Ag⁺ and Cu⁺ Cations Ligated by Zeolite Environment Enhancing Hydrogen Activation – ETS-NOCV Charge-Transfer Analysis

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Adsorption and activation of molecular hydrogen on cationic sites in zeolites was studied by performing theoretical analysis. of charge-transfer between various parts of a three-component complex system (H₂, silver or copper cation and a zeolite treated as a generalized ligand). ETS-NOCV analysis resolved electron density redistribution accompanying complex formation into independent electron transfer channels: electron donation from $\sigma(\text{H-H})$ to 4s (Cu) or 5s (Ag) orbitals, backdonation from 3d _{π} (for Cu) or 4d _{π} (for Ag) to $\sigma^*(\text{H-H})$ antibonding orbital and electron transfer into the bonding region between hydrogen and cation. All three electron transfer channels strengthen the bonding of hydrogen molecule while the first two are responsible for H-H bond activation. By embedding in zeolite framework donation of electrons from hydrogen bonding orbital is reduced and backdonation to hydrogen antibonding orbital is enhanced compared to free cations, stronger for Cu⁺ than for Ag⁺. This result rationalizes why copper sites in zeolites are exceptionally good absorbers and activators for hydrogen.

Keywords: DFT modeling, Hydrogen adsorption and activation, Electron transfer analysis, ETS-NOCV method, Zeolite, Copper and silver cationic sites, Donation and backdonation

1 Introduction

Interaction of hydrogen with adsorption or catalytic centers is a key issue from the point of view of storage, purification and activation leading to dissociation or to other reactions. Thus as well the binding energy as the activation of hydrogen molecule are of crucial importance here. Cationic sites are among the most promising adsorption centers leading to purification, storage or activation of hydrogen. In this aspect, zeolites and other microporous (nanoporous) materials equipped with cationic sites, are considered as possible materials, not only hosting cations but also strongly influencing their properties by the interaction with zeolitic framework. Since it has been revealed that Cu (I) sites in zeolite ZSM-5 exhibits unusual ability to bind H₂ [1], the H₂-Cu⁺ interaction has been widely investigated.[2–3,4] Present work illustrates decomposition of the interaction energy between copper or silver cations and hydrogen molecule into

meaningful components as well as important contributions to this interaction brought about by embedding in zeolitic framework. The role of zeolitic environment in modifying cationic properties and thus the electronic processes underlying hydrogen activation is explained by decomposing electron density flow between the molecule and the cationic site into independent electron transfer channels. Our results rationalize clearly why zeolitic framework strongly enhances as well adsorption as activation of hydrogen by coinage metal cations and explain why copper sites exhibit unusual ability to bind H₂.

2 Methodology

As models of cationic sites we used bare cations of silver (I) and copper (I) as well as cations coordinated to [Al (OH)₄][−] tetrahedral anion (T1) as the simple mimic of zeolitic environment. In accord with already accepted view, hydrogen molecule

Figure 1. Models presenting H_2 interacting with bare cations (left) or M (T1) (right); M stands for “Cu” or “Ag”

is bounded side-on either with bare cations or with cation sites (Figure 1): $(\eta^2-H_2) Ag^+$, $(\eta^2-H_2) Cu^+$, $(\eta^2-H_2) Ag(T1)$, $(\eta^2-H_2) Cu(T1)$.

Electronic structure calculations, geometry optimization and vibrational analysis has been done with Turbomole package [5] at DFT/B3LYP level with def2-TZVP basis set. The difference between electron density of the composed system and the sum of densities of non-interacting fragments, in the geometries they take in the complex (deformation density $\Delta\rho$), may be represented by deformation density matrix $\Delta\mathbf{P}$. Natural Orbitals for Chemical Valence (NOCV) are defined as the eigenvectors, ψ_i (appropriate combinations of fragment molecular orbitals ϕ_j), diagonalizing deformation density matrix, $\Delta\mathbf{P}$:

$$\Delta\mathbf{P}\mathbf{C}_i = \lambda_i\mathbf{C}_i$$

where $\mathbf{C}_i$ is a vector of the coefficients expanding ψ_i in the basis of N orthogonalized fragment orbitals ϕ_j , and λ_i is the i -th eigenvalue, a descriptor for the number of electrons transferred along selected channel. Deformation density can be expressed as a sum of pairs of complementary orbitals (ψ_{-k} , ψ_k) corresponding to eigenvalues equal in absolute value, but opposite in signs [6,7,8,9] that define independent density transfer channels ($\Delta\rho_k$):

$$\Delta\rho(r) = \sum_{k=1}^{N/2} \lambda_k [-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{N/2} \Delta\rho_k(r)$$

NOCV decomposition of the differential density given by above equation may be linked to Ziegler-Rauk energy decomposition approach (Extended-Transition-State, ETS) [10,11]. Within this scheme total interaction energy between two frag-

ments may be decomposed into the following terms:

$$\Delta E_{\text{int}} = \Delta E_{\text{dist}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$$

ΔE_{dist} is the energy needed to change the geometry of non-interacting fragments to the one they take in the complex and ΔE_{Pauli} is associated with repulsion of closed shells of fragments thus both terms are destabilizing. Next two terms are stabilizing: ΔE_{elstat} is an energy of interacting between electron densities on both fragments (promolecules) and ΔE_{orb} is an orbital interaction energy of the fragments, including inter- and intrafragment polarization. By applying ETS-NOCV method the last term (ΔE_{orb}), describing the part of adsorption energy due to direct electronic interactions may be decomposed into contributions corresponding to independent electron transfer channels, spanning deformation electron density.

ETS-NOCV analysis, linking the Extended Transition State (ETS) approach with the Natural Orbitals for Chemical Valence (NOCV) method [6–11] has been done for all studied systems within partition scheme into two fragments (S1//S2) in which hydrogen molecule was one fragment and the rest of the system, modeling free or embedded cation was the second fragment: $(\eta^2-H_2)//Ag^+$, $(\eta^2-H_2)//Cu^+$, $(\eta^2-H_2)//Ag(T1)$, $(\eta^2-H_2)//Cu(T1)$. For the models of cationic sites, we performed additional ETS-NOCV analysis for partition scheme in which hydrogen molecule and the cation stand for one fragment and T1 for the second one (modeling zeolite environment): $(\eta^2-H_2) Ag//(T1)$, $(\eta^2-H_2) Cu//(T1)$ – this fragmentation describes electronic interaction between hydrogen molecule bound to the cation and zeolitic framework where bridging oxygens act as generalized ligand to the cation.

Table 1. Experimental (Δv_{exp}) and calculated (Δv_{calc}) red-shifts of H-H stretching frequency, calculated elongation of H-H bond upon interaction (Δr_{calc}), calculated distances between a cation M and hydrogen atoms (R (M-H))

	ref.	{Cu (η^2 -H ₂)} ⁺	{Cu (η^2 -H ₂)}(T1)	{Ag (η^2 -H ₂)} ⁺	{Ag (η^2 -H ₂)}(T1)
Δv_{exp} (H ₂)/cm ⁻¹	a,b		-1082 ^a		-861 ^b
Δv_{calc} (H ₂)/cm ⁻¹	#	-600	-1133	-442	-769
	c	-	-	-430	-781
	d	-629, -624	-1207, -1129	-	-
	e	-	-1471	-	-845
Δr_{calc} (H ₂)/Å	#	+0.042 - -	+0.077	+0.031 - -	+0.051
	e		+0.107		+0.054
	c		-		+0.051
R (M-H)/Å	#	1.77	1.61	2.04	1.77

#: this work, a: Ref. [15], b: Ref [1], c: Ref. [17] d: Ref. [18], e: Ref. [16]

Table 2. Interaction energies between fragments (ΔE_{int}) together with various contributions corresponding to Ziegler-Rauk and ETS-NOCV decomposition scheme (kcal/mol)

	{Cu (η^2 -H ₂)} ⁺	{Cu (η^2 -H ₂)}(T1)	{Ag (η^2 -H ₂)} ⁺	{Ag (η^2 -H ₂)}(T1)
ΔE_{int}	-22.6	-23.8	-10.0	-11.3
ΔE_{dist}	0.4	3.0	0.2	3.1
ΔE_{Pauli}	33.9	63.6	25.5	75.5
ΔE_{elstat}	-29.6	-53.2	-20.4	-57.0
$\Delta E_{\text{dist}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}}$	3.4	13.4	5.2	18.6
$\Delta E_{\text{attr}} = \Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$	-56.9	-90.4	-35.6	-86.9
ΔE_{orb}	-27.3	-37.2	-15.3	-29.9
$\Delta E_{\text{orb}}^{\text{don}}$	-16.0	-11.4	-10.7	-8.7
$\Delta E_{\text{orb}}^{\text{pol}}$	-7.2	-9.9	-2.7	-8.6
$\Delta E_{\text{orb}}^{\text{bdon}}$	-3.7	-14.6	-1.4	-10.8

3 Results and Discussion

Both optimized structural parameters and vibrational frequencies bring the information about the adsorption and activation of the hydrogen molecule. Elongation of the H-H bond and red-shift of stretching frequency (with respect to gas-phase hydrogen molecule) are given in Table 1 as the measure of the extent of activation. Bond length is related to calculated value for free molecule (0.744 Å) while experimental values is 0.742 Å [12]. Red-shifts are calculated as the differences between the harmonic calculated frequency for H₂ of 4418 cm⁻¹ (experimental harmonic frequency is 4400 cm⁻¹ [13]). Experimental frequency for *para*-H₂ of 4161 cm⁻¹ is taken as the reference frequency for experimental shifts [14]. Hydrogen molecule adsorbed on Brønsted acid sites or sodium sites exhibit red-shift ca 60 cm⁻¹

[15,16] thus the values for hydrogen interacting with free silver and copper cations are 8–10 times larger. Embedding the cations in zeolite framework shifts the frequency even more toward lower values (by additional 400–550 cm⁻¹). It is worth to notify that calculated values of red-shifts for hydrogen interacting with embedded cations agree reasonably well with experimental and calculated ones [17,18]. Changes in the H-H bond length are parallel to calculated red-shifts.

The analysis of various contributions to total interaction energy (ΔE_{int}) brings better understanding of the interaction between silver and copper cations/cationic sites with hydrogen. In the Table 2 various energy contributions to adsorption energy are presented. This list of energy contributions allows to compare the interaction of hydrogen with two coinage metal cations (Ag⁺ and Cu⁺), as well free as embedded in tetrahedral

Figure 2. Contribution to deformation electron density for $(\eta^2\text{-H}_2)//\text{Cu}^+$ partition together with the corresponding orbital interaction energy contributions (ΔE_{orb}^i , kcal/mol) and NOCV charge-transfer estimates (λ_i). Atomic positions as in Figure 1. red (light gray) – density outflow, blue (dark gray) – density inflow (contour value 0.001 au, color Figures on-line)

models of zeolitic silver and copper sites. Even if total interaction energies (ΔE_{int}) for bare and embedded cations are close to each other, individual contributions are significantly different. Distortion energy (ΔE_{dist}) is larger when (T1) cluster is present because besides hydrogen also the cluster geometry must be distorted. Hydrogen molecule is closer to the cations when interacting with the cationic sites (Table 1) thus the Pauli repulsion (ΔE_{Pauli}) is also larger for H_2M (T1) than for H_2M^+ . This repulsion is partially compensated by the increase of electrostatic term, nevertheless, the sum $\Delta E_{\text{dist}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}}$ becomes even more positive (destabilizing) for embedded cations. The increase of direct electronic interaction by embedding, covered by ΔE_{orb} causes that ΔE_{ads} comes back to nearly the same values as for bare cations. Therefore the hydrogen molecule is very strongly bonded as well by free coinage metal cations as by cationic sites.

Even if the relative share of ΔE_{orb} in the sum of attraction terms (ΔE_{attr}) decreases after embedding, the influence of orbital interaction on the activation of adsorbed hydrogen molecule is tremendous, judging from as well red-shifts of infrared frequency as elongation of H-H bond. This effect can be understood by performing the analysis of electron density flow between the cation (free or embedded) and the adsorbed molecule. To this end, Figures 2–5 show the contributions to deformation electron density obtained from NOCV analysis for $(\eta^2\text{-H}_2)//\text{Cu}^+$, $(\eta^2\text{-H}_2)//\text{Cu}$ (T1), $(\eta^2\text{-H}_2)//\text{Ag}^+$ and $(\eta^2\text{-H}_2)//\text{Ag}$ (T1) systems, respectively.

In all cases three dominant electron flow channels come out

from ETS-NOCV analysis. In the case of a free cations (Figures 2 and 4) the first one may be depicted as electron donation from $\sigma(\text{H-H})$ to 4s (Cu) or 5s (Ag) which energy is ascribed as $\Delta E_{\text{orb}}^{\text{don}}$. This contribution covers also traces of electron density polarization toward the bonding region between M^+ and H_2 , with some admixture of depopulating $\text{d}z^2$ orbital and populating s orbital. Second contribution ($\Delta E_{\text{orb}}^{\text{pol}}$) covers mainly strong density transfer into the hydrogen – cation bonding region coming from depopulating cation $\text{d}z^2$ orbital and polarization of $\sigma(\text{H-H})$ toward the cation. Third contribution ($\Delta E_{\text{orb}}^{\text{bdon}}$) depicts backdonation from 3d_π (for Cu) or 4d_π (for Ag) to $\sigma^*(\text{H-H})$ antibonding orbital. The first and the third contribution weaken the H-H bond while the second slightly strengthens the H-H bond thus the interplay between these contradictory contributions will influence the hydrogen activation. However, all three contributions strengthen the bond between the cation and hydrogen molecule thus they should be responsible for exceptionally strong bonding of hydrogen by Cu and Ag, as well free cations as cationic sites.

Having a deeper insight into ΔE_{orb} within ETS-NOCV resolution, one can notice that not all orbital contributions become larger on embedding. When the cations are embedded in zeolite environment, the ordering of the three electron density flow channels change. The main difference between the interaction of free or embedded cations with hydrogen comes from $\Delta E_{\text{orb}}^{\text{bdon}}$ which means that backdonation from 3d_π (for Cu) or 4d_π (for Ag) to $\sigma^*(\text{H-H})$ becomes the dominant contribu-

Figure 3. Contribution to deformation electron density for $(\eta^2\text{-H}_2)/\text{Cu}$ (T1) together with the corresponding orbital interaction energy contributions (ΔE_{orb}^i , kcal/mol) and NOCV charge-transfer estimates (λ_i). Atomic positions as in Figure 1. red (light gray) – density outflow, blue (dark gray) – density inflow (contour value 0.001 au, color Figures on-line)

Figure 4. Contributions to deformation electron density for $(\eta^2\text{-H}_2)/\text{Ag}^+$ partition together with the corresponding orbital interaction energy contributions (ΔE_{orb}^i , kcal/mol) and NOCV charge-transfer estimates (λ_i). Atomic positions as in Figure 1. red (light gray) – density outflow, blue (dark gray) – density inflow (contour value 0.001 au, color Figures on-line)

tion ($|\lambda_i|=0.33$ and 0.28 , respectively for copper and silver). At the same time donation is suppressed and polarization to the bond area increases. For copper the first effect is bigger than the second one while for silver the ordering is opposite. However either for copper or for silver cations the ordering of the orbital interaction energy contribution changes from $|\Delta E_{\text{orb}}^{\text{don}}| > |\Delta E_{\text{orb}}^{\text{pol}}| > |\Delta E_{\text{orb}}^{\text{bdon}}|$ to $|\Delta E_{\text{orb}}^{\text{bdon}}| > |\Delta E_{\text{orb}}^{\text{don}}| > |\Delta E_{\text{orb}}^{\text{pol}}|$. Taking into consideration charge-transfer estimates (λ_i) we obtain similar picture. By embedding in zeolite framework, donation of electrons from hydrogen bonding orbital is reduced stronger

for copper ($0.36 \rightarrow 0.29$) than for silver ($0.27 \rightarrow 0.25$) and, at the same time, backdonation to hydrogen antibonding orbital is strongly enhanced as well for copper ($0.16 \rightarrow 0.33$) as for silver ($0.09 \rightarrow 0.28$) site. Hence, cooperation with framework bridging oxygens decreases the donation more efficiently for copper while the increase of backdonation is strong for both cations; both effects enhance activation of hydrogen and thus copper site is more efficient here than silver. Nevertheless, hydrogen molecule is very strongly bound by the two sites, as rationalized by as well interaction energy decomposition as the character of electron density deformation, therefore hydrogen may stay

Figure 5. Contribution to deformation electron density for (η^2 -H₂)/Ag (T1) partition together with the corresponding orbital interaction energy contributions (ΔE_{orb}^i , kcal/mol) and NOCV charge-transfer estimates (λ_i). Atomic positions as in Figure 1. red (light gray) – density outflow, blue (dark gray) – density inflow (contour value 0.001 au, color Figures on-line)

Figure 6. Contribution to differential electron density for (η^2 -H₂) Cu/(T1) partition scheme together with the corresponding orbital interaction energy contributions (ΔE_{orb}^i , kcal/mol) and NOCV charge-transfer estimates (λ_i). Atomic positions as in Figure 1. red (light gray) – density outflow, blue (dark gray) – density inflow (contour value 0.001 au, color Figures on-line)

adsorbed as non-dissociated molecules.

ETS-NOCV analysis performed for the second partition scheme brings the explanation of the alteration of charge density flow upon cation coordination to framework oxygen atoms. The important contributions to differential density are shown in Figures 6 and 7 for Cu (I) and Ag (I) sites, respectively. Only the first two density flow channels seem important for describing the impact of embedding on the properties of the cation

and its interaction with hydrogen molecule since the other two do not engage either the cation or the molecule orbitals and describe merely framework polarization. The first contribution enhances backdonation – the energetic effect is 12.0 kcal/mol for silver and 16.3 kcal/mol for copper site. This charge flow can be also characterized by the number of electrons transferred along this channel which is 0.34 and 0.38, respectively. The second important contribution opposes σ donation having ener-

Figure 7. Contribution to differential electron density for (η^2 -H₂) Ag/(T1) partition scheme together with the corresponding orbital interaction energy contributions (ΔE_{orb}^i , kcal/mol) and NOCV charge-transfer estimates (λ_i). Atomic positions as in Figure 1. red (light gray) – density outflow, blue (dark gray) – density inflow (contour value 0.001 au, color Figures on-line)

getic weights of 15.8 kcal/mol for silver and 20.3 kcal/mol for copper. As the both effects are larger for copper than for silver

thus the changes of ΔE_{orb}^{don} and ΔE_{orb}^{bdon} and corresponding eigenvalues are more pronounced for this cation. For copper ΔE_{orb}^{bdon} increases by 10.9 kcal/mol while for silver by 9.4 kcal/mol. The decrease of ΔE_{orb}^{don} is lower for silver (2.0 kcal/mol) than for copper (4.6 kcal/mol).

4 Conclusions

Our analysis rationalizes why coinage metal cations, especially copper, have a great potential toward adsorption and activation of hydrogen molecule that can be still strongly intensified by interaction with ligands. ETS-NOCV analysis of the interaction between zeolite treated as a generalized ligand and the cation allows to elucidate the mechanism of modifying properties of the cation upon embedding. By embedding in zeolite framework donation of electrons from hydrogen bonding orbital is reduced and backdonation to hydrogen antibonding orbital is enhanced as well for copper as for silver site, and both effects enhance activation of hydrogen. Moreover, cooperation with framework bridging oxygens decreases the donation more efficiently for copper while the increase of backdonation is strong for both cations.

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