

## Research Article

# Structure and Reverse Hydrogen Spillover in Mononuclear Au<sup>0</sup> and Au<sup>I</sup> Complexes Bonded to Faujasite Zeolite: A Density Functional Study

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We have studied the structure of mononuclear gold supported on acidic form of faujasite zeolite in two oxidation states, namely, 0 and +1, using density functional theory. The binding of the gold monomer to the zeolite support is stronger in the oxidation state +1 than in the oxidation state 0. For the oxidation state 0, the hydrogenated clusters AuH/(2H)-FAU, AuH<sub>2</sub>/H-FAU generated by stepwise reverse hydrogen spillover from bridging OH groups of zeolite are energetically preferred over the Au/(3H)-FAU structure. Reverse hydrogen spillover of all the three acidic protons from the zeolite to the Au monomer did not lead to a stable structure. The calculated reverse hydrogen spillover energy per hydrogen atom for zeolite supported AuH and AuH<sub>2</sub> clusters are -10.2 and -5.1 kJ/mol, respectively, in the oxidation state 0, while in the oxidation state +1 it is 20.9 kJ/mol for zeolite supported Au<sup>+</sup>H cluster.

## 1. Introduction

Oxide-supported transition metal clusters form an important class of system both for theoretical and experimental investigations mainly due to their very important applications as catalysts. The activity of supported metal clusters is found to be higher than bare clusters and these metal-support interfaces are believed to act as active sites for catalysis. The factors influencing the reactivity of supported clusters are the size, structure and oxidation state of the cluster, the nature of the support, and cluster support interaction. Zeolites form an important class of support material for nanoclusters because their pores and cavities facilitate the formation of size-selective clusters of nanometer and sub-nanometer dimensions. Also, the zeolite support enables the tuning of the charge state of the cluster, as it depends upon the concentration of the acidic centres on the support, which can be modified. Among the transition metals gold has been highly investigated due to its ability to catalyse a number of reactions like CO oxidation [1], water gas shift reaction [2], epoxidation of propylene, [3] vinyl chloride synthesis [4], and so forth. Spurt in research activities involving supported gold clusters

began after the pioneering discoveries of Haruta et al. [5] and Hashmi and Hutchings [6] demonstrating strong catalytic activities of highly dispersed gold. The common metal oxide supports used for gold cluster catalysis are MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and so forth.

It has been found by Vayssilov and Rösch [7] that transition metal clusters M<sub>6</sub> with hydrogen impurity adsorbed on a zeolite support have more nearest neighbour M-O contacts than the corresponding bare adsorbed clusters indicating that the presence of hydrogen in the adsorbed cluster leads to higher stability. Also, a comparison of the theoretically calculated M-M and M-O distances of a Rh<sub>6</sub> cluster supported on Y zeolite with experimentally measured structural information using EXAFS spectroscopy [8] shows that the bond distances of the hydrogenated supported cluster are closer to the experimental values compared to the bare supported cluster [9], indicating the fact that the experimental structures contain hydrogen impurity atoms. Mikhailov et al. [10] used quantum chemical methods to investigate the structure and reactivity of anion-radical site in HZSM-5 zeolite. In an earlier investigation [11] of Au<sub>6</sub> cluster supported on faujasite zeolite, we found that the

hydrogenated clusters generated by stepwise reverse hydrogen spillover from the support to the cluster are more stable than the bare supported clusters. Fierro-Gonzalez and Gates [12] demonstrated experimentally that NaY zeolite supported mononuclear cationic gold complexes Au<sup>I</sup> and Au<sup>III</sup> can be used as CO oxidation catalysts. They found that the Au<sup>III</sup> complex is an order of magnitude more active as a catalyst than the Au<sup>I</sup> complex. However, while using gold clusters or monomer on a zeolite support, there is a tendency of the acidic hydrogen of zeolite to migrate on to the cluster which is known as reverse hydrogen spillover. Although reverse hydrogen spillover has been studied for some metal clusters, no theoretical study has been performed on zeolite supported Au monomers yet. In view of the catalytic importance of the gold monomer for CO oxidation reaction, we were motivated to investigate the possibility of reverse spillover of hydrogen from the faujasite zeolite support to the gold monomer, by transferring hydrogen atoms, one at a time, from the support to the gold. As the activity of supported nanoparticles depends greatly on the oxidation state of the metal, we shall perform this investigation in two oxidation states, 0 and +1.

## 2. Method and Models

The framework of zeolite has been modelled with a 9T (T = tetrahedral unit of zeolite) cluster containing the six-member ring and three other Si atoms of the wall of the supercage of faujasite structure which is accessible by metal clusters and adsorbed molecules. Three Si atoms of the six-member ring are isomorphously substituted by three Al atoms in an alternating sequence according to the Löwenstein rule [13]. The excess negative charges generated due to three Al atoms are compensated by protons forming bridging OH groups with framework oxygen atoms. The charge on the adsorbed gold atom is varied by changing the number of compensating protons. Three compensating protons make the adsorbed gold atom neutral, while two compensating protons mean that the adsorbed gold atom carries charge of +1. The free valences of silicon and aluminum atoms are saturated with hydrogen atoms. At first, only Si-H, Al-H, and O-H bonds are optimized keeping the position of other atoms fixed at their crystallographic positions [14]. In subsequent calculations, the optimized positions of the terminating hydrogen atoms are held fixed and all other atoms are allowed to relax.

All calculations have been performed at the Density Functional Theory (DFT) level using the DMol<sup>3</sup> program package [15]. We have used the double numeric quality basis sets with polarization functions (DNPs) [16]. Our choice of exchange correlation functionals is guided by the fact that LDA functionals give a better description of geometry and GGA functionals are better suited to describe molecular properties in case of zeolite supported metal clusters. So in case of both gas phase and supported clusters, the geometry optimizations have been performed by using the VWN functional [17]. Single point calculations are then carried out at the VWN optimized geometry with the GGA functional BLYP, which incorporates Becke's exchange [18] and Lee Yang

Parr correlation [19], in order to determine energy and other properties.

We calculate the reverse hydrogen spillover energy per transferred acidic hydrogen atom,  $E_{RS}$ , to the supported Au monomer using the following equation:

$$E_{RS} = \frac{\{E [\text{AuH}_n / ((3-n) \text{HFAU})] - E [\text{Au} / (3\text{HFAU})]\}}{n}, \quad (1)$$

where  $n = 1$  and  $2$  and

$$E_{RS} = \left\{ E \left[ \frac{\text{Au}^+\text{H}}{(\text{HFAU})} \right] - E \left[ \frac{\text{Au}^+}{(2\text{HFAU})} \right] \right\}. \quad (2)$$

A negative value of the  $E_{RS}$  implies that the hydrogenated gold monomers, Au<sup>0,+</sup>H<sub>*n*</sub>, on zeolite support are more stable than their corresponding dehydrogenated counterparts.

## 3. Results and Discussion

We shall first report the optimized structures of bare monomers Au/3H-Fau and Au<sup>+</sup>/2H-Fau and the hydrogenated monomers AuH/2H-Fau, AuH<sub>2</sub>/H-Fau and Au<sup>+</sup>H/H-Fau. Thereafter we will give an overview of atomic charges on the supported clusters. Finally we shall discuss the energy of reverse hydrogen spillover,  $E_{RS}$ , from the zeolite support to the metal.

The optimized structures of bare and hydrogenated Au<sup>0</sup> and Au<sup>+</sup> monomers adsorbed on the six-member ring of faujasite zeolite are shown in Figure 1. Selected geometric parameters of the adsorbed gold atoms are summarized in Table 1. We have designated the framework oxygen atoms as Oz while the oxygen atoms with bridging OH groups are labeled as O<sub>H</sub>. Similarly the compensating protons of the zeolite framework are designated as H<sub>O</sub>, while those that have migrated to the gold monomer are labeled as H<sub>Au</sub>. As seen from Table 1, the Au-Oz distance for the Au/3H-Fau monomer is 2.429 Å which is significantly higher than the experimental EXAFS value of 2.08 Å in zeolite supported gold clusters [20]. This shows that the neutral gold monomer is weakly bound to the zeolite support. Moving over to the supported gold monomer in the oxidation state +1, the Au-Oz distance is 2.115 Å, indicating that that the bonding with the support is stronger in this case.

The hydrogenated clusters, AuH, AuH<sub>2</sub>, and Au<sup>+</sup>H, were formed by transferring acidic protons in a stepwise manner from the zeolite to the supported Au<sup>0,+</sup> atom. Attempts to simulate the transfer of three protons in case of the supported neutral monomer and two protons in case of the monomer in the oxidation state +1 failed. As seen from Table 1, the Au-Oz distance gets significantly reduced in presence of hydrogen spilled over from the zeolite to the gold atom. The Au-Oz distance for the supported monomer with one and two spilled over hydrogen atoms are 2.191 and 2.179 Å, respectively. Thus with increasing number of protons in the clusters, the Au-Oz distances decreases. This is in agreement with our observation on reverse hydrogen spillover in case of zeolite supported Au<sub>6</sub> cluster obtained in an earlier study [11] and those of Deka and Baishya [21]. The decreasing Au-Oz

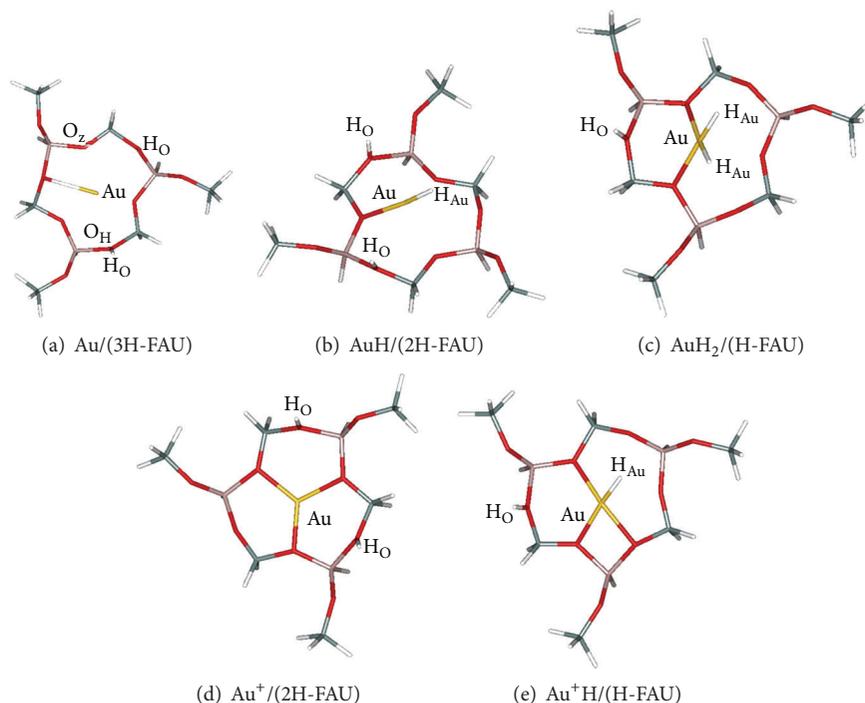


FIGURE 1: Optimized structures of (a), (d) bare and (b), (c), (e) hydrogenated monomers of Au and Au<sup>+</sup> adsorbed on the six member ring of faujasite zeolite.

TABLE 1: Computational results of zeolite supported Au and Au<sup>+</sup> monomer and complexes formed after stepwise reverse hydrogen spillover: average distances (Å), total charge of the clusters and energy characteristics (kJ/mol) per transfer of hydrogen atoms.

	Au/(3H)-FAU	AuH/(2H)-FAU	AuH <sub>2</sub> /H-FAU	Au <sup>+</sup> /(2H)-FAU	Au <sup>+</sup> H/(H)-FAU
Bond distances					
Au-O <sub>z</sub>	2.429	2.191	2.179	2.115	2.151
Au-O <sub>H</sub>	2.863	3.064	3.020	2.904	2.282
Au-Al	3.512	3.372	3.279	3.196	3.134
Au-Si	3.406	3.226	3.242	3.065	3.149
Au-H <sub>Au</sub>		1.527	1.519		1.530
Charges (Hirshfeld)					
q (Au)	0.081	0.243	0.381	0.278	0.240
q (H <sub>O</sub> )	0.145	0.288	0.205	0.305	0.208
q (H <sub>Au</sub> )		-0.045	-0.004		-0.017
E <sub>RS</sub>		-10.164	-5.118		20.938

O<sub>z</sub>: oxygen atoms of zeolite connected to the gold atom, O<sub>H</sub>: oxygen atoms where acidic hydrogen atoms are attached, H<sub>Au</sub>: acidic hydrogen of zeolite which has migrated to the gold atom, H<sub>O</sub>: acidic hydrogen of zeolite, E<sub>RS</sub>: reverse spillover energy.

distance with increasing migration of the protons to the gold monomer indicates that the hydrogenated monomer is more strongly anchored to the zeolite support compared to the bare monomer. However, in case of the gold monomer in the oxidation state +1 the Au-O<sub>z</sub> distance increases slightly from a value of 2.12 Å to 2.15 Å due to reverse hydrogen spillover. The Au-Al distance is found to decrease from supported Au<sup>0,+</sup> cluster to supported Au<sup>0,+</sup>H<sub>n</sub>. The Au-Si distance decreases due to reverse hydrogen spillover in case of the supported Au<sup>0</sup> while it increases in case of the supported Au<sup>+</sup> monomer. The distance of Au atom to the spilled over hydrogen atom

is found to decrease with the increase in the number of hydrogen atoms in the cluster indicating a strong interaction of the metal atom with hydrogen. Thus to summarize our observations on the optimized distances of the zeolite supported Au<sup>0,+</sup> and Au<sup>0,+</sup>H<sub>n</sub> clusters we conclude that in case of the neutral gold monomer all the three distances Au-O<sub>z</sub>, Au-Al and Au-Si decrease due to hydrogenation while in case of Au<sup>+</sup> only the Au-Al distance decrease on hydrogenation. Decreasing metal-support distances indicate stronger interaction of the cluster with the support. These observations point to the fact that reverse hydrogen spillover

from the zeolite to the  $\text{Au}^+$  monomer may not be a favourable process.

The Hirshfeld charges on the bare and hydrogenated mononuclear gold complexes are also presented in Table 1. For the bare supported gold monomer the charge carried by the Au atom is 0.081 e while for the hydrogenated monomers the values are 0.243 and 0.381 e. This increasing value of charges reveals oxidation of the gold atom on going from the bare to the hydrogenated cluster. The bridging hydrogen atoms in the supported  $\text{Au}^0$  monomer carry an average charge of 0.145 e. This charge reduces to  $-0.045$  and  $-0.004$  e when one and two hydrogen atoms migrate from the support to the cluster, respectively indicating a formal reduction of  $\text{H}^+$  to  $\text{H}^-$  due to reverse hydrogen spillover. Thus it can be inferred that reverse spillover of acidic hydrogen from the zeolite to the neutral gold monomer causes a reduction of hydrogen atoms with a concomitant oxidation of oxygen atoms. This is in keeping with our observation on reverse hydrogen spillover in case of zeolite support  $\text{Au}_6$  cluster. Our observations of charges of the supported monomer in the oxidation state +1 reveal a different picture. In this case while the acidic hydrogen of the zeolite framework gets reduced on migration to the gold monomer, the gold monomer itself gets reduced in the process.

Finally, we present the reverse spillover energy,  $E_{\text{RS}}$ , for migration of acidic hydrogen atoms of the zeolite cluster to Au atom. It is seen from Table 1 that in case of the supported gold monomer in the oxidation state 0,  $E_{\text{RS}}$  for the first proton is  $-10.16$  kJ/mol while the  $E_{\text{RS}}$  per atom for transfer of two protons from the zeolite cluster is  $-5.12$  kJ/mol. Thus the reverse hydrogen spillover process of one proton transfer is energetically more favourable than that of two protons in case of the faujasite zeolite supported neutral gold monomer. This is in agreement with our earlier study [11] on reverse hydrogen spillover in case of zeolite supported gold hexamer. As is evident from the above values of  $E_{\text{RS}}$ , the value for two proton transfers is almost half that of one proton transfer. This may be due to the fact that as the considered cluster is mononuclear migration of two protons is less favourable. However, in our earlier study the reverse spillover energy per transferred proton does not vary significantly, having values of  $-67.6$ ,  $-65.6$ , and  $-59.1$  kJ/mol, for the transfer of one, two, and three protons, respectively. This may be due to the fact that as the cluster in this case contains six Au atoms, it presents a large number of sites onto which the acidic hydrogen atoms of the zeolite support may migrate. For the gold monomer in the oxidation state +1, reverse spillover of a single proton takes place from the support to the gold atom. The reverse spillover energy is 20.94 kJ/mol. Thus this process is endothermic and hence is not energetically favoured. Vayssilov and Rösch [7] calculated reverse hydrogen spillover energy for  $\text{Au}_6$  supported on zeolites and obtained a value of  $-18.0$  kJ/mol per transfer of hydrogen.

#### 4. Conclusions

We have modeled the sequential migration of protons from the bridging OH groups of faujasite zeolite to the Au monomer in the oxidation states 0 and +1 without any

symmetry constraint. We have found that the migration of one and two protons are possible in the case of  $\text{Au}^0$  atom, while in the case of  $\text{Au}^+$ , migration of only one proton is possible. In case of  $\text{Au}^0$ , the Au-Oz, Au-Al, and Au-Al distances decrease due to reverse hydrogen spillover indicating that the hydrogenated atom is more stable than the dehydrogenated one, while in the case of  $\text{Au}^+$ , the dehydrogenated monomer is more stable. The process of reverse hydrogen spillover is exothermic in case of  $\text{Au}^0$  while it is endothermic for  $\text{Au}^+$ .

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