) were calculated by the generally used finite approximation X^x = IP+EA/2 and η = IP-EA and $\omega = x^2/2$, respectively. Interaction energy (ΔE_i) per hydrogen molecule (Kumar *et al*., 2009) adsorption energy (ΔE_{ads}), average desorption energy (ΔEDE) per hydrogen atom (Thomas, 2007) reaction enthalpies (ΔH_r) and Gibb's energies $(\Delta G)_r$ and electrophilicities ($\Delta\omega$) were calculated as the difference between the products and reactants according to Eq. 1-5 (Ochterski, 2000; Salam *et al*., 2013):

$$\Delta E_i = \left(\frac{1}{n}\right)\left[E_M(H_2)_n - \left(E_M + nE_{H_2}\right)\right] \quad (1)$$

E_M, E_{H_2} and $E_M(H_2)_N$ are the energy of reduced metal, hydrogen and hydride system, respectively:

$$\Delta E_{ads} = \left[E_M + nE_{H_2}\right] - E_{M(H_2)_n} \quad (2)$$

$$\Delta E_{DE} = E_H + \left(\frac{1}{2}\right)\left[E_{SH_{n-2}} - E_{SH_n}\right] \quad (3)$$

Gibbs energy and formation energy calculation have been performed using following expression:

$$\Delta H_r(298.15k) = \sum(\varepsilon_o + H_{corr})_{product} - \sum(\varepsilon_o + H_{corr})_{reactact} \quad (4)$$

$$\Delta G_r(298.15k) = \sum(\varepsilon_o + G_{corr})_{product} - \sum(\varepsilon_o + G_{corr})_{reactact} \quad (5)$$

RESULTS AND DISCUSSION

Hydride formation: ICP-MS analysis showed 44.19, 25.98 and 30.10 weight percent of magnesium, nickel and Aluminum (Al), respectively in mixed oxide solution that was consistent with molar ratios considered during synthesis of hydrotalcite. High crystalline magnesium hydrotalcite usually form in high pH condition. Aluminum was used as support therefore, slightly less amount of aluminum precipitated. So, amount of elements are enough to form the hydrotalcite based mixed oxide of $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$.

The mixed oxide was subjected to hydrogen adsorption analysis (Parr *et al*., 1999). Raman, FTIR and XPS analysis of hydrogen adsorbed reduced mixed oxides demonstrated the formation of MgH_2 and Mg_2NiH_4 mainly at applied condition and there was no hydride of aluminum since aluminum considered as support element of the hydrotalcite. So, the computational study of hydrogen adsorption kinetics and thermodynamics has been carried out below on hydrides of MgH_2 and Mg_2NiH_4 that were formed in adsorption process.

Characterization of hydride using DFT: The geometry of hydrides is optimized successfully. Optimized clusters of Magnesium Hydride (MgH_2) and ternary metal hydride (Mg_2NiH_4) are shown in Fig. 1.

Frequency, analysis demonstrated that all hydride phases are free from imaginary frequency and the minima on the potential energy surface. This scenario indicate that all hydride phases are stable. The electronic properties of hydride phases and feasibility of their application are discussed in next section below. To observe the stability of the hydride phases and interaction between metals and hydrogen, stability descriptors and energy descriptors have been studied via density functional theory based global reactivity descriptors.

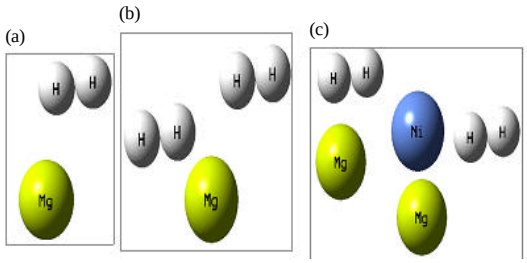

Fig. 1: Optimized structure of MgH_2 and Mg_2NiH_4: a) Mg-(H_2); b) Mg-$(H_2)_2$ and c) Mg_2Ni-$(H_2)_2$

Table 1: Hydride phases stability indicator

Cluster names	E (kJ/mol)	η (kJ/mol)	χ (kJ/mol)	ω (kJ/mol)
Mg-(H_2)	-5.280×10^5	86.74	911.92	605.47
Mg-$(H_2)_2$	-5.311×10^5	118.09	376.75	601.00
Mg_2Ni-$(H_2)_2$	-5.015×10^6	190.48	383.88	386.83

E: Total electronic energy, η: hardness, χ: Electronegativity, ω: Electrophilicity

Table 2: Different energy descriptors

Cluster names	ΔE_i (kJ/mol)	ΔE_{ads} (kJ/mol)	ΔE_{des} (kJ/mol)	Δω (kJ/mol)
Mg-(H_2)	-76.13	60.13	64.31	212.46
Mg-$(H_2)_2$	-43.93	58.84	61.00	104.43
Mg_2Ni-$(H_2)_2$	-25.11	40.22	45.72	65.95

ΔEi: Interaction energy, ΔE_{ads}: Adsorption energy, ΔE_{des} Desorption energy, Δω:Reaction electrophilicity

Physical and chemical properties of hydrides: Total electronic energy and thermodynamical stability descriptors such as the hardness, electronegativity and electrophilicity of Mg $(H_2)_2$ and Mg_2 Ni-$(H_2)_2$ are calculated and shown in Table 1 to explore the physical and chemical properties of hydrides.

Electronic Energy (E) of hydrides show increasing trend in Table 1 upon hydrogen captured subsequently which is an indication of addition/bonding hydrogen onreduced metals surface. Electron leaving from parity balance of hydride phases can be measured by chemical potential. Charge transfer stability of hydrides determined by Chemical hardness (η). According to, the stability descriptor principle, most stable hydride show bigger hardness (maximum hardness) and lower electrophilicity (minimum electrophilicity) values (Sibley and Albery, 2001). Thus, Mg-$(H_2)_2$ is stable hydride of Mg-$(H_2)_n$. Mg_2 Ni-$(H_2)_2$ is also stable compare to MgH_2.

Adsorption and desorption energy: Interaction energies between reduced magnesium, magnesium and nickel oxide and hydrogen molecules are reported in Table 2.

Interaction energies between reduced metal surface and hydrogen is in incremental mode. Interaction energies of Mg-$(H_2)_2$ is higher than Mg-(H_2). Moreover, interaction energy of Mg_2 Ni $(H_2)_2$ is -25.11 kJ/mole higher than other hydride phases. Similar trends is observed for hydrogen

adsorption energies shown in Table 2. Favorable hydride system shows ladder like energy phenomena for interaction and adsorption energies which attribute the hydride systems are able to capture possible best number of hydrogen molecules. The range of adsorption energies is 40.22-60.13 kJ/mole that are in chemisorption range.

Mg_2 Ni $(H_2)_2$ show the desorption energy of 45.72 kJ/mole which is less than that of Mg-(H_2). Magnesium Hydride (Mg-H_2) desorb hydrogen at higher temperature than complex hydride of Mg_2 Ni $(H_2)_2$. It is a significant outcome from calculation where Mg_2 Ni $(H_2)_2$ would desorb hydrogen at near ambient conditions. Maximum number of hydrogen loosely captured with Mg that desorb at lower temperature. Reaction electrophilicity is another descriptor to justify the hydrogen adsorption properties. Electrophilicity of Mg_2 Ni $(H_2)_2$ is 65.95 kJ/mole. Decreasing trend of electrophilicity values upon increasing number of captured hydrogen corresponds favorable adsorption system.

It is reasonable to explain the scenario goes behind for such kind of variation of adsorption and desorption. In the case of mixed oxides, the binding energy of the metals are generally replaced to one another. One of them might be more ionic and induce electric field that alternatively occur for second metal. Thus, hydrogen polarized by ionic metals that induces and adsorbs on the metal surface in quasi-molecular form. So, the adsorbed hydrogen can desorb in long range of temperature due to physical and chemical adsorption of hydride phases. Due to the complex hydride system, d-orbital electron of nickel help to dissociate the hydrogen molecules on the metal surface that adsorb and diffuse to bulk layer of the materials. A dipole difference between metals create enough interaction energies and reduce the activation barrier in adsorption process. Nickel catalyzes hydrogen adsorption onto magnesium by enhancing the dissociation of adsorbed hydrogen molecules. After forming a hydride layer, a linear MgH_2 molecule is polarized to be H^{δ}-Mg^{δ}-H^{δ} and molecular hydrogen can be associated to $H^{\delta-}$ and $Mg^{\delta+}$ to form a large cluster via ionic or covalent with the ligands (Wang and Andrews, 2004). Hydrogen capturing on magnesium ground state is difficult. Different states of magnesium (charge and multiplicity) offer to bind with hydrogen molecule easily without showing any imaginary frequency. Mg_2 Ni cannot capture hydrogen in its ground state but two molecules hydrogen can saturate on Mg_2 Ni with a positive charge and doublet state. Two or more hydrogen molecules can be adsorbed on each reduced metal surface with the minimum energy on potential energy surface in special orientation and conditions.

Hydrogen adsorption: Hydrogen adsorption on reduced mixed oxides or clean surface of metals depends on few factors. The reason behind to investigate the mixed oxides of the $Mg_{0.5}Ni_{0.25}Al_{0.25}O_{1.13}$ is detailed out below.

Surface of s-orbital electron and d-orbital electrons of atom/molecule play an important role in dissociation of H_2 on the adsorbent metals surface. H_2 molecules come to the metals surface in the adsorption process. The molecular orbitals of hydrogen ($1s^2$) start to overlap on the metals surface s-orbital electrons. According to the Pauli Exclusion Principle, hydrogen s-orbital electron repel due to the fully occupied valance electron of metals (Mg: $1s^22s^22p^63s^2$), resulting in the energy barrier. The metals with d-orbital electrons contribute in the dissociation of H_2. The electron density of magnesium distribute around the atom with a net charge near of (+2) and the negative charge of H atoms with a value of -0.94-0.26. The rest of electron density is distributed evenly in the interstitial region and showed charge deficiency to form covalent bond. Since, H_2 comes closer to the metal surface, the charge transfer from the H_2 s-orbital to the d-orbital of metal (Ni (28): $1s^22s^22p^63s^23p^63d^84s^2$) surface and simultaneously a back-donation of charge from the surface d-orbital to the H_2 anti-bonding state. Thus, the interaction b between d-orbital of nickel and s-orbital of H_2 enhances the H_2 dissociation on the adsorbent surface with a small energy barrier.

The main group element of Aluminum, (Al (13): $1s^22s^22p^63s^23p^1$) valance electron is three. The electron affinity of Al is -44 kJ/mol and show low affinity to H. Since, the p-state of Al can accommodate electron more it competes with H for the valence electrons of Mg (Mg $1s^22s^22p^63s^2$). The electron affinity of magnesium and hydrogen are 21 and 74 kJ/mol. So, hydrogen binds with weak interaction (lower bonding strength) with the Mg or Mg_2 Ni and form reversible hydride. The technique is considered to decrease desorption energy or decomposition temperature result in forming reversible hydride adsorbent.

The dissociated hydrogen bears enough energy to overcome the diffusion barrier in the adsorbent. Nano crystalline adsorbent allow the dissociated hydrogen to reach the bulk metals surface quickly due to shorter diffusion path compare to the big particle and enhance the adsorption and desorption kinetics. The different electronic structure of adsorbent offers different diffusivity. Therefore, metals selection in synthesizing of mixed oxide adsorbent is very important.

The dissociated hydrogen penetrates into magnesium and rapidly forms a layer of MgH_2 due to the negligible solid solubility of the hydrogen in the

Table 3: Adsorption thermodynamics and kinetics descriptors

Hydride names	ΔHr (kJ/mol)	ΔGr (kJ/mol)	ΔSr (kJ/mol)	k (s-1)
Mg-(H_2)	-48.18	-4.64	-135.00	6.0×10^{12}
Mg-(H_2)$_2$	-43.85	-2.42	-145.13	1.1×10^{12}
Mg_2Ni-(H_2)$_2$	-62.90	-13.41	-155.00	1.3×10^{13}

ΔHr: Reaction enthalpy, ΔGr: Gibb's free energy, k: rate of adsorption at 303 K

magnesium. In the binary and ternary reduced mixed oxides, hydrogen may diffuse along boundaries between the Mg_2 Ni and Mg_3Al_2 phases and inside the Mg_2 Ni phase. The hydrogen might be bonded with different phases of the magnesium compound and the resultant yields are MgH_n and Mg_2 NiH_n.

Hydrogen adsorption kinetics and thermodynamics: The thermodynamic descriptors of hydrogen adsorption of hydride phases such as change of Gibb's free energies (ΔG_r), enthalpy change (ΔH_r) and entropy change (ΔS_{rr}) are calculated to predict the feasibility of hydrogen adsorption on reduced metals surface. Gibb's free energies of Mg-(H_2), Mg-(H_2)$_2$, Mg_2 Ni-(H_2)$_2$ are 4.64,-2.42 and 13.41 kJ/mole, respectively. All values of Gibb's energies are negative correspond the systems are feasible and spontaneous in hydrogen adsorption at room temperature. Enthalpy change of hydride formation of Mg-(H_2), Mg-(H_2)$_2$ and Mg_2Ni-(H_2)$_2$ are -48.18, -43.85 and 62.90 kJ/mole, respectively. An increasing trend of reaction enthalpies and Gibb's energies (ΔG_r) indicating spontaneous hydrogen adsorption and negative enthalpy (Δh_{rr}) values predict the hydrogen trapping on metal surface is exothermic reaction. The range of enthalpy change are in the range (40-200 kJ/mole) of physical and chemical adsorption (Table 3).

System entropy is decreasing upon captured increasing number of H_2 on the reduced surface due to the decrease of freedom of movement of hydrogen. The system show moderate hydrogen adsorption kinetics those are in between physical and chemical adsorption level. The consistent values of different descriptors such as reaction enthalpies, Gibbs free energies and adsorption energies imply that 2 molecules hydrogen can be captured to the reduced nickel and magnesium octahedral side and with its legends without any more special conditions.

CONCLUSION

The DFT calculation on $Mg_{0.5}$ $Ni_{0.25}$ $Al_{0.25}O_{1.13}$ predicted the maximum hydrogen adsorption capacity 7.6 wt.% of H_2 on minimum Potential Energy Surface (PES) of mixed oxides.The Hydrogen adsorption study using the Density Functional Theory (DFT) based Quantum Molecular (QM) reactivity descriptors explored physical and chemical properties of hydrides. Variation of the different reactivity descriptor, enthalpies, Gibb's free energies and rate of constant of adsorption upon the increasing number of captured hydrogen molecules implies the stability of the clusters and feasibility of hydrogen adsorption. Finally, it can be concluded that oxygen vacancies (hydride impurities) or oxygen substitution (structural hydride) might be considered to produce suitable site for hydride formation stabilization. Demonstrated adsorption kinetics and thermodynamics is significant for reversible hydrogen storage materials.

ACKNOWLEDGEMENT

We would like to thanks for the financial support of MOSTI, Malaysia through the FRGS grant of 158-200-092.

REFERENCES

Berlouis, L.E.A., C. Jubin, B.G. McMillan, J. Morrow and M.D. Spicer *et al*., 2007. Enhanced Hydrogen storage in Ni/Ce composite oxides. Phys. Chem. Chem. Phys., 9: 6032-6039.

Frisch, M.J., G.W. Trucks, H.B. Schlegel, G.E. Scuseria and M.A. Robb *et al*., 2009. Gaussian 09, Revision A.1. Gaussian Inc., Wallingford, Connecticut.

Hanada, N., T. Ichikawa and H. Fujii, 2005. Catalytic effect of nanoparticle 3D-transition metals on Hydrogen storage properties in magnesium hydride MgH2 prepared by mechanical milling. J. Phys. Chem. B., 109: 7188-7194.

Hehre, W.J., 1986. Ab Initio Molecular Orbital Theory. John Wiley & Sons Publisher, New York, USA., Pages: 548.

Johansson, M., C.W. Ostenfeld and I. Chorkendorff, 2006. Adsorption of Hydrogen on clean and modified magnesium films. Phys. Rev. B., 74: 45-49.

Kim, H.S., K.S. Cha, B.K. Yoo, T.G. Ryu, Y.S. Lee, C.S. Park and Y.H. Kim, 2010. Chemical hydrogen storage and release properties using redox reaction over the Cu-added Fe/Ce/Zr mixed oxide medium. J. Ind. Eng. Chem., 16: 81-86.

Kumar, T.D., P. Tarakeshwar and N. Balakrishnan, 2009. Geometric and electronic structures of hydrogenated transition metal (Sc, Ti, Zr) clusters. Phys. Rev. B., 79: 205415-205426.

Li, C., X. Xiao, P. Ge, J. Xue and S. Li *et al*., 2012. Investigation on synthesis, structure and catalytic modification of Ca(AlH4)2 complex hydride. Intl. J. Hydrogen Energy, 37: 936-941.

Ochterski, J.W., 2000. Thermochemistry in Gaussian. Gaussian Inc., Wallingford, Connecticut.

Parr, R.G. and R.G. Pearson, 1983. Absolute hardness: Companion parameter to absolute electronegativity. J. Am. Chem. Soc., 105: 7512-7516.

Parr, R.G., L.V. Szentplay and S. Liu, 1999. Electrophilicity index. J. Am. Chem. Soc., 121: 1922-1924.

Pearson, R.G., 1997. Chemical Hardness: Applications from Molecules to Solids. 1st Edn., Wiley-VCH Publisher, Weinheim, Germany, ISBN-10: 3527294821, Pages: 208.

Salam, M.A., S. Sufian and T. Murugesan, 2013. Catalytic Hydrogen adsorption of nano-crystalline hydrotalcite derived mixed oxides. Chem. Eng. Res. Des., 91: 2639-2647.

Salam, M.A., S. Sufian and T. Murugesan, 2013. Characterization of nano-crystalline Mg-Ni-Al hydrotalcite derived mixed oxides as hydrogen adsorbent. Mater. Chem. Phys., 142: 213-219.

Salam, M.A., S. Sufian and Y. Lwin, 2013. Hydrogen adsorption study of mixed oxides using the density functional theory. J. Phys. Chem. Solids, 74: 558-564.

Salam, M.A., Y. Lwin and S. Sufian, 2013. Synthesis of nano-structured Ni-Co-Al Hydrotalcites and derived mixed oxides. Adv. Mater. Res., 626: 173-177.

Sen, K.D. and C.K. Jorgensen, 1987. Electronegativity: Structure and Bonding. Vol. 66, Springer, Berlin, Germany,.

Sibley, R.J. and R.A. Alberty, 2001. Physical Chemistry. 3rd Edn., John Wiley & Sons Publisher, New York, USA.,.

Thomas, K.M., 2007. Hydrogen adsorption and storage on porous materials. Catal. Today, 120: 389-398.

Wang, X. and L. Andrews, 2004. Infrared spectra of magnesium hydride molecules, complexes and solid magnesium dihydride. J. Phys. Chem. A., 108: 11511-11520.

Wiitala, K.W., T.R. Hoye and C.J. Cramer, 2006. Hybrid density functional methods empirically optimized for the computation of 13C and 1H chemical shifts in chloroform solution. J. Chem. Theor. Comput., 2: 1085-1092.