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Bonding of H atoms to Ir_4 clusters: the effect of Mg^{2+} ions

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We present local-density-approximation calculations of atomic hydrogen adsorption on tetrahedral Ir_4 clusters. The hydrogen atom prefers twofold or threefold coordination. The effect of the presence of a Mg^{2+} ion next to the Ir_4 on the adsorption is studied. It changes the calculated adsorption energy by less than 10%, but the Ir–H stretch frequencies may change as much as 25%. A comparison with earlier results of H_2 adsorption on the same tetrahedral Ir_4 clusters supports the hypothesis that polarization of the metal particle by a Mg^{2+} ion in zeolites promotes H_2 dissociation.

1. Introduction

The chemical reactivity of small metal clusters in zeolites is of practical and fundamental interest [1]. They are active hydrocarbon-conversion catalysts. Zeolites are alumino-silicates having a large internal surface. The negative charge of the zeolite lattice is compensated for by positively charged ions in the zeolite micropore. The catalytic activity of metal particles embedded in zeolite cavities has been reported to be a strong function of cation charge [2]. If cations of low charge are replaced by cations of high charge, the rate of hydrocarbon conversion may increase by an order of magnitude. This has been found especially for the zeolites X and Y [3,4].

In order to explore a possible explanation, we have initiated a quantum-chemical study of CO, H_2 and H adsorption on a Ir_4 particle in the presence and absence of a Mg^{2+} ion. Earlier, we reported the results of local-density-approximation calculations on the effect of a Mg^{2+} ion on CO and H_2 adsorption [5–7]. For a configuration with the CO adsorbed to the Ir_4 cluster opposite the Mg^{2+} ion, we found significant changes in the CO stretch frequencies but no change in CO adsorption energy. In distinction from CO, the adsorption energy of H_2 was found to be significantly affected by the presence of a Mg^{2+} ion.

For the particular adsorption geometry chosen, changes in adsorption energy are due to polarization of the metal particle by the cation. The Mg^{2+} polarizes the Ir_4 particle so that a negative charge develops on the cluster atoms close to the Mg^{2+} ion screening the cation. The resulting electron-density reduction between metal particle and adsorbate decreases repulsion between doubly occupied adsorbate and cluster orbitals. This is the dominating effect in the case of H_2 adsorption and results in an increase of the adsorption energy. For chemisorbed CO, this effect is counteracted by a reduced interaction with the $2\pi^*$ orbital. In order to estimate the effect of a Mg^{2+} ion on the dissociation of the H_2 molecule, the H_2-molecule-adsorption calculation will be compared with results for hydrogen-atom adsorption.

2. Computational details

We have done non-relativistic, restricted calculations using the local-density-approximation with the $X\alpha$ exchange-correlation potential ($\alpha=0.7$) using the implementation of Baerends' group [8]. Molecular orbitals are represented as linear combinations of atomic Slater-type orbitals. Integrals are computed numerically, and adsorption energies are computed with the Ziegler transition-state method [9].

For magnesium, the 1s core is kept frozen, and so are the orbitals for iridium electrons up to the 4f. The

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exponents of the STO basis sets and fitting functions we used in our calculations can be found elsewhere [6]. Single-ζ functions are used for core orthogonalization. The valence functions are of double-ζ quality with a triple-ζ d for iridium. Polarization functions have been added for iridium and hydrogen.

Fig. 1 shows the three Ir_4–H clusters studied, with and without a Mg^{2+} ion. The distance between two iridium atoms is taken equal to the nearest-neighbour distance in the bulk, 2.71 Å [10]. For this Ir–Ir distance, the calculated heat of formation of an Ir_4 cluster is −28.72 eV. The calculated cluster equilibrium distance from a quadratic fit is 2.695 Å with a calculated heat of formation of −28.74 eV, indicating that the cluster equilibrium Ir–Ir distance is in good agreement with the nearest-neighbour distance in the bulk. The distance between the Ir atoms and the Mg^{2+} ion is taken to be equal to the ionic radius (0.66 Å) [11] plus half the Ir–Ir distance (1.36 Å). The distance between the H atom and nearest-neighbour Ir_4 atoms has been optimized. The Mg^{2+} ion is located on the opposite side of the metal particle that is accessible to the adsorbing atom.

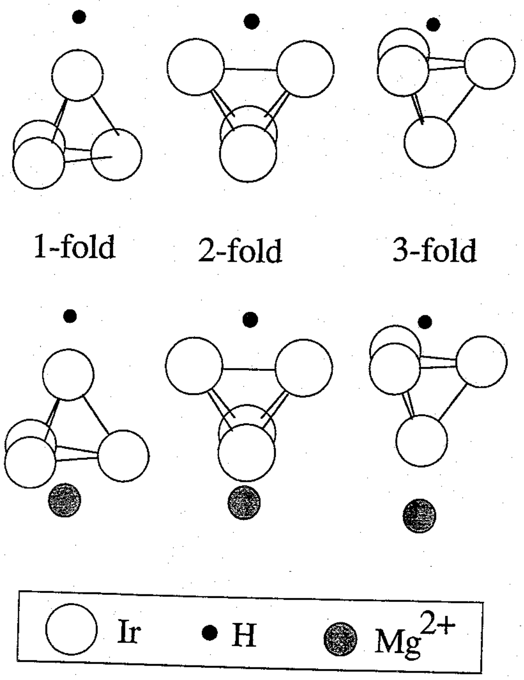

Fig. 1. Geometries of the three Ir_4H systems and the three Mg^{2+}–Ir_4H systems that have been studied.

One gets an estimate of the numerical error in the calculated adsorption energies from calculating the adsorption energy of a hydrogen atom and a Mg^{2+} ion on Ir_4 cluster in two different ways: In one case, Mg^{2+} is first adsorbed on Ir_4 and then H on Mg^{2+}–Ir_4. In the other case, H is first adsorbed on Ir_4 and then Mg^{2+} on Ir_4–H. The sum of the two adsorption energies thus obtained should be the same in both cases. The maximum difference between the two adsorption energies is 0.1 eV, and we thus estimate the error in our calculation at about 0.1 eV.

3. Results and discussion

The results of the H adsorption in the geometries of minimal energy are shown in tables 1, 2, and 3. The adsorption energy is defined as

$$\Delta E_{\text{ads}} = E(\text{Ir}_4\text{H}) - E(\text{Ir}_4) - E(\text{H}) ,$$

for the calculations without the Mg^{2+}, and as

$$\Delta E_{\text{ads}} = E(\text{Mg}^{2+}\text{–Ir}_4\text{H}) - E(\text{Mg}^{2+}\text{–Ir}_4) - E(\text{H}) ,$$

for the calculations with the Mg^{2+}. When comparing the three adsorption geometries, we see that the hydrogen atom has a strong preference for the twofold or threefold adsorption site over the onefold adsorption site. The adsorption energies for the twofold and the threefold sites are very close. The total adsorption energy depends only slightly on the presence of a Mg^{2+} ion. For the onefold adsorption ge-

Table 1
Calculated properties of Ir_4H and Mg^{2+}–Ir_4H for the onefold H geometry

	Without Mg^{2+}	With Mg^{2+}
electronic configuration	$a_1^{10}a_2^2e^{25}$	$a_1^{14}a_2^2e^{29}$
d(Ir–H) (Å)	1.64	1.64
ΔE_{steric} (eV)	2.02	1.89
ΔE_σ (eV)	−1.28 (−4.77)	9.61 (−4.21)
ΔE_π (eV)	−3.60 (−0.11)	−14.09 (−0.27)
ΔE_δ (eV)	0.00 (0.00)	0.00 (0.00)
ΔE_{int} (eV)	−4.88	−4.48
ΔE_{ads} (eV)	−2.86	−2.60
gross population H(1s)	0.93	0.75
ω of H (cm^{-1})	2337	1733

Table 2
Calculated properties of Ir_4H and Mg^{2+}–Ir_4H for the twofold H geometry

	Without Mg^{2+}	With Mg^{2+}
electronic configuration	$a_1^{14}a_2^6b_1^9b_2^8$	$a_1^{18}a_2^6b_1^{10.14}b_2^{10.86}$
d(Ir–H) (Å)	1.82	1.81
ΔE_{steric} (eV)	3.94	3.09
ΔE_σ (eV)	−4.46 (−7.69)	6.51 (−6.85)
ΔE_π (eV)	−3.47 (−0.24)	−13.68 (−0.32)
ΔE_δ (eV)	−0.01 (−0.01)	0.00 (0.00)
ΔE_{int} (eV)	−7.93	−7.17
ΔE_{ads} (eV)	−4.02	−4.11
gross population H(1s)	0.81	0.79
ω of H (cm^{-1})	1975	2002

Table 3
Calculated properties of Ir_4H and Mg^{2+}–Ir_4H for the threefold H geometry

electronic configuration	$a_1^{10}a_2^{2.57}e^{24.43}$	$a_1^{14.95}a_2^2e^{26.05}$
d(Ir–H) (Å)	1.91	1.91
ΔE_{steric} (eV)	5.17	3.34
ΔE_σ (eV)	−5.68 (−8.73)	−6.40 (−7.10)
ΔE_π (eV)	−1.56 (−0.24)	−0.87 (−0.17)
ΔE_δ (eV)	−1.82 (−0.09)	0.00 (0.00)
ΔE_{int} (eV)	−9.06	−7.27
ΔE_{ads} (eV)	−3.91	−3.94
gross population H(1s)	0.84	0.86
ω of H (cm^{-1})	2538	2384

ometry, this dependence is the largest, and is shown in fig. 2a. For the threefold adsorption geometry, this dependence is much smaller, as shown in fig. 2b. The contribution of the zero-point energy to the adsorption energy is of the same order as the error in our calculations (≈0.1 eV), and is ignored in this discussion. The Xα method generally suffers from overestimating adsorption energies. Together with the fact that the surface is modelled by a small cluster, the agreement between the calculated adsorption energies and the experimental values is expected to be poor.

The adsorption energy can be decomposed in two main contributions:

$$\Delta E_{ads} = \Delta E_{steric} + \Delta E_{int} .$$

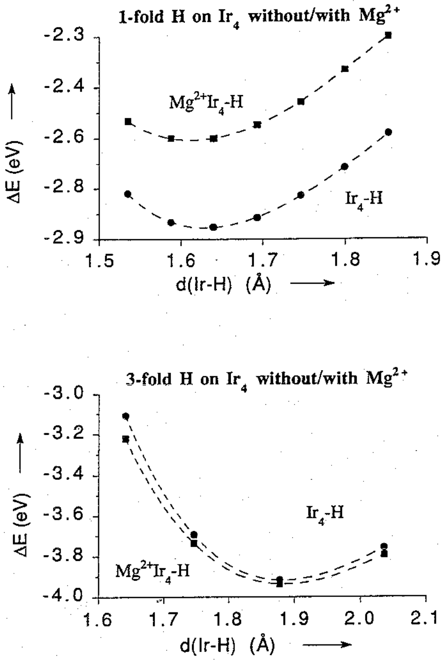

Fig. 2. Adsorption energies for various Ir–H distances for the onefold hydrogen adsorption on Ir_4 and Mg^{2+}–Ir_4 and for the threefold hydrogen adsorption on Ir_4 and Mg^{2+}–Ir_4.

Here, ΔE_{steric} is the energy change due to superposition of Ir_4 and H without changing their molecular orbitals. This can be considered the contribution due to steric repulsion. The steric repulsion is much larger for two- and three-fold adsorption than for the onefold, simply because the hydrogen atom in the two- and three-fold position is in contact with more iridium atoms than in the onefold position.

The other term, ΔE_{int}, is the interaction energy. This interaction energy can be split into various symmetries:

$$\Delta E_{int} = \Delta E_\sigma + \Delta E_\pi + \Delta E_\delta .$$

The changes in the orbital interaction energies shown in the tables are partly due to the fact that the number of electrons in an orbital with a certain symmetry changes with respect to Ir_4 and H or Mg^{2+}–Ir_4 and H at infinite separation. We can estimate the various symmetry contributions by transferring the electrons back to their original orbital [5]. The resulting values are the ones in parentheses in tables 1 through 3. We see that the σ orbitals are stabilized the most, the π orbitals are stabilized very little and the δ orbitals not at all. The latter orbitals do not participate actively in the bond formation.

In contrast to the total adsorption energy, the steric repulsion and the total orbital interaction show a strong dependence on the presence of the Mg^{2+} ion. In the presence of a Mg^{2+} ion, the steric repulsion, as well as the total attractive orbital interaction, decreases. These changes cannot be explained from a change in the adsorption geometry; thus, the Ir–H distance is found not to change. The reduction of the steric repulsion is caused by the polarization of the cluster by the cation, which moves electrons away from the adsorption site. This polarization also makes it harder for the cluster orbitals to interact with the H 1s-orbital, as the formation of a chemical bond has to shift the electron density in the cluster to a less favourable one for the interaction with the cation. The cancellation of the two effects is accidental. The calculated hydrogen stretch frequency for the onefold and threefold hydrogen adsorption shows also a strong dependence when a Mg^{2+} ion is present. For CO adsorption, we showed that the polarization of the cluster leads to a flatter well for the metal–carbon bond. The same mechanism is working here. The effect is, however, subtle, and for twofold adsorption, hardly any change in stretch frequency is found. For hydrogen adsorption on iridium, there exists no known experimental value for the stretch frequency. The calculated stretch frequencies for the twofold and threefold geometries seem to be rather large when compared to adsorption on other transition metals, for example, the frequencies obtained with inelastic neutron-scattering spectroscopy for the hydrogen adsorption on Ni [12], on Pd [13], and on Pt [14].

Figs. 3a–3c present H(1s) local-density-of-states (LDOS) on the different clusters. Of interest is the upward shift in average peak position for occupied levels when the coordination of the hydrogen atom decreases. This agrees with the trend predicted based on the concept of group orbitals [15]. The H 1s-orbital interacts with cluster orbitals, σ symmetric with respect to the hydrogen–metal particle symmetry axis. In high coordination, this constrains the interaction to low-energy orbitals, whereas in lower coordination, also higher-energy orbitals contribute [16]. The shift for onefold adsorption in average local density to higher energies when a Mg^{2+} ion is present agrees with the observed bond weakening. It is the effect of the increased energy difference between cluster and adatom orbitals that weakens the covalent interaction. For the two- and three-fold adsorption, this energy difference increases much less, as the distance between H and Mg^{2+}, and between Mg^{2+} and the Ir atoms that interact with H is almost the same. Hence, the small change in the LDOS for these adsorption geometries.

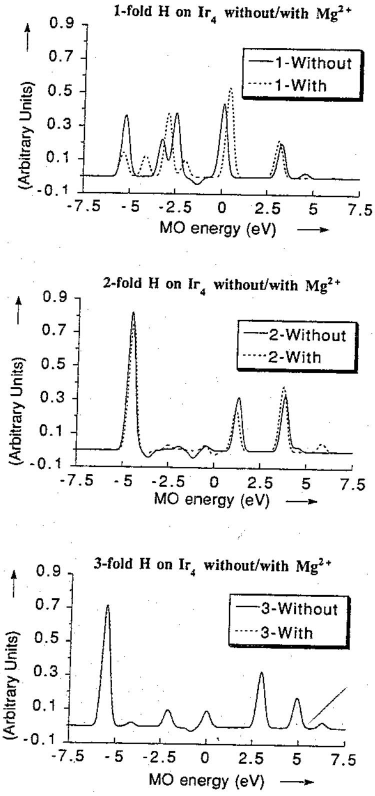

Fig. 3. Hydrogen 1s local-density-of-states (LDOS) for the onefold, twofold, and threefold hydrogen adsorption on the Ir_4 cluster without and with Mg^{2+}. For the threefold adsorption geometry, the LDOS calculated without and with the Mg^{2+} almost coincide.

Electron-density difference maps of all the geometries studied are shown in fig. 4. Some polarization of the hydrogen–metal bond density towards the Ir_4 cluster by the Mg^{2+} ion can be seen. However, these effects are small, in accord with the LDOS figures.

In a previous paper, we found that the adsorption energy of H_2 increases (in the absolute sense) when the cation is present [6]. Together with the results

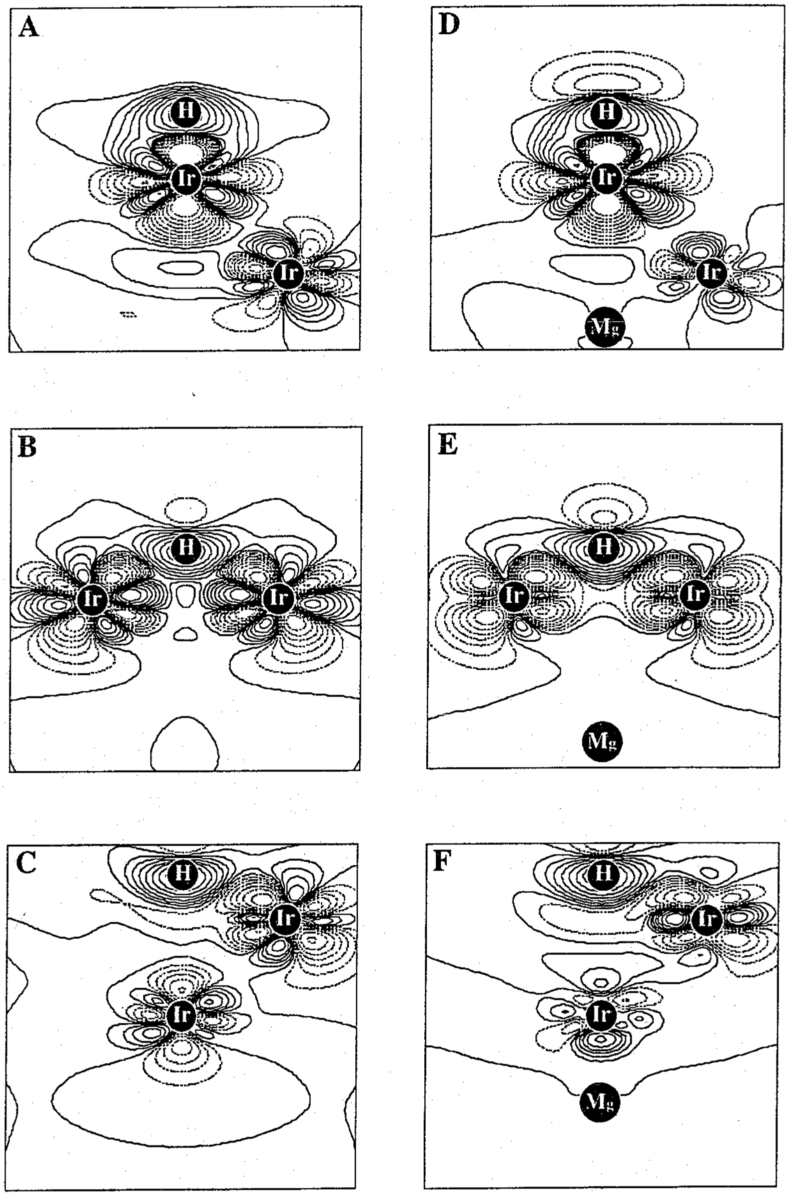

Fig. 4. Contour plots of the electron-density differences $\rho(Ir_4H)-\rho(Ir_4)-\rho(H)$ and $\rho(Mg^{2+}\text{-}Ir_4H)-\rho(Mg^{2+}\text{-}Ir_4)-\rho(H)$. Dashed lines show a decrease, solid lines an increase of the electron density, except for the solid lines next to dashed lines which depict nodal surfaces. Subsequent contours correspond to ±0.010, ±0.022, ±0.037, ±0.059, ±0.090, ±0.135, ±0.202, ±0.303, and ±0.452 electrons per Å^3. Shown are the contour plots for the onefold (A), twofold (B), and threefold (C) hydrogen adsorption on Ir_4 without Mg^{2+}, and the contour plots for the onefold (D), twofold (E), and threefold (F) hydrogen adsorption on Ir_4 with the Mg^{2+}.

for the H atom presented here, we find that the overall activation energy for H_2 adsorption and dissociation with respect to the gas phase should decrease, as predicted by the relation of Polanyi [2].

4. Conclusions

The local-density-approximation studies of hydrogen adsorbed to Ir_4 clusters show a small decrease in hydrogen-bond strength in the presence of a Mg^{2+} ion. The maximum decrease is 0.26 eV for a top-adsorbed hydrogen. For stronger bounded hydrogen atoms adsorbed in high coordination sites, only very small changes in bond strength are found.

As a result, the heat of dissociative adsorption for the particular clusters studied of hydrogen to Ir_4 particles will not change. For the particular cluster studied, the overall activation energy with respect to the gas phase is predicted to decrease due to the increased heat of adsorption of the H_2 molecule.

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