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Global nucleophilicity as electronic property for the study of Hydrogen storage materials capacities

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ABSTRACT

Our aim in the present work is to perform a theoretical study of the efficiency on hydrogen storage of a series of metal functionalized systems by means of global reactivity indices derived from density functional theory, and put in evidence the ability of the nucleophilicity whitch is a simple global index to explain material hydrogen storage. In the present paper theoretical calculations were carried out at the M05-6/6-311+G(d) level of the theory by means of Gaussian 09 software. All systems geometries were optimised at the same level and the global indices were then evaluated using the optimised structures. The studied systems were divided into two series where the first series contained 12 systems MX each (M=Li, Na, K; X=H, AlH_4, BH_4, NH_2) and the second one contained 8 systems MX_2 each (M=Mg, Ca). The obtained results and after comparison with experimental data, showed that nucleophilicity index is directly related to the predicted storage capacities by inversed trends. Considering the obtained results, it can concluded that Density Functional Theory (DFT) derived indices namely nucleophilicity is an important parameter which can be used for modelling and designing a potential new hydrogen storage material.

1. Introduction

We are currently noticing the use of mix energy in all countries of the world. Thanks to their low cost, renewable energies are gradually pushing gas, coal and uranium plants out of the market[1,2]. The rapid growth of renewable energy is causing a growing problem of synchronization between supply and demand [3,4]. Disturbingly, the supply of affordable energy storage is a very complex subject and also a challenge because of the very high prices in the market. Hydrogen is considered as one of the new alternative energy vectors which can be produced from the electrolysis of water [5]. As source of energy, hydrogen is clean and renewable source respecting the environment without releasing greenhouse gas emissions [6–8]. Compared to other actual sources of energy, the hydrogen combustion generates about three times more energy than other fossil fuels[9]. Regarding advantages offered by hydrogen, it can be considered as the best energy source to be developed and investigated [6]. On the other hand, the storage and transport of hydrogen efficiently, safely and without risk, remains a major challenge hindering its wide use and development in the energy field [10]. Currently, many research projects are underway in order to make the use of hydrogen as a safe and efficient source of energy accessible and without risk [11,12] . Hydrogen can be stored by compression in high-pressure gas cylinder, as a liquid in cryogenic tank, or stored in a host material [13,14]. It's highly recommended that researches be conducted, developed, and easily feasible for hydrogen storage purposes, such as gravimetric/volumetric hydrogen storage capacity,

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reversibility of storage, stability use and, cycle life [15]. Very recently, an innovative method of storing hydrogen in solid materials has emerged, enabling hydrogen atoms to be absorbed and stored in metallic matrixes such as metal hydrides, complex hydrides, inter-metallic, organic compounds and porous materials (activated carbons, carbon nanotubes and nanofibers and zeolites) [16–18]. Intermetallic hydrides in complex materials are attracting considerable interest for hydrogen-storage use because of their high gravimetric capacities[19]. However, the release of hydrogen in these materials requires a high temperature due to the chemical bonding of hydrogen in the interstitial sites of the host material for intermetallic compounds or covalent and ionic into the crystal structure of complex hydride

Table 1: Theoretical Gravimetric H_2 Density/Wt% [20]

Chemical hydride	Theoretical gravimetric H_2 density/wt%	
Alkali metals		
Hydride	LiH	12.7
	NaH	4.20
	KH	2.51
Complex hydride	LiAlH$_4$	10.6
	NaAlH$_4$	7.47
	KAlH$_4$	5.75
	LiBH$_4$	18.5
	NaBH$_4$	10.7
	KBH$_4$	7.47
	LiNH$_2$	8.78
	NaNH$_2$	5.17
	KNH$_2$	3.66
Alkaline earth metals		
Hydride	MgH$_2$	7.66
	CaH$_2$	4.79
Complex hydride	Mg(AlH$_4$)$_2$	7.34
	Ca(AlH$_4$)$_2$	7.9
	Mg(BH$_4$)$_2$	14.8
	Ca(BH$_4$)$_2$	11.6
	Mg(NH$_2$)$_2$	7.15
	Ca(NH$_2$)$_2$	5.59

Experimental and theoretical previous studies [20] showed that for two series of intermetallic hydrides in complex materials namely series 1 of alkali metals containing 12 system MX (M=Li, Na, K; X=H, AlH$_4$, BH$_4$, NH$_2$) and second series containing 8 alkaline earth metals complex MX$_2$ (M=Mg, Ca); the first series gave best hydrogen capacities storage   for

lithium complexes succeeded by sodium and potassium complexes classified as the last one. Those finding are noticed for all hydrides results obtained, showing that the BH$_4$ hydrides storage capacities are the best for the three metals. On the other hand and concerning the second series the magnesium complexes present the best storage capacities and where the BH$_4$ hydrides gave the best results as given by experimental results reported in Table 1. Current status of hydrogen capacity storage development research for effective molecular templates able of hydrogen storage at ambient conditions is still a challenging task for the scientific community[21]. The experimental research on the storage of hydrogen is very risky and difficult because of the pressure and the high temperature increasing probability explosion accident[22]. Nowadays, the development of computer tools and computational theories constitute an important and solid alternative for hydrogen storage research by reducing cost and saving considerable time. Among many methods, the density functional theory (DFT) is widely used for designing new material for hydrogen storage[23,24]. In our present paper we use the global DFT derived reactivity indices to prove and justify the experimental results reported in Table 1 and also to permit to researchers a simple tool allowing design of new hydrogen storage materials. To the best of our knowledge, our study is the first and unique one based on nucleophilicity as electronic properties for development of hydrogen storage materials using DFT theory allowing validation of ongoing experimental studies.

2. Materials and Methods

Within the DFT framework one can derive a number of global molecular quantities .The first one is the system electronegativity χ [25,26]

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \qquad (1)$$

μ is the Lagrange multiplier associated with the normalization constraint of DFT [27–29].
Hardness (η) is defined [30] as the corresponding energy second derivative,

$$\eta = \left(\frac{\partial^2 E}{\partial N}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \qquad (2)$$

Softness (S) is the reciprocal of hardness; $S = 1/\eta$.
Using a finite difference method, working equations for the calculation of μ and η may be given as [30]:

$$\mu = -\frac{I + A}{2} \qquad (3)$$

$$\eta = I - A \quad (4)$$

Using Koopmans' theorem[31], μ and η can be written as

$$\mu \approx \frac{\varepsilon_{HOMO} + \varepsilon_{LUMO}}{2} \quad (5)$$

$$\eta \approx \varepsilon_{HOMO} - \varepsilon_{LUMO} \quad (6)$$

The electrophilicity index, as defined by Parr *et al.* [32], is given by

$$\omega = \frac{\mu^2}{2\eta} \qquad (7)$$

The maximum charge transfer is defined as

$$\Delta N_{max} = -\mu/\eta \qquad (8)$$

This quantity can be considered as a measure of the electrophilic power of a system. Domingo et al [33]. introduced an empirical (relative) nucleophilicity index, *Nu*, based on the HOMO energies obtained within the Kohn–Sham scheme [29] and defined as:

$$Nu = E_{HOMO(Nuc)} - E_{HOMO(TCE)} \qquad (9)$$

This nucleophilicity scale takes tetracyanoethylene (TCE) as a reference. This choice allows us to handle a nucleophilicity scale with only positive values [34].

2.1. Computational details

Quantum chemical calculations reported in this work have been performed at M05-6/6-311G+(d) [35,36] level of theory using the Gaussian 09 series of programs [37]. All stationary points found were characterized as true minima by frequency calculations. The molecular geometries of all the systems were optimized.

3. Results and discussion

Global descriptors

HOMO and LUMO energies, global reactivity descriptors such as nucleophilicity (Nu), hardness (η), electrophilicity (ω), chemical electronic potential (μ), and the maximum charge transfer *ΔNmax* for the different metal hydrides and complexes are presented in Table 2.

Obtained result reported in Table 2 show that for the first Alkali metals series (Li, Na and K) the calculated indices for all hydrides and complexes are the same for the nucleophilicity trends. Concerning hydrides series 1; the nucleophilicities are classified in accordance with X=H, AlH$_4$, BH$_4$, NH$_2$. Those latter obtained results are similar for all studied systems by considering the Theoretical Gravimetric H$_2$ Densities Wt% given in Table 1 where the trends are directly inversed i.e. *Nu*(LiX)> *Nu*(NaX)> *Nu*(KX). Regarding first series obtained results we deduce that hydrogen storage capacities of a given system can be linked inversely to its nucleophilicity index. In order to confirm our obtained results we compared the obtained values *μ(au) ω (eV), η(au) , ΔNmax(au), S(au),* for all series, where no indices gave a corresponding trend compared to the theoretical gravimetric H$_2$ densities (Wt%) trends given in Table 1. On the other hand, the classification of the second series theoretical gravimetric H$_2$ Densities (Wt %) given in Table 1 showed that the magnesium hydrides complexes are the best. As consequence of our results reported in Table 2 we deduce that for all cases; the nucleophilicities of the calcium derived systems are greater than the Magnesium derived systems

Regarding Nucleophilicities of the second alkaline earth metals series, we notice that no other indices gave respected trends which this is in good agreement compared to the obtained results for the first series.

Table 2 shows that for all studied systems and considering the same metal hydrides and complexes; M(BH$_4$)n (M=Li,Na,K, Mg, Ca; n=1,2) the nucleophilicity indices values remain the lowest in total accordance to results reported in Table 1. In addition, M(BH$_4$)n derivatives from studied systems presents the greatest values of the theoretical gravimetric H$_2$ densities Wt%. All our obtained results from calculation lead to the same conclusion, where the Theoretical Gravimetric H$_2$ Densities (Wt %) is correlating inversely with the global nucleophilicity indices, excepted the case for M(BH$_4$)$_2$ systems.

Results also show that, for all studied systems and considering the same metal hydrides and complexes; M(BH$_4$)n (M=Li, Na, K, Mg, Ca; n=1,2) the nucleophilicity indices values remain the lowest in total accordance to results reported in Table 1. In addition, M(BH$_4$)n derivatives from studied systems presents the greatest values of the theoretical gravimetric H$_2$ densities Wt%. All our obtained results from calculation lead to the same conclusion, where the theoretical gravimetric H$_2$ densities (Wt %) is correlating inversely with the global nucleophilicity indices.

To more explain our obtained results, the nucleophilicity indices is generally used to explain the capability of a system to get an electrophilic attack or to be linked with a

electrophilic system, in our case the studied systems are all based on a series of metals whitch are known to be the most electrophilic species in the periodic table and they are the most able to reach a positive charge, so the inversed trends founded compared with the nucliophilicities is in good agreement with the chemical properties of the studied systems.

4. Conclusion

In the present paper and regarding the global nucleophilicity index proposed by Domingo *et al.* [33], the relative theoretical gravimetric H_2 densities (wt %) have been qualified which led to the conclusion that for the alkali metals, Li derivatives are better metal hydrogen storage than K derivatives. For the nucleophilicities the trends are inversed. Indeed, in the case of the Li derivatives, the calculations show that the *Nu* values are comprised between 1.75eV and 4.70eV. By contrast, in the case of the K derivatives, the calculations point out that *Nu* values are comprised between 2.79eV and 5.77eV is found the most nucleophile, one comparing with experimental outcomes the K derivatives are found as the less efficient

on H storage with a gravimetric H_2 density/wt% varying fom 2.51% to 7.47,15% compared to Li derivatives that are characterized by the best gravimetric H_2 density/wt% of 8.47% to 18.5%, so for better hydrogen storage materials it's more important to consider the lowest nucleophilicities. The same trends are observed in earth metals derivatives. On other hand, the Mg derivatives are considered as better hydrogen storage with a good gravimetric H_2 density/wt% varying from 7.15% to 14.8% compared to Ca derivatives that are characterized by the lowest gravimetric H_2 density/wt% of 4.49% to 11.06%. It has been also demonstrated that for the same metals the BH_4 complexes are better for hydrogen storage and present also the least nucleophilicity power. Our calculations showed that the gravimetric H_2 densities (wt %) are correctly reproduced and correlate inversely whith the nucleophilicity indices. As a conclusion, we can say that the global nucleophilicity as defined by Domingo's group is suitable for the prediction of the gravimetric H_2 densities wt% of metal hydrides and complexes allowing use of the design for new materials for hydrogen storage.

Table 2: Global indices of the metal hydrides and complexes

System	HOMO(au)	LUMO(au)	μ(au)	ω (eV)	η(au)	ΔNmax(au)	S(au)	*Nu*(eV)
LiH	-0.1994	-0.0478	-0.1236	1.37	0.1515	0.8156	6.59	3.93
NaH	-0.1874	-0.0535	-0.1205	1.47	0.1339	0.8995	7.464	4.26
KH	-0.1596	-0.0521	-0.1059	1.41	0.1075	0.9849	9.29	5.02
MgH$_2$	-0.2604	-0.0258	-0.1431	1.18	0.2345	0.6101	4.26	2.27
CaH$_2$	-0.2116	-0.0678	-0.1397	1.84	0.1437	0.9722	6.95	3.60
LiAlH$_4$	-0.2740	-0.0477	-0.1608	1.55	0.2263	0.7107	4.41	1.90
NaAlH$_4$	-0.2573	-0.0708	-0.1640	1.96	0.1864	0.8797	5.36	2.36
KAlH$_4$	-0.2413	-0.0525	-0.1469	1.55	0.1888	0.7779	5.29	2.79
Mg(AlH$_4$)$_2$	-0.3165	-0.0503	-0.1834	1.72	0.2661	0.6893	3.75	0.75
Ca(AlH$_4$)$_2$	-0.3018	-0.0761	-0.1890	2.15	0.2257	0.8373	4.42	1.15
LiBH$_4$	-0.2796	-0.0499	-0.1648	1.60	0.2297	0.7174	4.35	1.75
NaBH$_4$	-0.2593	-0.0723	-0.1658	2.00	0.1870	0.8870	5.34	2.30
KBH$_4$	-0.2407	-0.0512	-0.1460	1.53	0.1895	0.7705	5.27	2.81
Mg(BH$_4$)$_2$	-0.3379	-0.0446	-0.1913	1.69	0.2932	0.6523	3.41	0.16
Ca(BH$_4$)$_2$	-0.3163	-0.0909	-0.2036	2.50	0.2253	0.9034	4.43	0.75
LiNH$_2$	-0.1711	-0.0368	-0.1039	1.09	0.1342	0.7747	7.45	4.70
NaNH$_2$	-0.1494	-0.0636	-0.1065	1.79	0.0858	1.2408	11.64	5.29
KNH$_2$	-0.1318	-0.0387	-0.0852	1.06	0.0930	0.9165	10.74	5.77
Mg(NH$_2$)$_2$	-0.2223	-0.0387	-0.1305	1.26	0.1835	0.7112	5.44	3.31
Ca(NH$_2$)$_2$	-0.2003	-0.0583	-0.1293	1.60	0.1419	0.9109	7.04	3.91

Conflict of Interest

The authors declare that they have no conflict of interest

Author's contribution

All authors have contributed equally to this paper by collecting data, analysis, performing and writing the paper.

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