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Inelastic Neutron Scattering Study of the Activation of Molecular Hydrogen in Silver-Exchanged A Zeolite: First Step in the Reduction to Metallic Silver at Low Temperature

Cheok N. Tam,[†] Frans R. Trouw,[†,‡] and Lennox E. Iton*,[§]

Intense Pulsed Neutron Source and Materials Science Divisions, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

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The initial steps in the reduction of Ag^+ ions by H_2 to produce metallic silver nanoparticles in silver cation-exchanged type A zeolite has been investigated in a novel way using inelastic neutron scattering (INS) to follow the reaction. The rotational tunneling excitations of the hydrogen adsorbed at low temperature were measured. The neutron scattering spectra show rotational tunneling peaks from the librational ground states of the adsorbed hydrogen. A transition at 0.3 meV is the lowest energy excitation ever observed for hydrogen adsorbed in a zeolite, and is characteristic of a σ-bond complex between a metal center and molecular hydrogen. The transition is assigned to a chemisorption complex between molecular hydrogen and the Ag_3^{2+} linear complex cation that has been proposed in X-ray diffraction studies of dehydrated Ag-A. Rotational tunneling peaks from H_2 molecules physisorbed on individual Ag^+ ions located at different sites in the zeolite are also observed. Warming the sample allows the reduction reaction to proceed, causing the rotational tunneling peaks to decrease and disappear irreversibly. New INS features appear that are attributed to H_2 physisorbed on neutral Ag clusters. The results clearly demonstrate that the first step in the reduction of the silver is the formation of an intermediate $[Ag_3^{2+}\cdots H_2]$ complex rather than a dissociative adsorption of hydrogen, and that the reduction reaction proceeds via this complex.

Introduction

Metallic silver nanocrystals can be created in the cages of A-type zeolites (structure type LTA) by the reduction of the silver-exchanged zeolite Ag-A with hydrogen. The chemistry of this reduction reaction in Ag-A has previously been examined in some detail, from the perspective of the silver ions and their clustering and intermediates stages of the metal particle growth.[1−3] However, the mechanism by which the hydrogen effects the reduction has not been examined closely, although the stoichiometry of the hydrogen adsorption has been established.[4] Dissociative chemisorption of H_2 has been asserted; this implies that the situation resembles that of H_2 adsorption on a metal surface wherein the two atoms in the H_2 molecule coordinate to the two neighboring metal atoms in the surface, the H−H bond is broken, and the two dissociated H atoms form independent M−H bonds via a reaction with a negligible activation barrier. The situation in the zeolite might be different. In particular, there is the possibility that a molecular hydrogen complex is formed initially at low temperature, prior to electron transfer and H−H bond dissociation. Inelastic neutron scattering (INS) spectroscopy is a unique probe for examining the details of the early stages of the chemistry of this metal cluster formation from the vantage point of the adsorbed reductant. Thus, the identity of the intermediate formed in the first stage of the reduction reaction can be revealed. In this paper, we report a novel application of the INS technique to the in situ monitoring of the early stages of the reduction by hydrogen of precursor cations to the metallic state, a common mode of preparing highly dispersed metal catalysts in zeolites and on other supports.

In the decade since transition-metal complexes of molecular hydrogen (H_2) were discovered, the application of INS spectroscopic techniques has contributed greatly to the understanding of these compounds.[5−7] The dihydrogen in these complexes forms a three-center, two-electron bond with the metal center, resulting in an η^2-H_2 complex. Nicol, Eckert, and co-workers have applied INS spectroscopy to study the complexation of H_2 by charge-balancing cations in zeolites.[8−10] In these INS measurements, rotational tunneling transitions (between the para ($I = 0$, $J = 0$) and the ortho ($I = 1$, $J = 1$) rotational states) of molecular hydrogen in its librational ground state are directly observed. The tunneling splittings are well correlated with the model of hindered rotational motions of H_2 under a double minimum potential. In the earlier cases of cation-exchanged zeolites investigated, viz., Zn/Na-A, Co/Na-A, and Ca/Na-A zeolites, the H_2 has exhibited only weak interactions with the Zn^{2+}, Co^{2+}, and Ca^{2+} cations, and activation of the H−H bond was not manifested. Recently, however, Mojet et al. have presented evidence for the chemisorption of molecular H_2 in Fe-ZSM-5 zeolite.[11] When the dihydrogen is bound in an authentic chemical complex, or is chemisorbed, the magnitude of the rotational tunneling splitting can become very small, and transitions below 2.5 meV (20 cm^{-1}) can be observed in the INS spectra.[5−7,11]

Experimental Section

Zeolite Sample Preparation. A 7 g sample of Na-A zeolite was washed by stirring with 0.1 M NaCl solution overnight at 60 °C. The filtered, rinsed, and partially dried Na-A zeolite was ion-exchanged by being stirred overnight with 700 mL of 0.1

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* To whom correspondence should be addressed. Phone: (630) 252-5536. Fax: (630) 252-9555. E-mail: iton@anl.gov.

[†] Intense Pulsed Neutron Source Division.

[‡] Present address: Manual Lujan, Jr., Neutron Scattering Center, MS H805, Los Alamos National Laboratory, Los Alamos, NM 87545.

[§] Materials Science Division.

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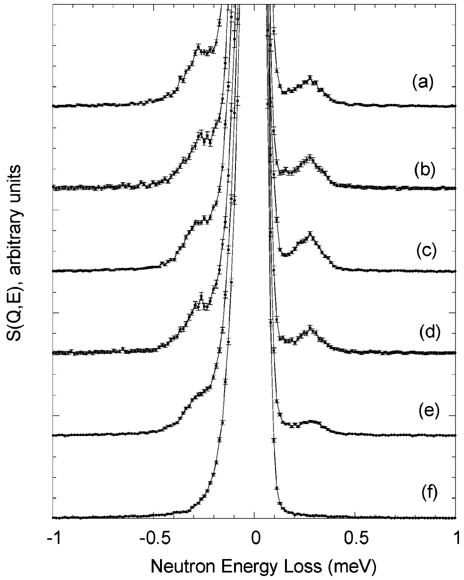

Figure 1. Rotational tunneling INS peak of H_2 in Ag-A zeolite measured at 20 K in a range from -1 to $+1$ meV: (a) a loading of 7.62 H_2 molecules per unit cell (0.71 H_2 molecule per Ag atom); (b) a loading of 4.21 H_2 molecules per unit cell (0.39 H_2 molecule per Ag atom); (c) a loading of 2.91 H_2 molecules per unit cell (0.27 H_2 molecule per Ag atom); (d) a loading of 4.21 H_2 molecules per unit cell (0.39 H_2 molecule per Ag atom) and after the reaction proceeded for 2 h at 200 K; (e) the sample in (d) reacted for an additional 2 h at 250 K; (f) the sample in (e) further reacted for 2 h at 298 K.

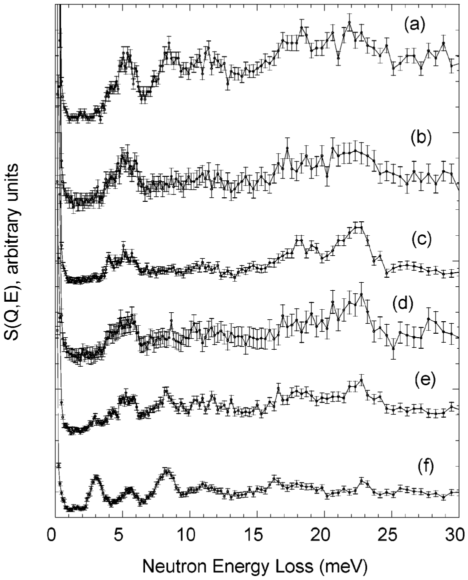

Figure 2. INS spectra of H_2 in Ag-A zeolite measured at 20 K in a range from 0 to 30 meV: (a) a loading of 7.62 H_2 molecules per unit cell (0.71 H_2 molecule per Ag atom); (b) a loading of 4.21 H_2 molecules per unit cell (0.39 H_2 molecule per Ag atom); (c) a loading of 2.91 H_2 molecules per unit cell (0.27 H_2 molecule per Ag atom); (d) a loading of 4.21 H_2 molecules per unit cell (0.39 H_2 molecule per Ag atom) and after the reaction proceeded for 2 h at 200 K; (e) the sample in (d) reacted for an additional 2 h at 250 K; (f) the sample in (e) further reacted for 2 h at 298 K.

M $AgNO_3$ solution at room temperature in the dark. Subsequent manipulations of the exchanged zeolite were conducted in dark or low-light conditions to minimize photoreduction of the silver. The filtered, rinsed, and partially dried Ag/Na-A zeolite was ion-exchanged for a second time by being stirred overnight with 700 mL of 0.2 M $AgNO_3$ solution at room temperature in the dark. The final, white Ag-A zeolite was then heated in a quartz tube in flowing nitrogen to 100 °C. The gas flow was changed to dry air, and the sample heating was continued stepwise to 400 °C over a period of 2 days. In occasional brief visual inspections, the sample color was observed to change from white to bright yellow, to orange, and back to yellow. The sample was cooled to 100 °C in the dry air flow, and then the air was replaced again by a flow of nitrogen. The sample was stored in a plastic bottle shielded from the light. Chemical analysis yielded the following anhydrous unit cell composition for the material: $[H_{1.07}]Ag_{10.7}Na_{0.03}(AlO_2)_{11.8}(SiO_2)_{12.2}$.

Inelastic Neutron Scattering. The calcined Ag-A zeolite sample was evacuated and heated gradually to 400 °C at a pressure of 2×10^{-5} Torr. A weighed quantity of the dehydrated zeolite was subsequently loaded (in a helium-filled glovebag) into a cylindrical aluminum sample can (0.9 cm diameter, 10 cm long). The sample can was fitted with a capillary tube at one end for connection to a gas-handling system. The sample was then evacuated. All INS spectra were measured at 20 K using the QENS spectrometer at the Intense Pulsed Neutron Source at Argonne National Laboratory.

The sample was first measured without adsorbate to provide a reference spectrum for the starting Ag-A material. Hydrogen was then introduced at 100 K to a loading of 7.62 H_2 molecules per unit cell (uc) (0.71 H_2 molecule per Ag atom). The sample was cooled to 20 K, and the INS spectrum was measured; it is shown in Figures 1a and 2a. (The spectra are shown in high resolution close to the elastic peak in Figure 1, while the full spectra up to energy transfers of 30 meV are shown in Figure 2.) The sample was then partially evacuated to reduce the H_2 loading to 4.21 H_2 molecules per unit cell (0.39 H_2 molecule per Ag atom) and the INS measurement repeated (Figures 1b and 2b). The hydrogen loading in the sample was reduced further to 2.91 H_2 molecules per unit cell (0.27 H_2 molecule per Ag atom) and the INS spectrum measured again (Figures 1c and 2c). The sample was then repressurized to a loading of 4.21 H_2 molecules per unit cell and, without further addition or removal of hydrogen, taken through a series of sequences wherein the sample was progressively warmed to allow the silver reduction reaction to proceed and then cooled back to 20 K for another measurement of the INS spectrum. The successive temperatures for the three reaction periods were 200, 250, and 298 K; the duration of each reaction period at elevated temperature was 2 h.

The resulting spectra are shown in Figures 1d−f and 2d−f. Following the INS measurement after the third reaction period (shown in Figures 1f and 2f, and again in Figure 3a), the sample was warmed to 100 K and the H_2 loading was increased to 5.49 H_2 molecules per unit cell (0.51 H_2 molecule per Ag atom). The sample was cooled and the INS spectrum measured (Figure 3b). The sample was warmed to 298 K and the reaction continued for an additional 2 h before the next INS spectrum (Figure 3c) was recorded at 20 K. At this juncture, the sample was evacuated at 100 K, and the INS spectrum was measured again (Figure 3d). To conclude the experiment, the sample was redosed with hydrogen to a loading of 3.57 H_2 molecules per unit cell (0.33 H_2 molecule per Ag atom) and heated to 298 K for a final reaction period of 4 h. The final INS spectrum was then measured at 20 K (Figure 3e).

Results

The spectrum obtained for the Ag-A initially dosed with 7.62 H_2 molecules per uc is shown in Figures 1a and 2a. There are seven peaks, at 0.3 meV (Figure 1a) and 4.1, 5.3, 8.4, 11.0, 18.0, and 22.6 meV (Figure 2a). As the amount of hydrogen is

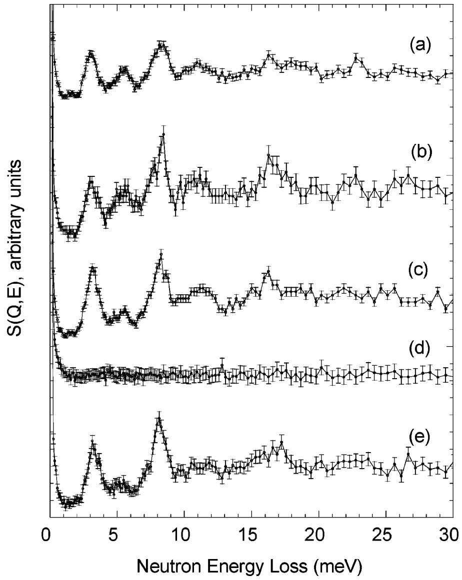

Figure 3. INS spectra of H_2 in Ag-A zeolite measured at 20 K in a range from 0 to 30 meV: (a) same as in Figure 2f, after reaction at 298 K for 2 h; (b) after the total loading was increased to 5.49 H_2 molecules per unit cell (0.51 H_2 molecule per Ag atom); (c) after further reaction for 2 h at 298 K; (d) after the sample was evacuated; (e) after redosing with hydrogen to a loading of 3.57 H_2 molecules per unit cell (0.51 H_2 molecule per Ag atom) and warming for the final reaction period of 4 h at 298 K.

reduced, first to 4.21 H_2 molecules per uc (Figures 1b and 2b) and then 2.91 H_2 molecules per uc (Figures 1c and 2c), all the peaks except for the 0.3 meV transition are reduced in intensity. In particular, the peaks at 8.4 and 11.0 meV, present at a loading of 7.62 H_2 molecules per uc, are absent at a loading of 4.21 H_2 molecules per uc. At the lowest H_2 coverage (2.91 H_2 molecules per unit cell), a distinct peak at 4.1 meV is resolved from the broader 5.3 meV peak. The intensities of the peaks observed at 18.0 and 22.6 meV have the same loading dependence as the intensity of the peak at 5.3 meV.

Warming the sample to 200 K for 2 h at a loading of 4.21 H_2 molecules per uc causes a decrease in the intensity of the 0.3 meV peak, which is further reduced by warming the sample to 250 K, as shown in Figure 1d–e. The peak is completely eliminated by warming to 298 K for 2 h (Figure 1f). The intensities of the peaks at 4.1 and 5.3 meV also diminish as the reduction proceeds (Figure 2d,e). The disappearance of the peak at 4.1 meV is complete after the first 2 h period of reduction at 298 K (Figure 2f). The peak at 5.3 meV is eliminated more slowly, and a vestige of it remains even after the third reduction cycle at 298 K (Figure 3e).

In addition to the disappearance of these peaks upon warming the sample, new features also appear. The dominant peaks in the INS spectrum after three cycles of warming for a total of 8 h at 298 K occur at 3.1 and 8.1 meV (Figure 3e). The latter peak emerged very weakly after the temperature had been raised to 200 K (Figure 2d) and became prominent after the reduction step at 250 K (Figure 2e), but the former only emerged very weakly after the temperature had been raised to 250 K. Other new weak INS peaks at 11.5 and 16.3 meV are visible following the reduction at 298 K for a total of 4 h (Figure 3c).

Discussion

The structural and electronic characterization of dehydrated Ag-A zeolite is still controversial. It had long ago been concluded that the pretreatment of the Ag-exchanged A zeolite, dehydration at high temperature in air as performed in our experiment (or in vacuo), results in a partial autoreduction of Ag^+ cations.[1−4] A characteristic trapped electron center, the trimeric complex Ag_3^{2+}, was proposed as being formed inside the sodalite cage of the zeolite.[2,4] This linear complex was composed of two Ag^+ cations in 6-ring sites, with the third, central Ag^0 atom in a 4-ring site of the zeolite framework. This structural model was developed by Gellens et al.[2] from X-ray powder diffraction studies. In a later single-crystal X-ray diffraction study, Gellens et al.[12] examined a Ag/H-A zeolite crystal that had been vacuum dehydrated at 683 K, a more drastic pretreatment that modifies the cation site distribution. Although they remained uncertain of the characterization of the silver clusters, linear trimers and more highly aggregated octahedral clusters were both plausible, the conclusion that ionic clusters were formed with reduced silver atoms occupying the 4-ring site in the sodalite cage was reiterated. The model of the Ag_3^{2+} linear trimer as being responsible for the yellow color was also adopted by Ozin and co-workers, who assigned vibrational peaks in the far-IR spectrum to this complex.[13,14]

A recent challenge to this model has been made by Calzaferri and co-workers, who have disputed the autoreduction scenario.[15,16] On the basis of a reinterpretation of the optical spectra and extended Hückel molecular orbital calculations,[16] they have concluded that the silver cations are not reduced during vacuum dehydration, attributing the yellow color to an isolated Ag^+ ion at the 4-ring site in the sodalite cage, and the red color to the Ag^+ ion at the 4-ring site with a second Ag^+ ion as a neighbor. Our view is that while a yellow color could indeed result from an isolated Ag^+ ion at the 4-ring site in the sodalite cage, the complementary evidence from chemisorption[4] properties favors the occurrence of the autoreduction reaction and the presence of the cationic clusters in the material.

The cation distribution in the Ag-A zeolite pretreated as we have described above, with a final evacuation at 400 °C, should correspond closely to that determined by Gellens et al.[2] for their yellow-gray Ag-A375 material. This material was shown to contain ∼1.8 Ag_3^{2+} clusters ($Ag^{+-}Ag^{0-}Ag^+$) per unit cell in the sodalite (β) cages of the LTA structure, accounting for 3.6 (nominally) Ag^+ ions in 6-ring sites (type II_β) and 1.8 (nominally) Ag^0 atoms in the 4-ring sites (type I). In addition, isolated Ag^+ ions were located at both 6-ring and 8-ring sites in the large α-cage. The 8-ring (type III) sites were fully occupied with 3 Ag^+ ions per unit cell, and the α-cage 6-ring sites (type II_α) contained ∼3.4 Ag^+ ions per unit cell. The same set of sites is occupied, but with different occupancies, for a variety of pretreatment conditions. The nomenclature for designating these sites has not always been consistent in the literature. In this paper, we are following the convention originally used by Gellens et al.[2] (the 6-ring and 8-ring sites have been designated as types I and II, respectively, for Na^+ ions in Na-A, and a site near the 4-ring in the α-cage has been designated as type III).

It has been convincingly argued in the early work that the chemisorptive interaction of molecular H_2 occurs specifically with the linear Ag_3^{2+} clusters[4,13,14] and not with the isolated Ag^+ ions.[4] If this chemisorption is molecular, then we should observe INS peaks corresponding to both the chemisorbed H_2 and to H_2 molecules interacting weakly with Ag^+ ions in the type II_α and the type III sites. On the other hand, if the initial chemisorption is dissociative (at 195 K), as concluded in the work of Jacobs et al.,[4] then the dissociated hydrogen will give rise only to high-frequency vibrations corresponding to energy transfers above the useful range of the QENS spectrometer (0–

50 meV). The experimental consequence of that would be the absence of a signature of the chemisorbed hydrogen in the rotational tunneling region of the INS spectrum. In the experiments from which dissociative adsorption of H_2 was deduced, Jacobs et al. adsorbed H_2 at 195 K and determined the amount that could not be desorbed at 293 K.[4] In our experiment, the adsorption of H_2 was performed at 100 K and the spectroscopic measurements were made at 15−20 K.

Low-Temperature Adsorption. The unambiguous signature of chemisorbed molecular H_2 is the appearance of a 0.3 meV peak in the INS spectra (Figure 1a−e). Physisorbed molecular H_2 interacting with Zn^{2+}, Co^{2+}, or Ca^{2+} ions in type A zeolite give rise to rotational tunneling splittings in the range of 3−9 meV,[8−10] while the tunneling splittings measured for the molecular hydrogen complexes lie in the range of 0.06−2.5 meV.[5−7] Therefore, the peak we observed at 0.3 meV (2.4 cm^{-1}) can be assigned to H_2 in a molecular complex. Consistent with this interpretation is the observation that the peak intensity is not diminished when the hydrogen loading is reduced from 4.21 to 2.91 H_2 molecules per unit cell (Figure 1b,c) at temperatures below 100 K, whereas the intensities of other independent peaks are diminished (Figure 2b,c). The amount of hydrogen adsorbed is at all steps less than 1 H_2 molecule per Ag atom. If we use as an approximation the site distribution determined by Gellens et al.[2] mentioned above, and reason that the chemisorption sites are all occupied in the initial dosing at 100 K, then 1.8 H_2 molecules per unit cell remain chemisorbed on the Ag_3^{2+} clusters in all the measurements (Figure 1a−c) made before the sample was warmed to 200 K. The amount of H_2 available for physisorption varies from 5.82 H_2 molecules per unit cell (Figure 2a) to 1.11 H_2 molecules per unit cell (Figure 2c). There are 6.4 isolated Ag+ ions per unit cell in the Gellens distribution, so the amount of H_2 adsorbed is insufficient for physisorption to occur at all the Ag^+ ion sites, even at the highest loading. The impact of reducing the hydrogen loading would be to modify the distribution of physisorbed H_2 molecules among the various sites.

The peaks at 5.3, 8.4, 11.0, 18.0, and 22.6 meV for H_2 adsorbed in the Ag-A zeolite are diminished in intensity by reducing the hydrogen loading at 100 K, and can therefore be assigned to the reversibly bound H_2 molecules interacting weakly with isolated Ag^+ ions in the type II_α and type III sites. (Should ions reside in the type I or type II_β and not belong to a complete linear Ag_3^{2+} complex, they will constitute additional inequivalent sites not specifically addressed in our ensuing discussion.) In particular, the peaks at 8.4 and 11.0 meV, which are present at a loading of 7.16 H_2 molecules per unit cell but absent at a loading of 3.96 H_2 molecules per unit cell, are assigned to H_2 molecules physisorbed on Ag^+ ions in the type III sites. At the lowest H_2 coverage (2.76 H_2 molecules per unit cell), a distinct peak at 4.1 meV is resolved from the broader 5.3 meV peak in the spectrum. The peaks are both attributed to H_2 molecules weakly coordinated with Ag^+ ions in the type II_α sites, but two types of complexation are implied. The intensities of the peaks observed at 18.0 and 22.6 meV have the same loading dependence as the intensity of the peak at 5.3 meV. Therefore, these two energy transitions are related to the H_2 physisorbed on Ag^+ at the type II_α sites.

One issue to be considered in discussing the mechanism of the reduction of silver cations by hydrogen in zeolite A is whether to invoke the need for access of H_2 to the linear Ag_3^{2+} cluster in the sodalite cage at room temperature or below. The effective diameter of the 6-ring access to these cages is 2.2 Å, and the kinetic diameter of the H_2 molecule is 2.89 Å (2.75 Å at 273 K). It might seem unlikely that H_2 molecules would diffuse into β-cages at the loading temperature of 100 K; however, Jacobs et al. attributed the much greater chemisorption capacity for hydrogen versus oxygen at 195 K to the inability of O_2 to enter the 6-ring window, whereas H_2 could. If we assume this to be the case, then a possible structure for the $[Ag_3^{2+}\cdots H_2]$ chemisorption complex that is formed initially would be one in which the H_2 molecule is inside the sodalite cage and interacting either with one of the terminal Ag^+ ions (type II_β site) in the linear complex or with the central reduced Ag^0 atom (type III site) in the linear complex. On the other hand, if the possibility that the H_2 enters the 6-ring at 100 K is discounted, then we can only allow that the $[Ag_3^{2+}\cdots H_2]$ chemisorption complex that is formed initially has a structure in which the H_2 molecule is on the α-cage side of the 6-ring window and forms the bond with a terminal Ag^+ ion in the type II_β site in the 6-ring. A bond to the Ag^0 in the type III site is not possible in this case. The Ag_3^{2+} complex to which the H_2 molecule is bonded is likely to relax its position so that the terminal silver atom coordinated to the H_2 molecule is closer to or in the plane of the 6-ring. The other terminal Ag^+ ion in the complex would not be able to interact strongly with a second H_2 molecule through its 6-ring window. This picture is consistent with the stoichiometry of the chemisorption determined by Jacobs et al., which is one H_2 molecule per Ag_3^{2+} complex.[4]

The model for analyzing these rotational tunneling transitions is adopted from Eckert and co-workers.[5−7] A double minimum potential is used:

$$\boldsymbol{V} = (V_2/2)(1 - \cos 2\theta) \tag{1}$$

where V_2 is the barrier height and θ is the angle of internal rotation. In the $[Ag_3^{2+}\cdots H_2]$ chemisorption complex, this is likely to be an oversimplification, and is perhaps best realized in the model in which the diatomic H_2 molecule is inside the sodalite cage and interacting with the central reduced Ag^0 atom (type III site). If the H_2 molecule is on the α-cage side of the 6-ring window and forms the bond with a terminal Ag^+ ion in the type II site in the 6-ring, then the 3-fold symmetry of the 6-ring must be deemed of negligible consequence in this approximation. Then, the rotational motion of the chemisorbed H_2 is limited to a plane parallel to the plane of the 6-ring, and a 2-dimensional hindered rotor model is appropriate. In a chemisorption complex, the H−H bond is expected to be stretched beyond the free molecule value of 0.74 Å as is found for the η^2-H_2 complexes.[6] This elongated H−H bond length is assumed to be 0.82 Å, which is taken from the diffraction data of some metal complexes with molecular hydrogen.[17] The rotational constant (B_c) of H_2 becomes 6.01 meV. The energy levels of this model as a function of rotational barrier height are shown in Figure 4. The fit of the excitation at 0.03 meV corresponds to a rotational barrier of 1.7 kcal/mol. Clot and Eckert[18] have described a refined 2-dimensional dynamical parametrized model that allows the H−H bond distance to be determined from the INS measurements. This method requires that transitions to higher lying torsional states be measured in the INS spectra. On the basis of the energy level diagram presented in Figure 4, these excitation energies would exceed 33 meV and are outside the energy range of the data shown in the experimental spectra. They were not observed.

For H_2 physisorbed on isolated Ag^+ ions, a hindered rotor model which has been used for the adsorption of H_2 on Co^{2+} in type A zeolite is adopted from Nicol et al.[9] The model is one in which the H_2 molecule adsorbs on the Ag^+ ion in an end-on geometry and rotates about its center of mass. This model

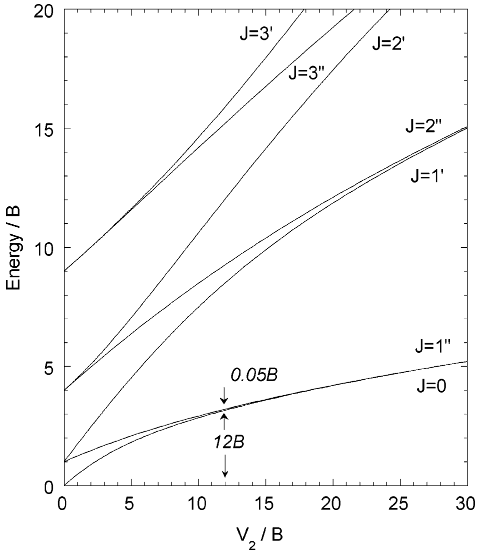

Figure 4. Energy levels for hindered rotational motion of H_2 in a plane parallel to the H−H axis, with a double minimum potential.

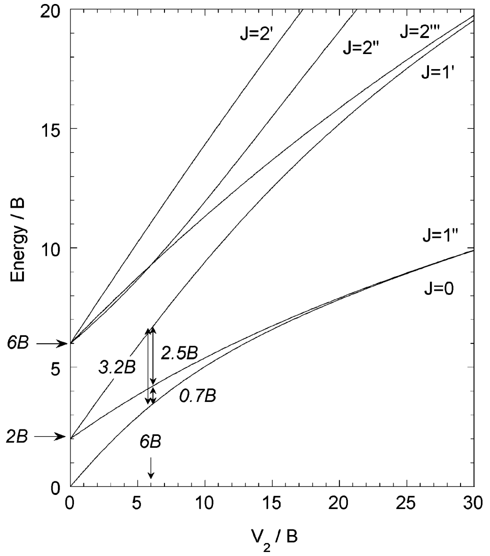

Figure 5. Energy levels for hindered rotational motion of H_2 physisorbed in an end-on manner (the σ model), with a double minimum potential.

TABLE 1: Peak Assignments and Barriers to Rotational Tunneling for Chemisorbed and Physisorbed H_2 in Ag-A Zeolite upon Initial Adsorption at 100 K

Energy Transfer (meV)	Assignment	Rotational Barrier	Transition
0.3	chemisorbed H_2/Ag_3^{2+} (II_β site)	$12B_c$[a]	$0 \rightarrow 1''$
4.1	physisorbed H_2/Ag^+ (II_α site)	$7.5B$[b]	$0 \rightarrow 1''$
5.3	physisorbed H_2/Ag^+ (II_α site)	$6.0B$	$0 \rightarrow 1''$
18.0			$1'' \rightarrow 1'$ (18.2 meV)[c]
22.6			$0 \rightarrow 1'$ (23.5 meV)[c]
8.4	physisorbed H_2/Ag^+ (III site)	$3.7B$	$0 \rightarrow 1''$

[a] $B_c = 6.01$ meV, the rotational constant of H_2 with an elongated H−H bond (0.82 Å). [b] $B = 7.36$ meV, the rotational constant of free H_2 (bond length 0.74 Å). [c] The neutron energy transfer calculated from the hindered rotation model with the $J = 0 \rightarrow J = 1''$ transition fitted to the observed value.

has also been used by Curl et al.[19] for the problem of end-to-end disorder of CO in the solid state.[16] The energy levels are shown in Figure 5. In this case, the H−H bond length is that of free H_2 (0.74 Å), and the rotational constant (B) is 7.36 meV. The results of the analyses along with the assignments discussed above are summarized in Table 1. Peaks at 18.0 and 23.5 meV are assigned as higher lying rotational tunneling excitations for H_2 physisorbed on Ag^+ ions in the type II_α sites, the first excitation of which occurs at 5.3 meV with a rotational barrier equivalent to 1.0 kcal/mol. The weakly physisorbed H_2 on Ag^+ ions in the type III sites giving rise to the peak at 8.4 meV is determined to have a rotation barrier of 0.63 kcal/mol.

Silver Reduction above 200 K. The reduction of the silver begins at 200 K as indicated by the decrease in intensity of the rotational tunneling peak at 0.3 meV (Figure 1d,e). We attribute the loss of intensity to the dissociation of the elongated, activated H−H bond in the chemisorption complex, a process that progresses as the temperature is raised further to 250 K and then to 298 K. Electron transfer from the dissociated hydrogen atoms to the Ag_3^{2+} complex results in the formation of a neutral Ag_3^0 complex, as suggested by Ozin et al. from far-IR spectroscopic measurements.[13] As remarked above, adsorbed dissociated H atoms or protons that migrate to form framework hydroxyl groups would not be manifested in our INS spectra.

The intensities of the peaks at 4.1 and 5.3 meV diminish as the reduction proceeds (Figure 2d,e). The disappearance of the peak at 4.1 meV is completed after the first 2 h period of reduction at 298 K (Figure 2f). The peak at 5.3 meV is eliminated more slowly, and a vestige of it remains even after the third reduction cycle at 298 K. Clearly, the reducibility of the isolated Ag^+ ions is site-dependent. On the basis of our assignments offered in the previous section, the Ag^+ ions in the type II_α sites are the most difficult to reduce.

The absence of any peaks in the INS spectrum of Figure 3d indicates that all the peaks observed after the reaction is allowed to proceed at 298 K for 2 h (Figure 3a,b) are due to weakly bound H_2. The dominant peaks in the INS spectrum after the reduction had proceeded (three cycles for a total of 8 h) at 298 K occur at 3.1 and 8.1 meV (Figure 3e). The latter peaks emerged very weakly after the temperature had been raised to 200 K and became prominent after the reduction step at 250 K, but the former only emerged very weakly after the temperature had been raised to 250 K. These two INS features are attributed to H_2 weakly bound to metallic silver clusters. Weaker peaks in the final spectrum were also observed at 5.3 and 22.5 meV and arise from the physisorbed molecular hydrogen on residual Ag^+ ions. A new, weak INS peak at 11.5 meV, which is related to the peak at 8.1 meV, is also observed. The new INS peak at 16.3 meV is not a rotational tunneling peak for gaseous hydrogen because the transition energy is higher than $2B$ (14.7 meV), the highest possible value for free H_2. Thus, it must be due to librational excitations of H_2 in a well-defined potential. A tentative assignment to the center of mass motion of H_2 in its adsorption site is proposed.

The rotational tunneling splittings observed at the termination of the reduction are also analyzed using the general hindered rotational model described above for physisorption on an isolated ion. However, we assign the peaks to H_2 physisorbed on small metallic clusters, on the basis of the chemistry of the system. Ozin and co-workers[12] concluded that the linear Ag_3^{2+} cluster in the sodalite cage is first reduced by hydrogen at room temperature to a Ag_3^0 cluster that remains in the sodalite cage. We assign the peak at 3.1 meV (Figures 2f and 3a−c,e) to H_2 physisorbed on the Ag_3^0 cluster in the sodalite cage. A barrier of 1.6 kcal/mol is determined. We assign the peak at 8.1 and 11.5 meV (Figures 2f and 3a−c,e) to H_2 physisorbed on zerovalent clusters that have formed in the large α-cage by Ag^0 atoms diffusing out of the sodalite cage. A barrier of 0.68 kcal/

TABLE 2: Peak Assignments and Barriers to Rotational Tunneling for Physisorbed H_2 in Ag-A Zeolite upon Termination of the Reduction at 298 K

Energy Transfer (meV)	Assignment	Rotational Barrier	Transition
3.1	physisorbed H_2/Ag_3^0 cluster	$9.5B^a$	$0 \rightarrow 1''$
8.1	physisorbed H_2/neutral Ag_n^0 cluster	$4.0B$	$0 \rightarrow 1''$
11.5			$1'' \rightarrow 1'$ (11.4 meV)[b]
16.3	H_2 center of mass motion		

[a] $B = 7.36$ meV, the rotational constant of free H_2 (bond length 0.74 Å). [b] The neutron energy transfer calculated from the hindered rotation model with the $J = 0 \rightarrow J = 1''$ transition fitted to the observed value.

mol is determined. The results of the analyses of the tunneling spectra in this approximation are summarized in Table 2.

Reaction Mechanism. At the beginning of the experiment, before the reduction reaction occurs, molecular hydrogen diffused into the zeolite framework and was adsorbed at the sites of both cationic silver complexes and the isolated silver ions. In the experimental INS spectra, chemisorbed and physisorbed H_2 species were observed before the reduction began. Identification of $Ag_3^{2+}\cdots H_2$ as the reactive intermediate was based on the rotational tunneling transition peak observed at 0.3 meV; this is a characteristic signature of dihydrogen bound in a transition-metal molecular complex.[5-7] The existence of this complex provides critical evidence for the mechanism of this reduction reaction. The proposed (barrier-free) dissociative chemisorption of H_2 onto the Ag_3^{2+} cluster is inconsistent with the INS results presented here. Instead, H_2 molecularly chemisorbed onto Ag_3^{2+} is activated by elongation of the H−H bond, but the complete dissociation is an activated process requiring a temperature in excess of 200 K.

When the reaction starts at 200 K, the intensity of the 0.3 meV INS peak decreases dramatically (Figure 1d), and the peak disappears irreversibly by the end of the first reaction period at 298 K (Figure 1f). During the same period, the intensities of the other main INS peaks assigned to physisorbed H_2 at type II_α sites (5.3 meV) and type III sites (8.4 meV) remain relatively unchanged (Figure 2d−f). Thus, the $Ag_3^{2+}\cdots H_2$ complex clearly is the reactive intermediate which drives the reduction reaction that is known to occur in this temperature range. The charge transfer from hydrogen to Ag_3^{2+} takes place as the H−H bond is broken. Meanwhile, new INS peaks growing in the spectra during the same period can be assigned to weakly bound H_2 on neutral silver (metal) clusters, both in the sodalite cage and in the large α-cage of the zeolite structure.

As the reaction proceeds at 298 K, Ag^0 atoms from the reduced trimers (Ag_3^0 clusters) evidently diffuse out of the sodalite cages and combine with isolated Ag^+ ions to form silver clusters with low charge. The charge transfer continues until most of the silver ions are reduced. After a total of 8 h of reaction at 298 K, the INS peaks due to the physisorption of H_2 on the silver metal clusters dominate the INS spectrum (Figure 3e). Only very weak residual intensity is observed for the 5.3 meV peak that corresponds to the physisorbed H_2 on isolated Ag^+ ions at the type II_α sites.

Unlike the simple reversible physisorption process, the adsorption processes that we are describing are irreversible. The chemisorbed molecular H_2 can only be observed following the initial loading of the sample at 100 K and before it is warmed to 298 K. Thereafter, the chemisorbed molecular H_2 species, $[Ag_3^{2+}\cdots H_2]$, cannot be regenerated because the original adsorption site, the Ag_3^{2+} cluster, has itself been chemically transformed. Thus, the chemisorbed molecular H_2 does not reappear when additional hydrogen is introduced at 100 K following the initial warming to 298 K (Figure 3b). In addition, as shown in Figure 3d, after the sample has been heated to 298 K the adsorbed molecular hydrogen can be completely removed by evacuation at 100 K. Redosing the sample with hydrogen at 100 K at this juncture does not result in the formation of the chemisorbed molecular hydrogen species. Chemical reversal is possible via high-temperature reoxidation of the reduced Ag-A zeolite with oxygen to restore the Ag_3^{2+} complexes.[13]

Hindered Rotation of Chemisorbed H_2. The barrier height for the chemisorbed H_2 species is $12B_c$, equivalent to 1.7 kcal/mol. The chemisorbed H_2 rotates under a higher barrier than the physisorbed H_2, which is consistent with the fact that the chemisorbed H_2 is more tightly bound. The barrier height arises mainly from the interaction of the H_2 molecule with the charged silver cluster. We have neglected the influence on the barrier height of the framework environment of the site where the silver species are located. Thus, the chemisorbed H_2 may interact with the framework atoms of the zeolite 6-ring. However, we have tried models with 6-fold and 12-fold potentials, neither of which gave reasonable fits to the observed rotational tunneling frequencies. Thus, we conclude that the interaction of H_2 with the framework atoms makes only a minor contribution. Unfortunately, there are no crystallographic data to provide a concrete measure of the distance between the hydrogen atom and the framework atoms.

As discussed by to Eckert et al.,[5] the H_2–M σ-donation and the M−H_2 σ^* back-bonding are the main source of the binding energy of the metal−molecular hydrogen complex. This situation is best described by a model with a double minimum potential.[5] On the other hand, this rotational barrier is determined by fitting only one transition frequency (0.3 meV) to the 2-dimensional hindered rotation in a plane with a double minimum potential, so we concede that our solution may not be a unique answer to the observed rotational tunneling frequency for the $[Ag_3^{2+}\cdots H_2]$ chemisorption complex. Nevertheless, the model is reasonable; moreover, it seems to suit best a geometry for the complex in which the H_2 molecule remains on the outside of the sodalite cage. Therefore, we favor the proposed structure of the $Ag_3^{2+}\cdots H_2$ complex with the H_2 bonded to the Ag_3^{2+} cluster via a Ag^+ ion in a 6-ring window.

Hindered Rotation of Physisorbed H_2. The barrier heights of different physisorbed H_2 species are in a wide range from $3.7B$ to $9.5B$. There are two possible geometries for the physisorption of H_2 onto Ag^+ ions or metallic Ag clusters in type A zeolites. The H_2 can be bound to the metal either end-on or side-on.[8] We term these the σ model and the π model, respectively. The most general model for hindered rotation would be to take into account both "in-plane" and "out-of-plane" hindered rotation (regarding the metal as a surface) and give two separate barrier heights accordingly.[20] However, such a model does not give a unique set of barrier heights that fit our data. If the π model is applicable, a 6-fold potential and an 8-fold potential will be required for the adsorbed H_2 at the type II and type III sites. These potentials also do not fit our data. Another possibility is that H_2 interacts negligibly with the zeolite framework. H_2 can then undergo free rotation in a plane, which gives rotational levels BJ^2. Again, this is not consistent with our data. Therefore, the π model cannot describe the H_2 adsorption correctly. Indeed, the σ model, whose energy levels are shown in Figure 5, fit our data satisfactorily. The same scenario is present in the reported case of the adsorption of H_2 in Co/Na-A zeolite.[9] The barrier heights for the case of Ag-A zeolite derived from this model are in a range similar to those for the adsorption of H_2 in Co/Na-A and Ca/Na-A zeolites.[9,10]

Conclusion

We have followed the reduction by H_2 of silver ions in Ag-A zeolite in a novel way using inelastic neutron scattering spectroscopy. A fairly complete set of rotational tunneling transitions are observed. The reduction reaction was shown to start as low as 200 K. The reaction intermediate formed before the charge transfer takes place has been unambiguously identified as a complex of a charged silver cluster and molecular hydrogen, $Ag_3^{2+}\cdots H_2$. Therefore, the mechanism of the reduction reaction does not begin with the dissociative chemisorption of H_2. Instead, the reduction reaction starts with the activation of the H−H bond by the formation of the silver−molecular hydrogen complex, followed by charge transfer from hydrogen to silver as the H−H bond breaks.

Besides the chemisorptive species, other physisorbed H_2 species have also been found in various sites of the zeolite framework. Most of the INS peaks can be assigned and are consistent with a model of hindered rotational motion of molecular hydrogen with a double minimum potential.

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