Probing the Locations of Ag^+ and Hydroxy Groups in AgA Zeolites by in situ FTIR Spectroscopy

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Hydroxy groups formed on AgA zeolites upon H_2 (D_2) adsorption exhibited infrared bands at different frequencies depending on the degree of Ag^+ exchange. The hydroxy groups formed by H_2 adsorption were found to occur mainly inside the β-cages of AgA-30, as evidenced by the inaccessibility of CO.

Ag-exchanged zeolites exhibit pronounced catalytic activity in various reactions.[1] Although their excellent reactivity has been suggested to be related to the redox properties of Ag^+, the active sites are still far from being fully understood. Additionally, some debate still exists on the nature and locations of the silver cations and silver cationic clusters. In this work, we investigated H_2 (D_2) adsorption on AgA zeolites at various degrees of Ag^+ exchange by FTIR. The H_2- or D_2-adsorbed AgA was further examined by CO adsorption at low temperature in order to probe the presence of various active sites and their locations.

AgA zeolites were prepared from NaA zeolite ($SiO_2/Al_2O_3 = 2.0$) as previously reported.[1] The degrees of Ag^+ exchange were 30, 60, and 100%, hereafter denoted as AgA-30, AgA-60, and AgA-100. All IR spectra were recorded on a JASCO WS/IR-7300 spectrometer with an MCT detector. The samples were pretreated in situ with O_2 at a heating rate of $0.4\,K\cdot min^{-1}$ from room temperature to 673 K, maintained for 1 h, and then evacuated for a further 1 h. After pretreatment, the color of the sample changed from gray-white to yellow then to brick-red, indicating the formation of silver cationic clusters inside β-cages.[2] H_2 (D_2) and CO adsorption was performed at 298 and 150 K, respectively. H_2- or D_2-adsorbed AgA refers to AgA samples that were subjected to H_2 or D_2 adsorption at 298 K for 30 min followed by pumping off of gaseous H_2 or D_2. All the IR spectra given here are background subtracted. The XRD patterns reveal that the crystall structure of AgA remains unchanged after the present H_2 adsorption.

After adsorption of D_2 on AgA at 298 K for 30 min, sharp bands due to the formation of bridging OD groups were observed (Figure 1). The OD band appeared at $2667\,cm^{-1}$ on AgA-30 and at $2664\,cm^{-1}$ on AgA-60. On the fully Ag^+-exchanged AgA-100 sample, a relatively large OD band was observed, which was well deconvoluted using a Lorentzian function into three bands at 2665, 2649, and $2632\,cm^{-1}$. The frequencies of hydroxy groups generated during H_2 (D_2) adsorption on various AgA and NaA samples are summarized in Table 1. Neither OH nor OD bands were formed on NaA under the same conditions due to the absence of Ag^+ cations.

Clearly, the OD bands occur at different frequencies depending on the degree of Ag^+ exchange (Figure 1). Three strong OD bands were identified for the AgA-100 sample, which can be explained in terms of the different locations of Na and Ag cations inside the zeolite cavity (see Graphical Abstract). During the Ag^+–Na^+ exchange processes, Ag^+ ions first replace the Na^+ ions at the four- (Site III) and six-oxygen ring sites (Site I) (Ag^+-exchange $\leq 75\%$), and then those at the eight-oxygen ring sites (Site II) (Ag^+-exchange $> 75\%$).[3] When Ag^+ cations are reduced to Ag^0 atoms upon H_2 adsorption, protons replace the Ag^+ ions and become incorporated into the zeolite in order to balance the negative charge of the zeolitic framework. Therefore, it is suggested that the three OD bands in Figure 1c originate from Ag^+ ions located in different sites. However, an unambiguous assignment of these hydroxy groups requires further investigation.

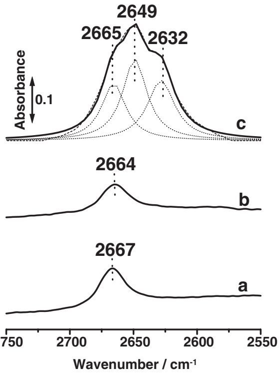

Figure 1. IR spectra of D_2 adsorbed on (a) AgA-30, (b) AgA-60, and (c) AgA-100 (dotted lines correspond to deconvoluted spectra, and dashed line is the fitted peak).

Table 1. Frequencies of hydroxy group peak after H_2 (D_2) adsorption on AgA and NaA at 298 K

Sample	ν_{OH}/cm^{-1}	ν_{OD}/cm^{-1}	ν_{OH}/ν_{OD}
AgA-30	3619	2668	1.356
AgA-60	3613	2664	1.356
AgA-100	3602	2665	1.352
	3591	2649	1.356
	3576	2632	1.359
NaA	Not observed	Not observed	—

Interaction between CO and Ag^+-exchanged zeolites at room temperature has been reported, and the bands observed at $2200\text{-}2150\,cm^{-1}$ were attributed to Ag^+–CO species.[4] Because CO adsorption is favored at low temperatures, some carbonyls (such as CO H-bonded to hydroxy groups) that are not stable at ambient temperature can thus be detected. In addition, the adsorption of CO at low temperature can suppress the subsequent reduction of Ag^+ by CO at room temperature or higher. To our best of knowledge, no report of CO adsorption on AgA

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at low temperature is available so far.

Figure 2a shows the IR spectra of CO adsorption on AgA-30 (before H_2 adsorption) at 150 K for 15 min followed by gradual warming of the IR cell under vacuum. A set of bands at 2182, 2165, 2156, 2136, and 2110 cm^{-1} emerged at 150 K. In the course of elevating the temperature, the three bands at 2110, 2136, and 2165 cm^{-1}, which were also observed for CO adsorption on NaA at 150 K (not shown for the sake of brevity), quickly disappeared. The band at 2136 cm^{-1} corresponds to typical physi-adsorbed CO inside the zeolite channel, and the band at 2110 cm^{-1} could represent the rotovibrational contribution of quasi-free CO molecules trapped in nanocavities.[5] The band at 2165 cm^{-1} should be assigned to CO adsorbed on Na^+ sites, which can be removed at ca. 220 K. The band at 2156 cm^{-1} gradually weakened with increasing temperature, but remained observable up to room temperature. The band at 2182 cm^{-1}, which is attributed to the CO–Ag^+ species as discussed below, first progressively increases in intensity up to 295 K, then weakens with further increase in temperature to finally disappear at around 423 K. Because there is no supply of CO from the gas phase, CO–Ag^+ species (2182 cm^{-1}) are formed by conversion of CO appearing at 2156 cm^{-1}, by increase in temperature.

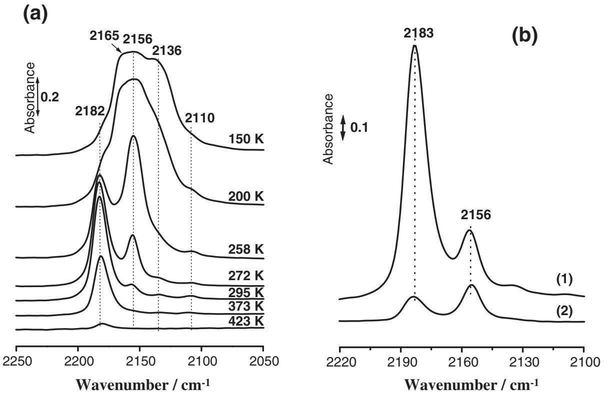

Figure 2. (a) IR spectra of CO adsorbed on AgA-30. CO was adsorbed at 150 K followed by gradual warming the IR cell under vacuum. (b) IR spectra (collected at 272 K) of CO adsorbed on AgA-30 (as in Figure 2a): (1) before H_2 adsorption; and (2) H_2-adsorbed AgA-30.

Considering that the CO molecule (ca. 0.38 nm in kinetic diameter[6]) is too large to penetrate into β-cages through the six-oxygen ring window (0.23 nm in diameter), the CO–Ag^+ species are not likely to be located inside the β-cages. Rather, they would be situated inside the larger α-cages consisting of eight-oxygen rings (0.41 nm in diameter). However, three Na^+ ions are known to be present near the center of eight-oxygen rings (Ag^+-exchange $\leq 75\%$), which would partially block CO from entering the α-cages through the eight-oxygen ring windows at low temperature. With gradual warming of the IR cell to 295 K, this retardation of Na^+ ions becomes less, because of weakening of the interaction between Na^+ ions and CO and an increase in Na^+ mobility and excitation of zeolite lattice vibration. This allows CO molecules to enter the α-cages with an accompanying increase in intensity of the band at 2182 cm^{-1} with temperature. With further increasing temperature (above 295 K), the amount of CO on Ag^+ decreased, and thus the intensity of the 2182-cm^{-1} band decreased. No bands attributed to silver cationic clusters were detected by CO adsorption, indicating that these silver clusters are located in the β-cages, which is consistent with the proposal by Gellens et al.[2]

The assignment of the band at 2182 cm^{-1} to Ag^+–CO species is further supported by the IR results of CO adsorbed on AgA after H_2 adsorption. CO adsorption on H_2-adsorbed AgA-30 sample at 150 K led to similar spectra as those observed in Figure 2a, only differing in intensity of the band at 2182 cm^{-1}. Figure 2b compares the IR spectra of CO adsorption collected at 272 K on AgA-30 before (Figure 2b(1)) and after adsorption of H_2 (Figure 2b(2)). The comparison reveals that H_2 adsorption weakened the band at 2182 cm^{-1} in intensity by 95%. When the sample was re-oxidized with O_2 at 673 K followed by CO adsorption under the same conditions, the intensity of this band was restored. This is attributable to the redox properties of silver cations: Ag^+ was reduced to Ag^0 upon H_2 adsorption on AgA, and Ag^0 was then reoxidized into Ag^+ when treated with O_2. No band related to the formation of Ag^0–CO species was observed in this work. This is because adsorption of CO on Ag^0 can only form a very weak bond with a predominant π-character. An IR band due to CO adsorbed on Ag^0 is expected at ca. 2060 cm^{-1}, but is rarely observed.[7]

The band at 2156 cm^{-1} in Figure 2a can be assigned to CO species H-bonded to OH groups.[4] This provides evidence that a small amount of hydroxy groups exist in the dehydrated AgA samples, although it is difficult to distinguish directly from the background IR spectra. These hydroxy groups are thought to originate from the dissociation of water molecules by Ag^+ ions because no such band (2156 cm^{-1}) was detected on NaA. It is worth noting that the intensity of the band at 2156 cm^{-1} remains almost unchanged for AgA-30 before and after H_2 adsorption (Figures 2b(1) and (2)), which suggests that the additional OH groups generated upon H_2 adsorption are not responsible for the IR band of absorbed CO at 2156 cm^{-1}. A possible explanation of this phenomenon is the inaccessibility of these OH groups to CO molecules. It can therefore be considered that these hydroxy groups produced upon H_2 (D_2) adsorption on AgA-30 are mainly located inside the β-cages, where CO could not reach easily through the small six-oxygen ring windows. In contrast, the hydroxy groups already present on AgA-30 before H_2 (D_2) adsorption may be located on the external surface or inside α-cages in zeolite A.

In summary, hydroxy groups producing different IR bands depending on the Ag^+-exchange degree of AgA were formed upon H_2 adsorption. At 30% exchange, these hydroxy groups were found to mainly locate inside β-cages, which are inaccessible to CO.

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