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# A density functional study of some silver cluster hydrides

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## Abstract

A density functional study of some silver cluster hydrides of general formulae  $\text{Ag}_n\text{H}$  is presented, in order to help the identification of species possibly formed in the interior of zeolites. Two correlation-exchange functionals were employed with two different basis sets and effective core potentials in order to investigate their influence on the final results. The calculated frequencies of the Ag–H stretching modes suggest that this property could be used to help the characterization of the silver hydride species formed inside zeolites.

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## 1. Introduction

In the last 25 years there has been a growing interest in the behavior of metal atoms and ions entrapped in zeolites, particularly in silver-exchange zeolites [1–9]. It is known [4,10,11] that silver cations in zeolites can be reduced with hydrogen to generate protons and silver metal, according to the reaction:



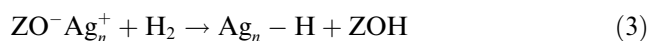
where ZOH stands for the Bronsted acid site in the zeolite. However, it has been suggested [2,5–7,12,13] that this reduction process can be more complex, and some authors believe that the silver metal further reacts with  $\text{Ag}^+$ , giving rise to silver cationic clusters



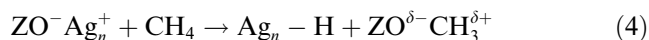
The silver atoms produced, according to reaction (1), at different points in the zeolite structure, could either be immobilized at the precursors  $\text{Ag}^+$  ions sites or diffuse through the zeolite channels to subsequently interact with other  $\text{Ag}^0$  atoms, giving rise to silver clusters which,

in turn, could further react at another metal-exchange site, as shown in Eq. (2). These metal clusters would be stabilized by the zeolite structure [14] and their formation would be greatly facilitated by the very regular crystalline structure of the zeolite, with pores of well-defined shapes and sizes.

More recently Baba et al. [15,16] presented evidence that the cationic silver clusters formed in reaction (2) can promote heterolytic cleavage of the  $\text{H}_2$  bond, producing silver hydride and reconstructing the original Bronsted acid site of the zeolite



This result prompted them to investigate the possibility of using silver-exchanged zeolites to activate C–H bonds in alkanes [16]. Indeed, the reaction of Ag–Y zeolite with  $\text{CH}_4$  was observed and the products characterized as being silver hydride and methyl alkoxide:



However, the mechanisms for all these reactions are mostly unknown. Not even the sizes of the silver clusters that could participate in the process are well determined. Although the formation of  $\text{Ag}_3\text{H}$  has been recently established [15,16], in the same experiment other unidentified  $\text{Ag}_n\text{H}$  species have also been observed. It is clear that the sizes of the clusters will somehow be

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limited by the dimension of the channels in the interior of the zeolite. However, one should keep in mind that the zeolite structure is not as rigid as it might look [17], and shape readjustments could take place to accommodate larger guests.

Due to the importance of reaction (4) it would be interesting to examine the whole process in detail. In order to accomplish that, one should investigate the diffusion of silver atoms through the zeolite structure, their combination to form larger metal clusters and the nature of the  $\text{ZO}^-\text{Ag}_n^+$  site. Once this site has been well characterized, one could proceed to investigate the activation of alkanes by the silver-exchanged zeolite.

In this Letter we will concentrate our attention at examining the structure of some silver-cluster hydrides that could be formed along the process. The characterization of such hydrides would be valuable for establishing the nature of silver-exchanged zeolite sites. The diffusion of silver atoms, their combination to form larger metal clusters are also under investigation and, together with the activation reaction, will be the subject of other publications.

## 2. Methodology

The sizes of the cluster hydrides to be considered were selected taking into account the size of the pores of the most frequently used zeolites in petrochemical and oil industries, and the geometry of the silver metal clusters as determined by Fournier [18]. Thus, cluster hydrides of general formula  $\text{Ag}_n\text{H}$  ( $1 \leq n \leq 5$ ) were considered, and for any value of  $n$  within this range, a full search of the potential energy surface (PES) was performed in order to obtain all possible stable isomers.

Although one cannot rule out the possibility of larger silver clusters being formed, due to their larger masses and volumes, they should diffuse much more slowly than the smaller clusters, as indicated by our preliminary studies. Also, because the smaller clusters diffuse faster, chances are that they will reach an exchanged site, where reaction (2) takes place, much before they can add another silver atom. Therefore, we decided to focus our

attention on the clusters containing up to five silver atoms.

It should also be mentioned that we are not, at this stage, considering the influence of the zeolite cavity on the structure of the silver-cluster hydride. However, as pointed out by Gurin et al. [14], EXAFS data indicate a weak  $\text{Ag} \cdots \text{O}$  interaction, and an even smaller  $\text{Ag} \cdots \text{Si}$  interaction should be expected. As for the  $\text{Ag}-\text{H} \cdots \text{O}$  interaction, it should be also small since as long as stable hydrides are formed their charge distribution will preferentially be  $\text{Ag}_n^{\delta+}\text{H}^{\delta-}$ .

The calculations have been performed using the DFT methodology at the local spin density approximation (LDA) [19,20] implemented via the VWN exchange-correlation functional. As pointed out by Fournier [18], newer functionals produce better results for geometries and binding energies of organic molecules but very little is known about their performance for metallic systems. The B3LYP functional was also considered in spite of producing disappointing results for transition metal dimers [21–23].

Two basis sets were considered, the 6-31G(p,d) [24–27]/LACVP(p,d) [28] and the 6-311G(p,d) [29,30]/LACV3P(p,d), for the hydrogen and silver atoms, respectively. For some calculations, basis sets containing diffuse functions were also considered for both the hydrogen (6-311G++(p,d)) and silver (LACV3P++(p,d)) atoms.

The starting geometries were constructed by adding one hydrogen atom to the silver clusters obtained by Fournier [18]. For each value of  $n > 1$ , several initial geometries were selected, considering all the different ways of adding the H atom to the silver clusters obtained by Fournier, and a full search for stationary points on the PES was performed, with the local minima being identified by the absence of imaginary frequencies. The search for these local minima was considerably hampered by the flatness of the potential energy surfaces along the Ag–H coordinate, which allows changes in energy of less than 5 mh for displacements of the order of 0.15 Å or 5° around the minima. For a given value of  $n$ , all the local minima differing by less than 6 mh ( $\approx 3.8$  kcal/mol) from the most stable one were considered for further analysis

Table 1  
Results for the AgH molecule

Parameter	B3LYP 6-31G(p,d)/ LACVP(p,d)	B3LYP 6-311G++(p,d)/ LACV3P++(p,d)	LDA 6-31G(p,d)/ LACVP(p,d)	LDA 6-311G++(p,d)/ LACV3P++(p,d)
Symmetry		$C_{\infty v}$		
$R$	1.631	1.631	1.588	1.590
Frequency <sup>a</sup>	1709	1728	1841	1858
$E$	−146.34384	−146.35028	−146.44275	−146.44947

Interatomic distances in Å, angles in degrees, frequencies in  $\text{cm}^{-1}$  and energy in a.u.

<sup>a</sup> Experimental frequency:  $1717.0 \text{ cm}^{-1}$  [35].

since they cannot be distinguished at the levels of calculation employed. The geometry optimization convergence criteria were set to  $1 \times 10^{-4}/2 \times 10^{-4}$  hartree/Å (RMS/Max). For a small number of cases, SCF convergence was only achieved after introducing some level shift in the earlier steps of the iterative process.

All the calculations were carried out using the programs JAGUAR v4.2 [31] and GAUSSIAN 98 [32].

### 3. Results and discussion

Tables 1–5 show the results obtained for the silver hydride geometries as well as the vibration frequencies related to the Ag–H stretching and some other modes involving the H atom. Fig. 1 shows the geometries for the calculated silver hydrides, the numbers indicating the silver atoms. The full sets of geometric parameters

Table 2  
Results for the Ag<sub>2</sub>H molecule, isomers 1 and 2

Parameter	B3LYP 6-31G(p,d)/ LACVP(p,d)	B3LYP 6-311G++(p,d)/ LACV3P++(p,d)	LDA 6-31G(p,d)/ LACVP(p,d)	LDA 6-311G++(p,d)/ LACV3P++(p,d)	LDA 6-311G++(p,d)/ LACV3P++(p,d)
Isomer 1					
Symmetry	D <sub>∞h</sub>		C <sub>2v</sub>		D <sub>∞h</sub>
R <sub>12</sub>	3.523	3.508	2.920	2.896	3.362
R <sub>1H</sub>	1.761	1.754	1.704	1.690	1.681
Θ <sub>1H2</sub>	179.9	180.0	118.0	117.9	180.0
Frequencies	1451	1499	1064; 1409	1104; 1516	128; 1868
E	−292.12595	−292.13998	−292.32608	−292.34170	−292.34032
Isomer 2					
Symmetry	C <sub>s</sub>				
R <sub>12</sub>	2.750	2.762	2.585	2.642	
R <sub>2H</sub>	1.661	1.653	1.620	1.595	
Θ <sub>12H</sub>	133.4	133.1	130.5	131.3	
Frequencies	197; 1560	196; 1610	209; 1695	598; 2463	
E	−292.12072	−292.13229	−292.32219	−292.33435	

Interatomic distances in Å, angles in degrees, frequencies in cm<sup>−1</sup> and energy in a.u.

Table 3  
Results for the Ag<sub>3</sub>H molecule, isomers 1 and 2

Parameter	B3LYP 6-31G(p,d)/ LACVP(p,d)	B3LYP 6-311G++(p,d)/ LACV3P++(p,d)	LDA 6-31G(p,d)/ LACVP(p,d)	LDA 6-311G++(p,d)/ LACV3P++(p,d)
Isomer 1				
Symmetry	C <sub>2v</sub>		C <sub>s</sub>	
R <sub>12</sub>	2.640	2.647	2.537	2.549
R <sub>13</sub>	2.868	2.864	2.688	2.654
R <sub>23</sub>	2.868	2.864	2.713	2.723
R <sub>3H</sub>	1.669	1.664	1.632	1.633
Θ <sub>123</sub>	62.6	62.5	61.5	60.4
Θ <sub>132</sub>	54.8	55.1	56.0	56.6
Θ <sub>213</sub>	62.6	62.5	62.5	63.1
Θ <sub>13H</sub>	152.6	152.5	147.1	136.6
Frequencies	156; 222; 1634	175; 265; 1674	166; 257; 1750	138; 272; 1798
E	−437.94565	−437.96065	−438.26228	−438.27845
Isomer 2				
Symmetry	C <sub>2v</sub>			
R <sub>12</sub>	2.517	2.513	2.514	2.514
R <sub>13</sub>	2.685	2.685	2.686	2.685
R <sub>23</sub>	2.685	2.685	2.682	2.684
R <sub>1H</sub>	1.896	1.870	1.895	1.871
Θ <sub>123</sub>	62.1	62.1	62.2	62.1
Θ <sub>132</sub>	55.9	55.8	55.9	55.8
Θ <sub>12H</sub>	48.4	47.8	48.4	47.8
Frequencies	334; 1080	353; 1062	325; 1167	434; 1194
E	−437.93542	−437.95028	−438.25372	−438.26952

Interatomic distances in Å, angles in degrees, frequencies in cm<sup>−1</sup> and energy in a.u.

Table 4  
Results for the Ag<sub>4</sub>H molecule

Parameter	B3LYP 6-31G(p,d)/ LACVP(p,d)	B3LYP 6-311G++(p,d)/ LACV3P++(p,d)	LDA 6-31G(p,d)/ LACVP(p,d)	LDA 6-311G++(p,d)/ LACV3P++(p,d)
Symmetry	$C_s$			
$R_{12}$	2.648	2.648	2.648	2.648
$R_{13}$	2.737	2.716	2.735	2.716
$R_{23}$	2.612	2.609	2.612	2.609
$R_{34}$	2.635	2.652	2.635	2.652
$R_{4H}$	1.850	1.814	1.850	1.814
$\theta_{123}$	62.7	62.2	62.7	62.2
$\theta_{234}$	120.3	119.9	120.3	119.9
$\theta_{H43}$	42.4	41.3	42.4	41.3
Frequencies	327; 839; 1113	333; 896; 1135	361; 850; 1239	369; 969; 1268
$E$	−583.75123	−583.77163	−584.18599	−584.20904

Interatomic distances in Å, angles in degrees, frequencies in cm<sup>−1</sup> and energy in a.u.

Table 5  
Results for the Ag<sub>5</sub>H molecule, isomers 1 and 2

Parameter	B3LYP 6-31G(p,d)/ LACVP(p,d)	B3LYP 6-311G++(p,d)/ LACV3P++(p,d)	LDA 6-31G(p,d)/ LACVP(p,d)	LDA 6-311G++(p,d)/ LACV3P++(p,d)
Isomer 1				
Symmetry	$C_{2v}$			
$R_{12}$	2.813	2.804	2.663	2.655
$R_{13}$	2.741	2.743	2.616	2.610
$R_{25}$	2.741	2.743	2.616	2.611
$R_{34}$	2.774	2.771	2.635	2.633
$R_{45}$	2.774	2.771	2.635	2.634
$R_{1H}$	1.823	1.833	1.807	1.785
$\theta_{134}$	63.4	63.1	62.9	62.8
$\theta_{142}$	58.1	58.1	58.2	58.2
$\theta_{245}$	57.8	58.0	58.2	58.3
$\theta_{314}$	58.9	58.9	58.9	59.0
$\theta_{1H2}$	98.8	98.8	95.0	96.2
Frequencies	358; 941; 1121	365; 1000; 1147	393; 1004; 1260	395; 1067; 1278
$E$	−729.58881	−729.61425	−730.14205	−730.17049
Isomer 2				
Symmetry	$C_s$			
$R_{12}$			2.664	2.664
$R_{13}$			2.683	2.692
$R_{25}$			2.656	2.656
$R_{34}$			2.582	2.575
$R_{45}$			2.619	2.606
$R_{3H}$			1.870	1.844
$\theta_{134}$			66.4	65.2
$\theta_{142}$			57.6	58.3
$\theta_{245}$			60.9	61.1
$\theta_{314}$			55.1	55.4
$\theta_{3H4}$			90.2	91.4
Frequencies			376; 783; 1289	395; 855; 1322
$E$			−730.12422	−730.15298

Interatomic distances in Å, angles in degrees, frequencies in cm<sup>−1</sup> and energy in a.u.

and vibration frequencies are available from the authors upon request. Not all of the silver clusters obtained by Fournier [18] give rise to stable cluster hydrides.

The first point to be noted is that all the systems studied are planar, retaining some structural relation-

ship with the related silver cluster [18]. All attempts at starting from geometries containing at least one out-of-plane atom converged to one of the planar structures shown in Fig. 1. Since this tendency to planarity is maintained at least up to  $n = 5$  [18], it is quite unlikely

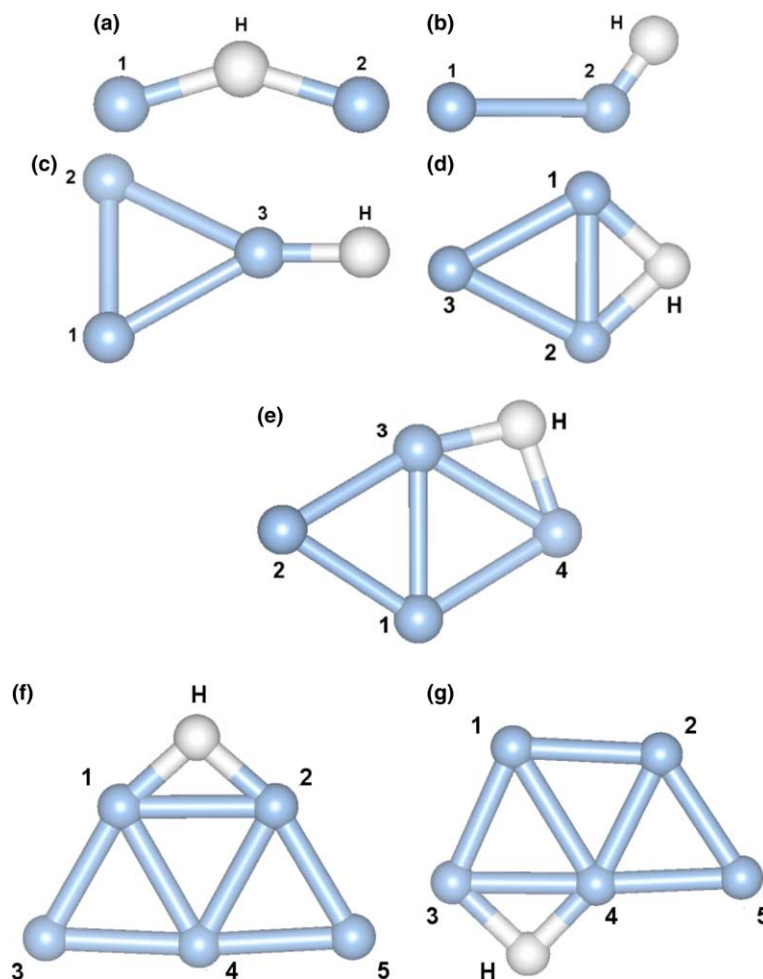


Fig. 1. Silver hydride clusters: (a)  $\text{Ag}_2\text{H}$  isomer 1, (b)  $\text{Ag}_2\text{H}$  isomer 2, (c)  $\text{Ag}_3\text{H}$  isomer 1, (d)  $\text{Ag}_3\text{H}$  isomer 2, (e)  $\text{Ag}_4\text{H}$ , (f)  $\text{Ag}_5\text{H}$  isomer 1, (g)  $\text{Ag}_5\text{H}$  isomer 2.

that larger non-planar cluster hydrides will be formed in a step-by-step process in the pores of the zeolites. Another common feature is the fact that, except the  $\text{AgH}$  molecule, all the cluster hydrides exhibit stable conformations where the hydrogen atom is shared by two silver atoms. The same phenomenon has been already observed on simulations with gold, where in a nanowire contaminated by hydrogen, the H atom was found angularly bridging two neighbor Au atoms of a colinear chain of five gold atoms [33], causing an increase of the Au–Au bond. In our calculations, it has been also verified that the average Ag–Ag bond distances – 2.78 Å (B3LYP) and 2.67 Å (LDA) are longer than those found in the silver dimer (2.53 Å [22]), but contrary to what was observed by Yanagisawa et al. [23], in the case of the dimers, we obtained shorter bond lengths with the hybrid DFT method when compared to the ones obtained with the non-hybrid method.

As it can be seen in Table 2, different results were obtained for the  $\text{Ag}_2\text{H}$  (isomer 1) depending on the exchange-correlation functional used. This effect was

only observed for this particular isomer. The only stable geometry observed with the B3LYP functional has  $D_{\infty h}$  symmetry. On the other hand, the LDA functional generates a  $C_{2v}$  geometry, for both basis sets, but also a  $D_{\infty h}$  stable structure when the 6-311G++(d,p)/LACV3P++(d,p) is used. This last structure is 2 mH less stable than the  $C_{2v}$  one and due to the accuracy of the used functionals, one cannot tell which one is the most stable. In particular, for the isomer 1, the Ag–Ag bond distance is the largest among all the clusters studied.

The results in Table 3 indicate that the geometries for  $\text{Ag}_3\text{H}$  (isomer 1), obtained with the LDA functional, are not strictly symmetric. If constrained to  $C_{2v}$  symmetry, the calculations produced unstable geometries with imaginary frequencies. However, the same problem is not observed with the B3LYP functional.

Another difference between LDA and B3LYP functional is shown in Fig. 1(g). This particular isomer for the  $\text{Ag}_5\text{H}$  molecule is only found when using the LDA functional. With the B3LYP functional, starting with

the H atom bridging atoms 3 and 4 leads, after a geometry optimization, to isomer (F). The same is true, for both functionals, if one starts the calculations with H atom bridging atoms 1 and 3 (see Fig. 1).

As a whole, once the same functional is used, the geometry and other properties of the clusters do not show a significant dependence on the size of the basis set. The only noticeable exception has to do with the internuclear distances in the  $\text{Ag}_2\text{H}$  (isomer 2), much shorter when the larger basis set is used. This has, of course, immediate consequences on the vibrational frequencies. Comparing the results obtained with both functionals, bond lengths are typically shorter with LDA, except for the case of the  $\text{Ag}_2\text{H}$  (isomer 1).

The examination of the Ag–H stretching frequencies for the clusters studied reveals that these could be very helpful for determining the possible clusters formed in reaction (3) and consequently the nature of the Ag-exchanged sites. As can be seen from Tables 1–5, these frequencies, in italics, cover a specific range of values and vary according to the way the Ag atoms are bound to the hydrogen. Flanigen et al. [34] correlated bands from 1250 to 300  $\text{cm}^{-1}$  to functional groups present in zeolites, as well as to structural aspects of these compounds, like framework arrangement and Si/Al relationship. From our results, it can be seen that silver hydrides containing only one silver atom bound to the hydrogen present a band above 1550  $\text{cm}^{-1}$ , outside the zeolite absorption region and, therefore, easily identifiable. The other compounds present two bands in the region from 1300 to 850  $\text{cm}^{-1}$ , except for the  $\text{Ag}_2\text{H}$  isomer 2. In this case, a comparative study of the IR spectra must be carried out, before and after reaction (3) takes place. In addition, oscillator strengths for the Ag–H vibration modes are usually high, which makes these bands easily identifiable. Just for comparison, a recent experimental study [35] assigned a 1717.0  $\text{cm}^{-1}$  absorption band to the Ag–H stretching in the mono-hydride, in very good agreement with our results. Some other vibration frequencies involving the H atom are also shown in Tables 1–5. They are much less intense than the stretching modes and occur in regions of spectra which overlap the bands due to the zeolite structure. Therefore, they will be not very useful for identification purposes.

#### 4. Conclusions

The calculations reported try to elucidate some aspects of the silver-cluster hydrides, identifying their structures and typical vibration spectra. The clusters share the same planar structure, maintaining a closed relation with the original silver cluster. Whenever possible the hydride structure is better stabilized when the hydrogen atom is shared with more than one silver atom. The same calculations also show that a simple examination of the IR

spectra of the products obtained in reaction (3) can provide with useful information about the structure of the silver-cluster hydrides inside zeolites and a better understanding of the Ag-exchanged sites.

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