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Properties of chemisorbed hydrogen species on Ag-A zeolite partially reduced with hydrogen as studied by ^{1}H MAS NMR

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Abstract

Heterolytic dissociation of H_2 proceeded to form acidic protons and silver hydride species, Ag_3–H upon exposing Ag-A to hydrogen. The effects of the degree of Ag^+ ion exchange and the temperature of hydrogen exposure on the formation of hydrogen chemisorbed species were examined with ^{1}H MAS NMR. Furthermore, the thermal stability of silver hydride species and the temperature dependence of the line shape of the peak due to acidic protons were studied with raising the temperature stepwise from 298 to 513 K. The thermal stability of Ag_3–H and the mobility of acidic protons decreased with increasing the Ag^+ content in zeolite. Ag_3–H reacted with acidic protons to form H_2 and ${Ag_3}^+$ at 353 K. This result was in conformity with the mechanism of hydrogen adsorption proposed in our previous work. © 2001 Published by Elsevier Science B.V.

Keywords: Hydrogen; Ag-A; ^{1}H MAS NMR; Acidic proton; Silver hydride

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1. Introduction

Recently, we have reported that ^{1}H MAS NMR gives unequivocal evidence for the heterolytic dissociation of hydrogen on Ag-A reduced with hydrogen [1]. Thus, acidic protons and silver hydride species, i.e. Ag_3–H were observed by exposing Ag-A to H_2 at 313 K. Furthermore, the amounts of Ag_3–H and acidic protons were reversibly changed by eliminating hydrogen from gas phase and exposing the sample to hydrogen again. On the basis of these experimental results, we proposed the mechanism of the reversible hydrogen chemisorption on Ag-A at 313 K as follows [1].

$$2Ag^+ + H_2 \rightleftarrows 2Ag^\circ + 2H^+ \tag{1}$$

$$2Ag^\circ + Ag^+ \rightleftarrows {Ag_3}^+ \tag{2}$$

$$Ag_3{}^+ + H_2 \rightleftarrows Ag_3H + H^+ \tag{3}$$

The formation of silver clusters in zeolites such as Ag-A has been studied with some instrumental techniques [2–14]. Gellens et al. [2–4] studied X-ray powder diffraction (XRD) of Ag-A, Ag-X and Ag-Y, degassed and treated with oxygen, and suggested that in Ag-A, isolated ${Ag_3}^{x+}$ clusters were the origin of the yellow color and the red color originated from two interacting Ag_3 clusters. Kim and Seff [5,6]

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determined the crystal structure of Ag-A ($Ag_{4.6}Na_{7.4}$-A) dehydrated, treated with H_2 and evacuated at 623 K by single-crystal XRD methods. They showed that Ag_6^{3+} clusters were present in each large cavity. The cluster is in the form of a nearly linear Ag_6^{3+} molecule, and each atom of which is coordinated to an Ag^+ ion. The authors also studied the structure of Ag-A ($Ag_{7.6}Na_{3.4}$-A) treated in a similar manner and found the presence of Ag_6^{3+} and Ag_5^{4+} clusters.

According to the various experimental results as mentioned above, the formation of silver clusters seems to depend on the degree of Ag^+-exchange and the conditions of hydrogen exposure.

The formation of silver hydride species has rarely been investigated. In our previous work, we reported the formation of Ag_3–H in Ag-A (the degree of Ag^+-exchange $= 54\%$) and the reversible change of the amounts of protons and Ag_3–H [1]. In the recent work, we investigate the effect of the degree of Ag^+-exchange and the temperature of hydrogen exposure on the formation of chemisorbed hydrogen species on Ag-A with ^1H MAS NMR. Furthermore, we examine the influence of temperature on the line shape of chemisorbed hydrogen species with variable temperature ^1H MAS NMR. In our previous work, ^1H MAS NMR spectra of Ag-A was measured only at 298 K and the thermal stability of chemisorbed hydrogen species on Ag-A has not been examined.

2. Experimental

Ag-A was prepared from Na-A using a conventional ion-exchange procedure with a silver nitrate solution at room temperature. The degrees of Ag^+-exchange were determined with atomic adsorption analysis, being 30, 60, and 100%. These zeolites are denoted hereinafter as Ag(30), Ag(60), and Ag(100), respectively.

Samples for ^1H MAS NMR measurements were prepared as follows: Ag-A zeolite (0.40 g) was packed in a glass tube with side arms, each of which was connected to a glass capsule used for ^1H MAS NMR measurements. The sample was heated under oxygen with a heating rate of 0.6 K min^{-1} from room temperature to 673 K, kept at the same temperature for 3 h, and then heated under vacuum at 673 K for 2 h. The Ag-A was exposed to 40 kPa of H_2 at 313, 353, and 393 K. The evolution of water during reduction was negligible. The consumption of hydrogen was manometrically monitored. Unless otherwise noted, the amount of hydrogen consumption corresponded to 21% of Ag^+ exchanged in Ag-A zeolites. Thus, the amounts of hydrogen consumption were 0.174, 0.350, and 0.584 mmol/g in Ag(30), Ag(60) and Ag(100), respectively. The amount of hydrogen consumption changed by changing time of hydrogen exposure at prescribed temperatures. These samples are denoted hereafter as Ag(30)-*T*, Ag(60)-*T*, and Ag(100)-*T*. Here, *T* represents the temperature of hydrogen exposure.

After cooling the sample to room temperature, it was transferred under hydrogen into a glass capsule to fill it completely and evenly. The capsule was then sealed, while the sample itself was maintained at 77 K.

^1H MAS NMR spectra were recorded on a Chemagnetics CMX-Infinity spectrometer operating at 400 MHz. In order to reduce ^1H-background signals from the probe material, the DEPTH2 pulse sequence was used [15]. The $\pi/2$ pulse width and the recycle delay were 2.0 μs and 20 s, respectively. The glass capsule containing the sample was inserted into a zirconia rotor (5 mm diameter). The rotation frequency of the glass capsule was 4.0 kHz. The chemical shift was referenced to tetramethylsilane (TMS) with the usual conventions. ^1H MAS NMR spectra were recorded at 298 K, unless otherwise noted.

3. Results and discussion

3.1. Effect of the degree of Ag^+-exchange on the formation of chemisorbed hydrogen species at 313 K

^1H MAS NMR spectra of Ag-A zeolites were recorded in the presence of H_2 (40 kPa), after exposing them to H_2 (40 kPa) at 313 K. Time of hydrogen exposure were 15, 10 and 9 min for Ag(30)-313, Ag(60)-313, and Ag(100)-313, whose spectra are shown in Fig. 1(a), (b), and (c), respectively.

In the case of Ag(30)-313, three kinds of peaks were observed at (3.9 ± 0.1), (-0.6 ± 0.1), and (-1.8 ± 0.1) ppm. On the other hand, in the cases of Ag(60)-313 and Ag(100)-313, two kinds of peaks

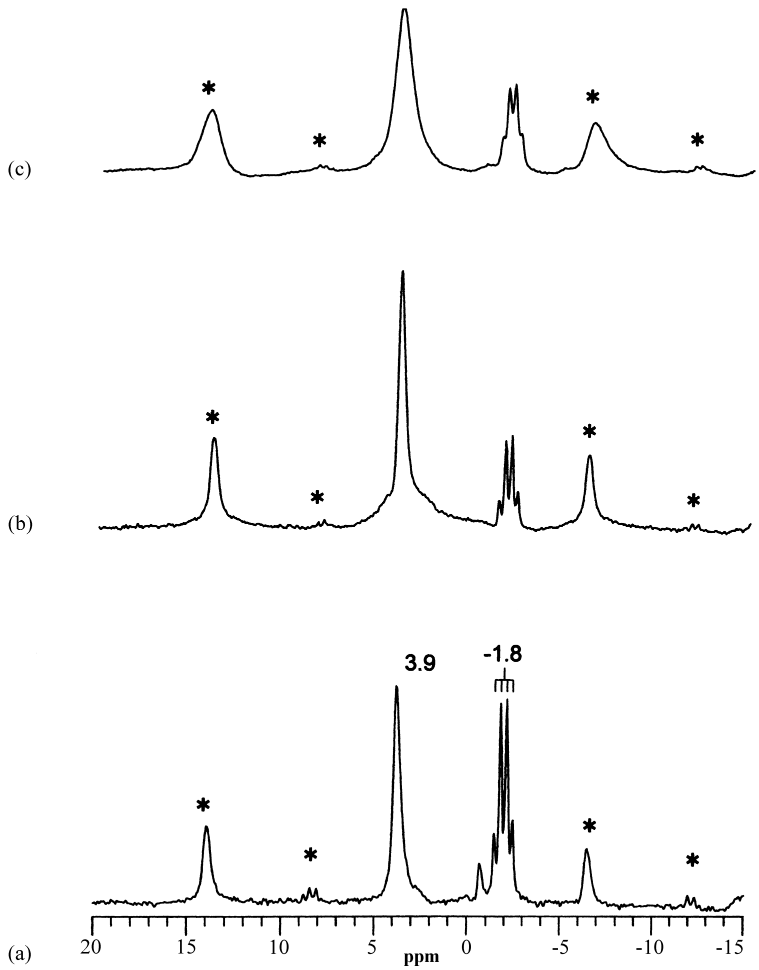

Fig. 1. ^1H MAS NMR spectra of Ag-A: (a) Ag(30)-313, (b) Ag(60)-313, (c) Ag(100)-313; (*)shows spinning side bands.

were observed at (3.9 ± 0.1) and (−1.8 ± 0.1) ppm, and the peak was not observed at −0.6 ppm. The peaks around −1.8 ppm separated into four peaks. The ratio of the peak intensities was 1:3:3:1, and their coupling constants were (131 ± 1) Hz. We have already assigned the peaks at 3.9 and −1.8 ppm to be attributed to acid protons and Ag_3–H, respectively [1]. Since the peak at −0.6 ppm was not observed by exposing H-Y to H_2, but was observed by exposing Ag(30) to H_2, it can be attributed to silver hydride species, which might be Ag–H. This result suggests that the formation of silver clusters depends on the degree of Ag^+-exchange in Ag-A zeolite and that silver hydride species other than Ag_3–H are also formed.

3.2. Effect of the amount of the hydrogen consumption on the formation of chemisorbed hydrogen species

The dependence of both the amounts of acidic protons and Ag_3–H on the amount of hydrogen consumption was examined by exposing Ag(60) to H_2 (40 kPa) at 313 K. The areas of the peaks due to acidic protons (3.9 ppm) and Ag_3–H (−1.8 ppm) were plotted against the amount of hydrogen consumption, which was changed with changing time of hydrogen exposure. As shown in Fig. 2, the amount of Ag_3–H linearly increased with increasing hydrogen consumption. The amount of acidic protons almost linearly increased with increasing hydrogen

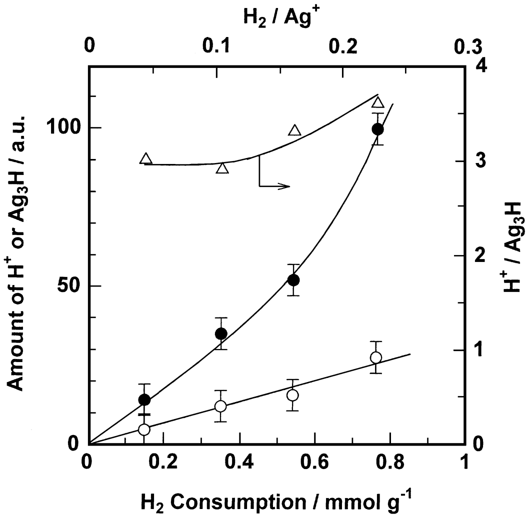

Fig. 2. The amounts of acidic protons and Ag_3–H were plotted against that of hydrogen consumption; Ag(60)-A was exposed to 40 kPa of hydrogen at 313 K: (●) acidic protons (3.9 ppm), (○)Ag_3–H(-1.8 ppm), and (□) the ratio of acidic protons to Ag_3–H.

consumption, while the linear relation was not observed at the amount of hydrogen consumption larger than ca. 0.54 mmol/g, which corresponded to 32% of Ag^+ cations exchanged in Ag(60). These results show that the formation of acidic protons and Ag_3–H depend on the amount of hydrogen consumption.

According to the mechanism expressed by Eqs. (1)–(3), the ratio of the amount of acidic protons to Ag_3–H is 3. At the amount of hydrogen consumption smaller than 0.54 mmol/g, the ratio of acidic protons to Ag_3–H is nearly equal to 3. However, the amount of acidic protons increased with increasing amount of hydrogen consumption as shown in Fig. 2, and the ratio of acidic protons to Ag_3–H is more than 3. These results suggest that the formation of acidic protons and of Ag_3–H are expressed by Eqs. (1)–(3) at the initial stage, and that of silver hydride species other than Ag_3–H are presumably formed by the reaction of $Ag_3{}^+$ with Ag^+ ions and/or silver metal, as the hydrogen consumption increased.

In the cases of Ag(30)-313 and Ag(100)-313 as shown in Fig. 1(a) and (c), the ratios of H^+/Ag_3–H were 2.3 and 3.8, respectively. Thus, the ratio also increased with increasing the degree of Ag^+-exchange. There is a possibility that $Ag_3{}^+$ further reacts with Ag^+ ions and/or silver metal to form silver cationic clusters with increasing the degree of Ag^+-exchange. Kim and Seff [5,6] also reported the formation of $Ag_6{}^{n+}$ such as $Ag_6{}^{3+}$.

3.3. *Effect of temperature of hydrogen exposure on the formation of chemisorbed hydrogen species*

The formation of chemisorbed species also depends on the temperature of hydrogen exposure. The spectra of Ag(60)-T were recorded in the presence of 40 kPa of hydrogen. As mentioned before, acidic protons and Ag_3–H were observed at 3.9 and -1.8 ppm for Ag(60)-313 (Fig. 3(a)). In the case of Ag(60)-353 as shown in Fig. 3(b), three peaks were observed at 3.9, -0.6, and -1.8 ppm. The peak at 3.9 ppm and the four peaks around -1.8 ppm are attributed to acidic protons and Ag_3–H, respectively. The peak at -0.6 ppm is presumably attributed to silver hydride species. However, in the case of Ag(60)-393, the silver hydride species were not observed, as shown in Fig. 3(c), while only one peak due to acidic protons was observed at 3.9 ppm. The line shape of the peak at 3.9 ppm was broad, as compared with that of the peak observed for Ag(60)-313. However, this reason is not clear at this stage.

According to the spectra shown in Fig. 3(a)–(c), the intensity of the peak due to acidic protons increased with increase in the temperature of hydrogen exposure, while the peak intensity of the peaks at -1.8 and -0.6 ppm decreased and these peaks were not observed for Ag(60)-393. At the temperature of hydrogen exposure higher than 313 K, $Ag_n{}^+$ ($n > 3$) might be generated by the reaction of $Ag_3{}^+$ with silver metal, which was formed by the reaction expressed by Eq. (1). It seems that the amount of $Ag_3{}^+$ decreased and that of acidic protons increased by the formation of $Ag_n{}^+$.

3.4. *Influence of measurement temperature of ^{1}H MAS NMR spectra on the line shape of chemisorbed hydrogen species*

^{1}H MAS NMR spectra of Ag(30)-313, Ag(60)-313, and Ag(100)-313 were recorded as the sample temperature was raised stepwise in the temperature range

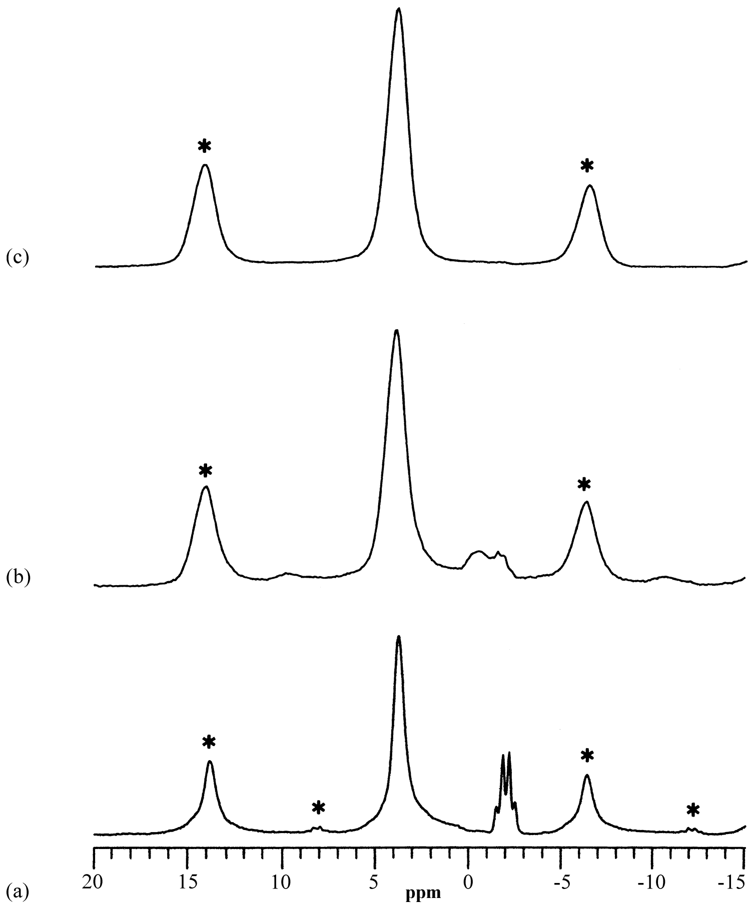

Fig. 3. The effect of temperature of hydrogen exposure on the formation of chemisorbed hydrogen species on Ag(60)-A: (a) Ag(60)-313, (b) Ag(60)-353, (c) Ag(60)-393; (*) shows spinning side bands.

from 298 to 473 K. Thus, the measurement was started in the presence of 40 kPa of H_2 at 298 K, and the sample was heated at prescribed temperatures for 15 min, and then the spectrum was measured. The variation of the amounts of acidic protons and Ag_3–H can be estimated by comparing the areas of these peaks with that of the background peak observed at 1.2 ppm.

^{1}H MAS NMR spectra of Ag(30)-313, Ag(60)-313, and Ag(100)-313 in the presence of 40 kPa of hydrogen are shown in Figs. 4–6, respectively. In the case of Ag(30)-313, the line shapes of the peak at -1.8 ppm and the peak at -0.6 ppm due to silver hydride species did not change with rising temperature, and their chemical shifts did not change either (Fig. 4). However, the intensity of the peak due to Ag_3–H (-1.8 ppm) increased up to 453 K, while it decreased and disappeared at 573 K. Thus, Ag_3–H in Ag(30)-313 is stable up to 453 K. On the other hand, the peak at -0.6 ppm decreased with decrease in temperature and disappeared at 393 K. Thus, Ag–H is stable up to 393 K. The chemical shift of the peak due to acidic protons did not change with changing temperature, while the line shape of the peak strongly depended on temperature. Thus, the line width began to increase around 393 K, and through maximum around 453 K, it decreased. This phenomenon may be due to the increased mobility of acidic protons at higher temperatures as found in H-ZSM-5 [16], and/or the exchange between acidic protons and hydrogen molecules in the gas phase.

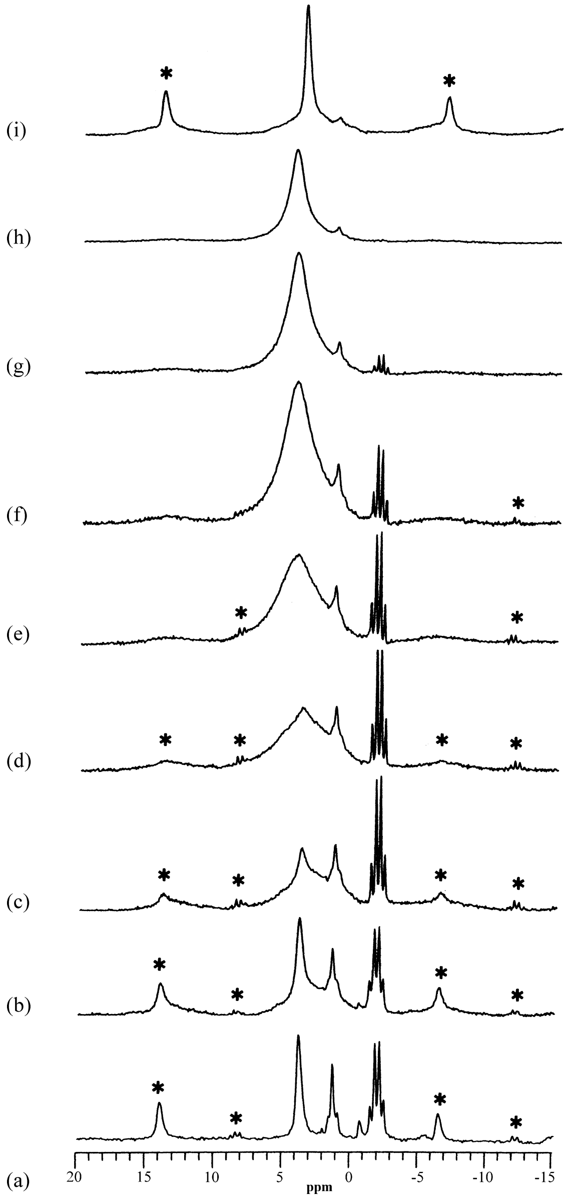

Fig. 4. The effect of temperature on the line shapes of acidic protons and silver hydride species in Ag(30)-313: (a) 298 K, (b) 353 K, (c) 393 K, (d) 423 K, (e) 453 K, (f) 473 K, (g) 493 K, and (h) 513 K. (i) The sample (h) cooled to 298 K. Sensitivity: (a)–(e) = 1, (f) and (g) = 1/2, (h) and (i) = 1/4; (*) shows spinning side bands.

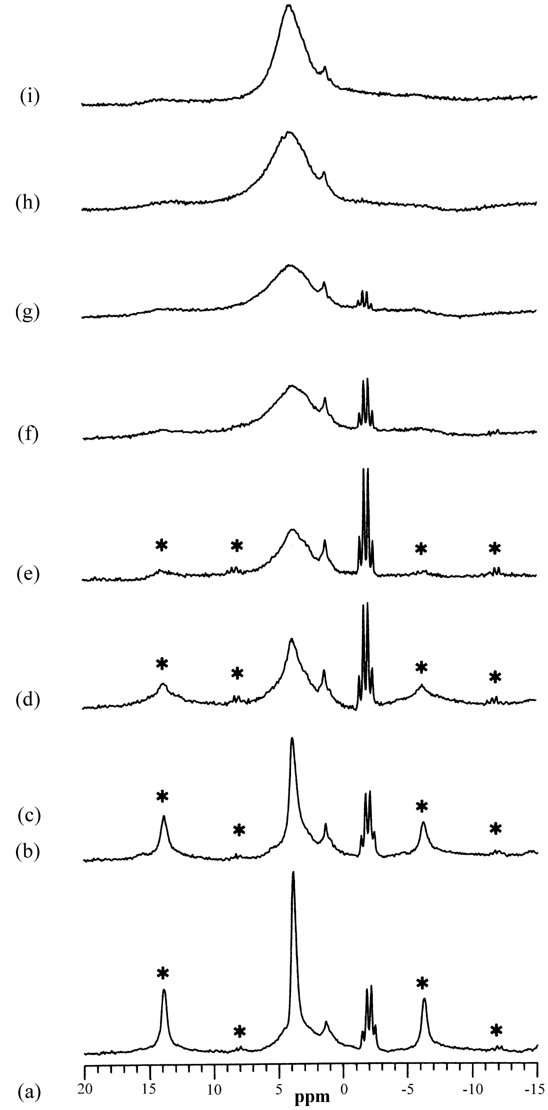

Fig. 5. The effect of temperature on the line shapes of acidic protons and silver hydride species in Ag(60)-313: (a) 298 K, (b) 353 K, (c) 393 K, (d) 423 K, (e) 453 K, (f) 473 K, (g) 493 K, and (h) 513 K. Sensitivity: (a)–(f) = 1, (g) and (h) = 1/2; (*) shows spinning side bands.

In the case of Ag(60)-313, the two kinds of peaks were observed as mentioned before (Fig. 5(a)). In this case, the line shape of the peak due to Ag_3–H and its chemical shift did not change with rising temperature as well as the case of Ag(30)-313, while the intensity of the peak reached maximum at 423 K and disappeared at 493 K. Thus, Ag_3–H was stable up to 423 K. The chemical shift of the peak due to acidic protons did not depend on temperature, while the maximum line width was observed around 423 K.

In the case of Ag(100)-313, silver hydride species were observed at −0.6 and −1.8 ppm (Fig. 6(a)). The peak at −0.6 ppm disappeared on raising the temperature to 393 K, while Ag_3–H was stable up to 353 K. In this case, the line width of the peak due to acidic protons, also depended on temperature as well as in the cases of Ag(30)-313 and Ag(60)-313. However, the line width increased with increase in temperature up to 513 K. This means that the maximum line width is observed at a temperature higher than 513 K. The chemical shift did not depend on the degree of Ag^+-exchange.

On the basis of the results of the temperature dependence shown in Figs. 4–6, both the thermal stability

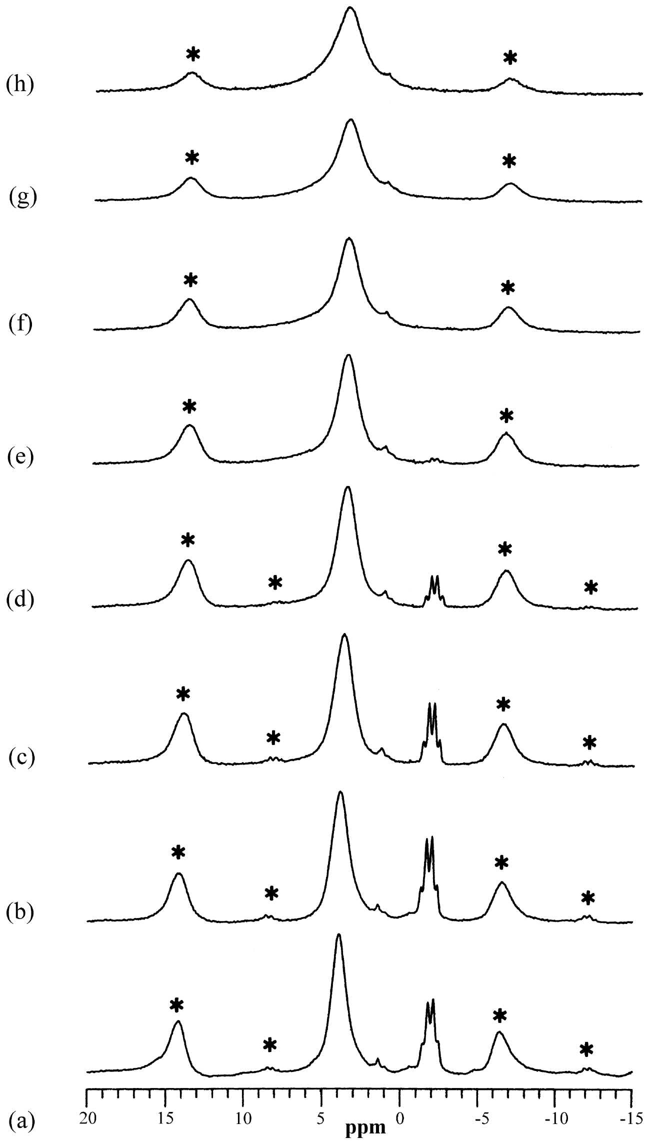

Fig. 6. The effect of temperature on the line shapes of acidic protons and silver hydride species in Ag(100)-313: (a) 298 K, (b) 353 K, (c) 393 K, (d) 423 K, (e) 453 K, (f) 473 K, (g) 493 K, and (h) 513 K; (*) shows spinning side bands.

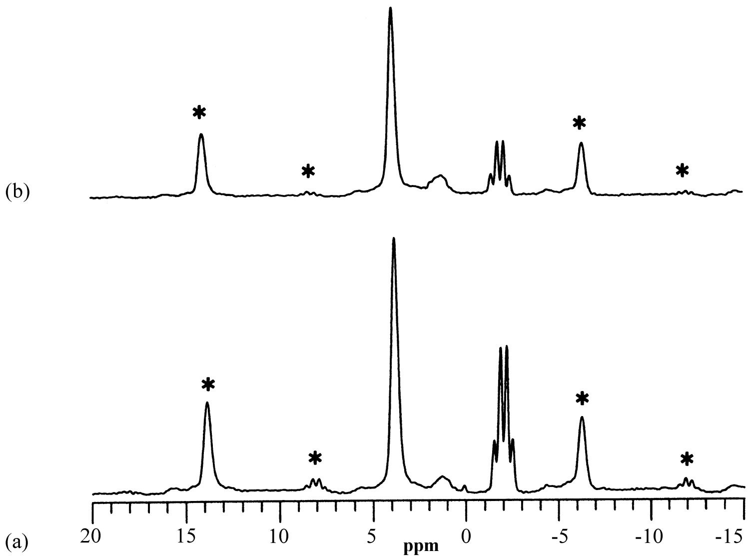

Fig. 7. The reaction of acidic protons with Ag_3–H: (a) Ag(60)-313 evacuated at 313 K for 5 min; (b) The sample (a) heated at 423 K for 15 min; (*) shows spinning side bands.

of Ag_3–H and the mobility of protons increase with decreasing degree of Ag^+-exchange.

The sample in Fig. 4(h) was cooled to 298 K and ^1H MAS NMR spectrum was measured as shown in Fig. 4(i). The intensity of the peak due to acidic protons (3.9 ppm) increased. This suggests that Ag^+ is further reduced with hydrogen to form acidic protons and silver metal. Furthermore, Ag_3–H was not observed, as shown in Fig. 4(i). There is a possibility that the reverse reaction expressed by Eq. (3) proceeds at a high temperature.

To examine the reverse reaction, the amounts of acidic protons and of Ag_3–H were measured, before and after heating Ag(60)-313 at 353 K in the absence of hydrogen in the gas phase. Fig. 7(a) shows ^1H MAS NMR spectrum of Ag(60)-313 evacuated for 5 min at 313 K. The acidic protons and Ag_3–H were observed at 3.9 and -1.8 ppm, respectively. This sample was then heated at 353 K for 30 min. As shown in Fig. 7(b), the intensities of both peaks due to acidic protons and Ag_3–H decreased. The amount of consumption of acidic protons was almost equal to that of Ag_3–H, indicating that the reverse reaction expressed by Eq. (3) proceeds at 353 K. This result was in conformity with the mechanism of hydrogen adsorption proposed in our previous work [1].

4. Conclusions

^1H MAS NMR gave evidence for the formation of acidic protons and silver hydride species when Ag-A was exposed to hydrogen. On the basis of the measurements of ^1H MAS NMR spectra and hydrogen consumption, we found novel properties of the chemisorbed hydrogen on Ag-A partially reduced with hydrogen in addition to the results of our previous work as follows.

1. The formation of Ag_3–H is influenced by the temperature of hydrogen exposure and the degree of Ag^+-exchange.
2. Silver hydride species (Ag–H) other than Ag_3–H were observed at -0.6 ppm.
3. The formation of these silver hydride species also depends on the temperature of hydrogen exposure and the degree of Ag^+-exchange. This suggests that the reactions other than those expressed by Eqs. (1)–(3) proceed to form hydrogen chemisorbed species.
4. The thermal stability of Ag_3–H increases with decreasing degree of Ag^+-exchange and the line shape of the peak due to Ag_3–H does not depend on the temperature.

5. The line width of the peak due to acidic protons depends on the temperature. As the degree of Ag^+-exchanged increases, the maximum line width is observed at higher temperature.
6. The chemical shift due to acidic protons is independent of the degree of Ag^+-exchanged and the temperature.

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