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Towards Hydrazine Based Hydrogen Storage Materials Incorporating Late Transition Metals: a DFT Study

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Abstract

Our established method of modeling transition metal based H_2 storage materials is extended to include the desirable and achievable targets of hydrazine linked Cu(I), Cu(II) and Ni(II). Two coordinate Cu(I) H_2 binding site representations bind two H_2 molecules through the reversible Kubas interaction with a theoretical maximum storage capacity of 4.27 %wt.

Keywords: Density Functional Theory; Kubas; Hydrogen Storage;

1. Introduction

Low weight, low volume hydrogen storage still presents a problem for road vehicle applications and there is on going research to obtain a hydrogen storage material that can be incorporated in a system that meets the U.S.A's Department of Energy targets for 2015 of 5.5 %wt, a volumetric storage capacity of 40 g L^{-1} and a 3.3 minute refueling time for a 5 kg tank.[1] It has been calculated that, in order to achieve these targets, a storage material would need a hydrogen adsorption enthalpy in the 20-30 $kJmol^{-1}$ range[2-3] to ensure a sufficiently large room temperature H_2 capacity while allowing H_2 to be easily removed without the need to heat the material. This adsorption enthalpy represents a bond strength somewhere between the covalent bond of metal hydrides and the Van der Waals bond of materials that physisorb hydrogen, such as zeolites and metal organic frameworks. A type of bond that meets this criterion is the Kubas interaction.[4-5] This is a synergic bond between a metal and a H_2 molecule formed of a σ-

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donation from the H-H σ-bonding orbital into a vacant metal d orbital and a π-back-donation from a filled metal d orbital into the σ* anti-bonding orbital of the H_2.

In order to achieve materials that bind H_2 in a Kubas fashion, metal centers have been incorporated into large surface area materials that would otherwise interact with H_2 by physisorption. We have studied materials of this sort, including amorphous silica based materials with benzylated Ti(III) H_2 adsorption sites,[6] and hydrazine linked materials with V(III) and Cr(II) metal binding sites.[7-8] These materials have shown, experimentally, promising adsorption enthalpies that have been reproduced computationally by modeling the binding sites as molecules,[9-10] and also impressive hydrogen storage capacities at room temperature. They are, however, air sensitive and some are pyrophoric; thus it would be advantageous to make hydrazides from less air sensitive late transition metals.

Here we extend our modeling of the hydrazine linked materials to include molecular binding site representations (BSRs) with Cu(I), Cu(II) and Ni(II) centers with between two and six hydrazine based ligands, with the aim of assessing their H_2 binding properties and thus of guiding future experimental work. Homoleptic alkyls or allyls of all of these metals are known,[11-13] and in all cases react with mild proton sources (HX) including alcohols to liberate the hydrocarbon ligand and form compounds of the type MX_n. Thus, treatment of these precursors with hydrazine followed by thermolysis should also lead to elimination of the hydrocarbon ligands, and any remaining ligand should be readily removed by hydrogenation as per the Cr analogue.[7]

2. Computational details

All calculations were performed using spin-unrestricted DFT, with the Perdew-Burke-Ernzerhof (PBE)[14-15] exchange correlation functional. The Gaussian 09 code[16] was used for all geometry optimizations, and the 6-311++G** basis sets[17-23] were used on all atoms. An ultrafine integration grid was used and the RMS force geometry convergence criterion was set to 0.000667 a.u. using IOP 1/7. Stationary points were analyzed by performing analytical frequency calculations.

Atoms in Molecules (AIM) calculations were performed using the AIMALLPro[24] program on the electron densities at the Gaussian optimized geometries. Partial atomic charges were quantified using the Mulliken, Voronoi and Hirshfeld scales. These were calculated at the Gaussian optimized geometries using the Amsterdam Density Functional (ADF) program,[25-27] with the PBE functional, TZ2P basis sets[28-32] on all the atoms, and the parameter controlling the integration grid set to 6.0. Mulliken charges were also calculated using the Gaussian code and Bader charges were taken from the AIMALLPro output.

The average energy of interaction between the metal and the H_2 units (M-H_2) was calculated in ADF as follows. Using the same calculation settings employed for the partial charges, a single point calculation on the geometry of the BSR with H_2 molecules bound (BSR(H_2)$_n$) was performed. Two further single point calculations were then performed breaking the molecule into two fragments; the metal-containing fragment (spin-unrestricted) and the (H_2)$_n$ fragment (spin restricted). The average energy of interaction between the metal and the H_2 units was calculated as

$$E_{H_2}^{int} = \frac{E_{BSR(H_2)_n} - E_{BSR} - E_{(H_2)_n}}{n} \tag{1}$$

E for all species was taken as the SCF energy.

3. Results and discussion

For Ni(II) the octahedral six coordinate BSR is the most stable (Tables 1 and 2). This BSR does not have a vacant coordination site to bind hydrogen. For Cu(II) the four coordinate BSR is the most stable but it was not possible to bind H_2 to this BSR. The implication for experiment is that, assuming hydrazide gels incorporate Ni(II) or Cu(II) centers with their most stable molecular coordination number, they would be poor hydrogen storage materials.

Table 1. Relative energies of the Cu and Ni BSRs with no bound H_2, compared with the two coordinate BSR, corrected for the differences in the number of hydrazine based ligands. /=result not computationally accessible, – = calculation not attempted.

	Relative Energy/kJ mol⁻¹		
Coordination No.	Cu(I)	Cu(II)	Ni(II)
2	0	0	0
3	/	-25.58	-79.35
4	-	-62.07	-113.41
5	-	-56.81	-137.53
6	-	-	-193.54

Table 2. Total energies (H) of the Cu and Ni BSRs with no bound H_2. /=result not computationally accessible, – = calculation not attempted.

|	Total Energy/kJ mol⁻¹		
Coordination No.	Cu(I)	Cu(II)	Ni(II)
2	-1863.093464	-1862.501902	-1730.323820
3	/	-1974.223762	-1842.066159
4	-	-2085.949778	-1953.791250
5	-	-2197.675989	-2065.512555
6	-	-	-2177.246005

For Cu(I) the two coordinate BSR was the only one that could be converged (Table 1) and a maximum of two H_2 molecules were found to bind to it (Table 3 and Figure 1 C) giving it a theoretical storage capacity of 4.27 %wt. The M-H_2 binding energy of the first H_2 molecule, -114.10 kJ mol⁻¹ (Table 3), is higher than those of four coordinate Ti(II) (-46.22 kJ mol⁻¹), V(II) (-37.33 kJ mol⁻¹) and Cr(II) (-37.75 kJ mol⁻¹) BSRs with hydrazine ligands studied previously.[10] However, the energy of the separated BSR

and H_2 is essentially the same as that of the complex with one bound H_2 (Figure 1 B, +5.6 kJ mol^{-1} *vs* separated BSR and H_2), suggesting that H_2 binding should be an easily reversible process. In addition, our previous Cr hydrazide material,[7] even with a M-H_2 interaction energy of over 40 kJ mol^{-1}, only achieved a storage capacity of 3.2 %wt at 298 K without saturation at 170 bar. Therefore, even though the present M-H_2 interaction energy is much higher than the ideal hydrogen storage enthalpy for room temperature applications, a higher M-H_2 interaction (> ~40 kJ mol^{-1}) may be desirable in materials of this type, where the amount of hydrogen stored depends on the pressure applied, such that higher H_2 capacities are achieved at lower pressures (*i.e.* less than 170 bar).

Table 3. H-H bond lengths, stretching frequencies, BCP electron densities and average M-H_2 interaction energies for the 2 coordinate BSRs. /=result not computationally accessible. [a] $2 \times$ Cu-H

	Cu(I)		Cu(II)		Ni(II)	
No. of H_2 bound	1	2	1	2	1	2
H–H bond lengths/Å	0.877	0.808	[a]	0.809	0.847	0.832
		0.821		[a]		0.832
H–H stretching frequencies/cm^{-1}	2720	3460	N/A	3457	2996	3185
		3298		N/A		3146
H-H BCP densities/e bohr^{-3}	0.195	0.223	N/A	0.224	0.206	0.212
		0.217		N/A		0.212
M-H_2 interaction energies/kJ mol^{-1}	-114.10	-56.37	-502.22	/	-59.24	-60.36

The bulk of the gel, which has not been modeled, may permit metal coordination geometries other than the most stable found for isolated molecules. If this were the case and two coordinate binding sites were generated for Ni(II) and Cu(II), then this would alter the hydrogen storage properties of the materials. For example, the two coordinate Cu(II) BSRs bind up to two H_2 molecules with the first as two hydride ligands (Figure 1 F). Extrapolation to the bulk implies that half of the H_2 would be irreversibly bound so this is not encouraging. However, the Ni(II) two coordinate BSR binds up to two H_2 molecules in a similar fashion to the Cu(I) BSR (Figure 1 I), giving a theoretical storage capacity of 6.76 %wt; potentially useful for H_2 storage.
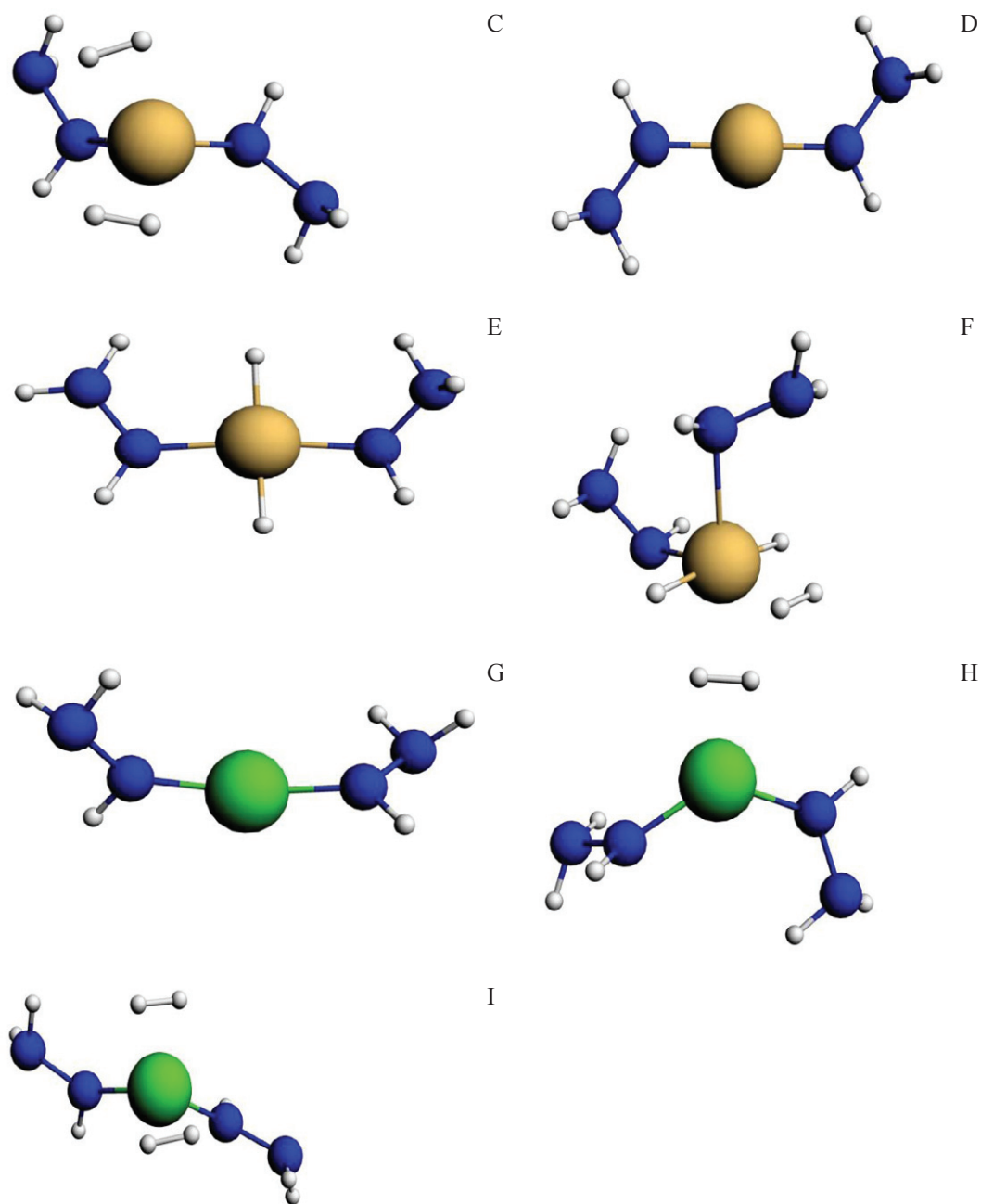

A

B
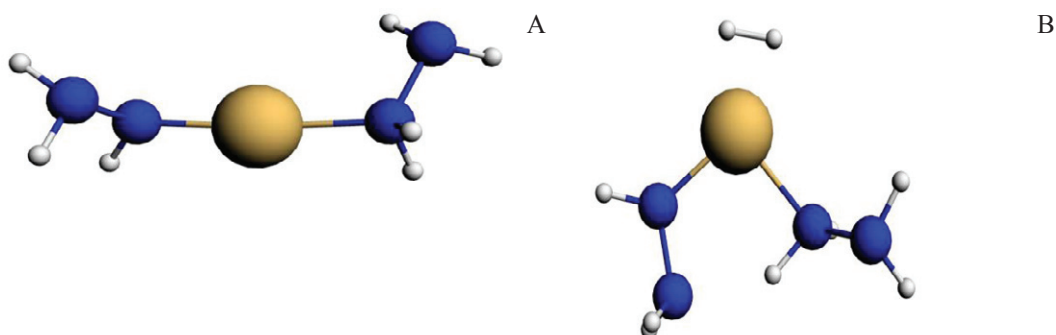
Fig. 1. Optimised geometries of BSRs of Cu(I) with A 0, B 1 and C 2 H_2 bound; Cu(II) with D 0, E 1 and F 2 H_2 bound; Ni(II) with G 0, H 1 and I 2 H_2 bound.

The Kubas interaction is characterized experimentally by a lengthening of the H-H bond without breakage and a simultaneous lowering of its stretching frequency. Here, the H_2 bond lengthens upon binding to the two coordinate Ni(II) and Cu(I) from its free value[10] of 0.752 Å to between 0.808 and

0.877 Å with a corresponding lowering of its stretching frequency from its free value[10] of 4317 cm^{-1} to between 3460 and 2720 cm^{-1} (Table 3). Molecular orbitals are present featuring the two synergic components of the Kubas interaction, the π-back donation (Figure 2 A) and the σ-donation (Figure 2 B).
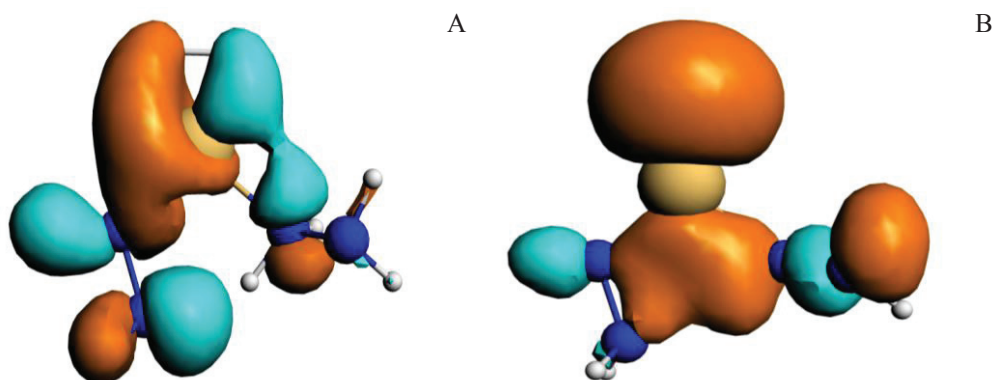

Fig. 2. Molecular orbitals of the Cu(I) BSR with 1 H$_2$ bound showing A HOMO-2 and B HOMO-26.

AIM theory tells us that two atoms are considered to be bonding when there is a bond critical point (BCP) between them. The BCP is the minimum on the line of maximum electron density connecting two nuclei (the bond path), and is a maximum in a plane perpendicular to the bond path. The electron density at the BCP is typically correlated with the strength of the bond, and values greater than ca. 0.2 e bohr^{-3} are taken to indicate covalent bonding. During Kubas binding the electron density at the BCP of the H$_2$ molecule reduces from its free value[10] of 0.256 e bohr^{-3}. Here the density lies between 0.195 and 0.223 e bohr^{-3} for the Ni(II) and Cu(I) BSRs (Table 3). We have previously benchmarked the electron density at the BCP of the H-H bond of the bound H$_2$ in some classically Kubas systems[10] and found it to be between 0.202 and 0.219 e bohr^{-3}. The range for the present Ni and Cu BSRs is comparable with the classically Kubas systems, by contrast to the early transition metal systems we have previously studied, in which the H-H BCP density was less reduced from the value for free H$_2$.[10] This is consistent with the stronger M-H$_2$ interactions found here for Ni and Cu.

In our previous work on early transition metals we found either a balance between the two synergic components of the Kubas interaction, or that σ-donation is slightly the stronger,[9-10] as have others.[33] Figure 3 indicates that the partial charge on the formally Cu(I) center either does not alter significantly or becomes slightly more positive as more H$_2$ molecules are bound, depending on the charge analysis method employed. This suggests that the M-H$_2$ interaction is a balance between the two synergic Kubas components or perhaps that the interaction has a slight excess of π-back-donation. This has been seen by Eckert *et al.* with extra framework Cu(I) binding hydrogen in zeolites.[34] π-back-donation could be even more substantial for Ni(II), for which almost all measures of the metal's partial charge become more positive as more H$_2$ molecules are bound (Figure 4).
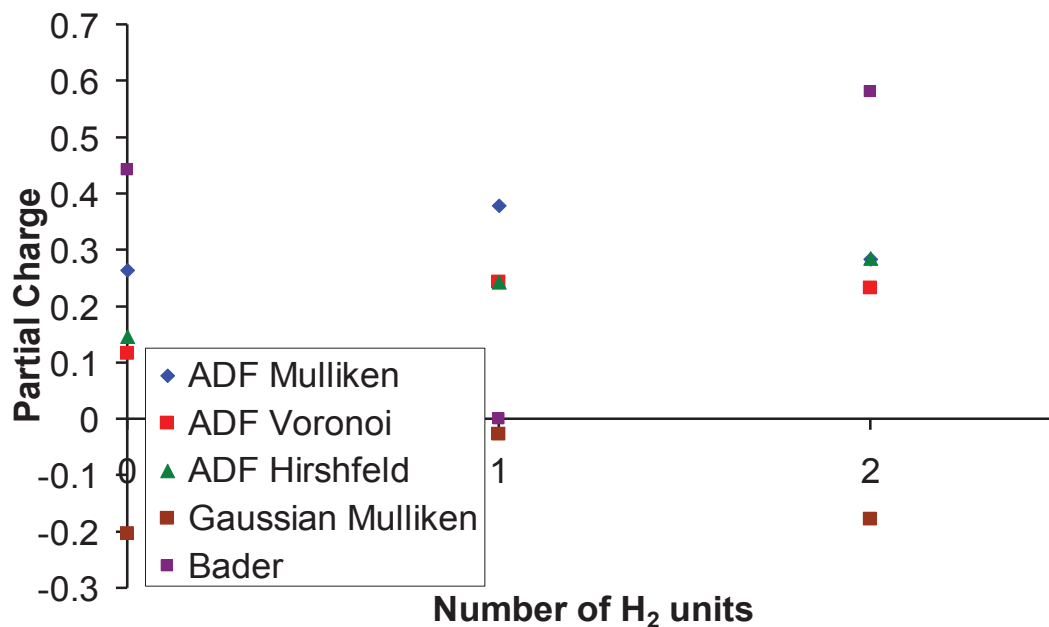
Fig. 3. Partial charge on the Cu atom of the two coordinate Cu(I) BSR as a function of the number of H$_2$ units bound.
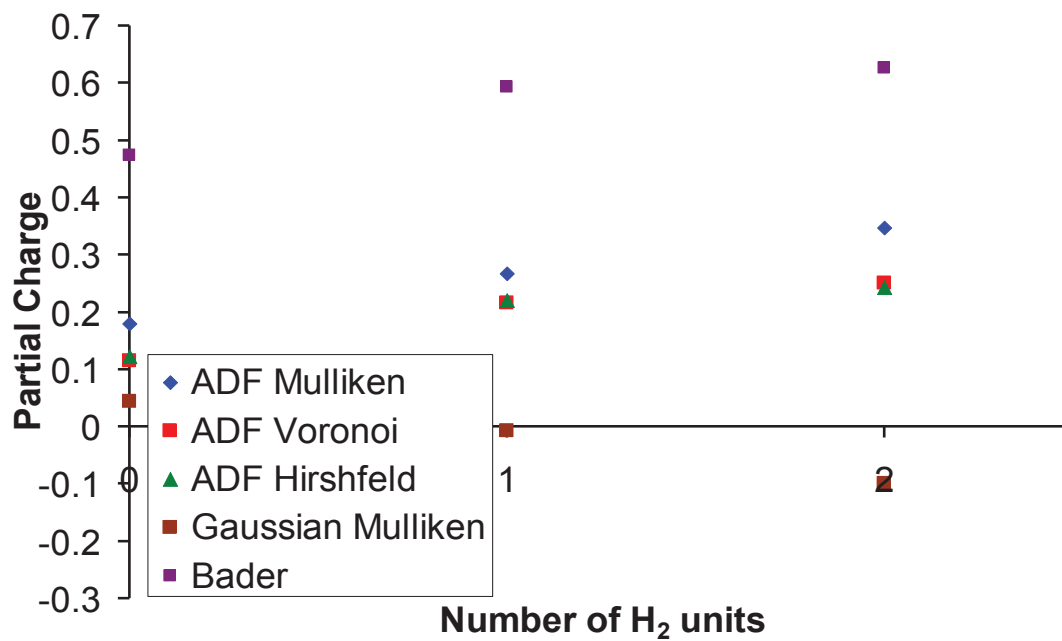

Fig. 4. Partial charge on the Ni atom of the two coordinate Ni(II) BSR as a function of the number of H$_2$ units bound.

4. Conclusion

In conclusion, a computational study of Cu(I), Cu(II) and Ni(II) analogues of experimentally realized V(III) and Cr(II) hydrazine linked systems has been undertaken, as systems incorporating later transition metals have the potential benefit of being much more stable than those with early transition metals. The calculations suggest that the H_2 binds to the metal centers through the Kubas interaction and that its synergic nature compensates for the fewer unfilled d orbitals of the later transition metals such that the π-component of the M-H_2 bond is the stronger. The overall interaction is as strong as in classically Kubas systems. We suggest that two coordinate binding sites would be most stable for Cu(I) and that two H_2 molecules could bind to them with high enthalpy. These potentially experimentally realizable gels could be stable, high capacity hydrogen storage materials, cheaper than our previous early transition metal analogues, and with this in mind we are exploring their synthesis and characterization.

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