Characteristics of Silver Ions Exchanged in ZSM-5-Type Zeolite, Aluminosilicate, and SiO₂ Samples: In Comparison with the Properties of Copper Ions Exchanged in These Materials

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Received: February 22, 2002

The IR technique in combination with adsorption microcalorimetry was used to picture the bonding nature of silver ion exchanged or supported on solid materials, such as ZSM-5-type zeolite, aluminosilicate, and SiO_2 , by utilizing CO as a probe molecule. It has become apparent that there exists an adsorption site on which the CO molecule is adsorbed to give an IR absorption band: IR band at around 2193 cm⁻¹ for silver-ion exchanged ZSM-5 (AgZSM-5) and aluminosilicate (Ag/SiO₂·Al₂O₃), and at 2177 cm⁻¹ for silver-ion supported SiO₂ (Ag/SiO₂). The CO adsorption took place accompanying a large heat evolution of 100-80 kJ mol⁻¹ on the former two samples and relatively small heat of 70-40 kJ mol⁻¹ on the latter sample; silver ions exchanged with protons acting as Brønsted acid sites are responsible for the strong adsorption sites for CO adsorption. Taking account of the relationship between the differential heat of adsorption (q_{diff}) and the stretching vibrational frequency of adsorbed CO ($\nu_{\rm CO}$), it was concluded that the electrostatic interaction is dominantly operative in these systems. The large adsorption heats in the initial stage of CO adsorption on the AgZSM-5 and Ag/ $SiO_2 \cdot Al_2O_3$ samples may be successfully explainable by considering a little contribution of σ -bonding in addition to the electrostatic interaction. The quantum chemical calculation was performed to justify the two types of ion-exchange model for silver ion coordinated to two or three lattice oxygen atoms in AgZSM-5, as well as to clarify the bonding nature between the exchanged silver ion and CO molecule. As the results, the two-coordinated silver ions in AgZSM-5 can adsorb CO molecules and give the values of about 100 kJ mol⁻¹ and 2193 cm⁻¹, and the three-coordinated silver ions weakly adsorb CO to give the values of about 80 kJ mol⁻¹ and 2184 cm⁻¹. These adsorption energies are much smaller and the stretching frequencies due to the adsorbed CO are higher, compared with the case of CO adsorption on copper-ion exchanged ZSM-5 (CuZSM-5). From these results it can be interpreted that the dominant force operating in the AgZSM-5–CO system is electrostatic attraction, as is different from the case of CuZSM-5–CO system in which the σ -donation is dominant in the bonding. This difference is explained by taking account of the differences in energy gap between 4d-5s for silver ion and 3d-4s for copper ion; in the former case the hybridization of orbital is limited to result in a large σ -repulsion. The present experiment clearly proved that the evaluation of bonding nature from the relationship between q_{diff} and ν_{CO} is useful in the characterization of exchanged ions. The specific bonding nature between copper ion (Cu⁺) exchanged in ZSM-5 and CO molecule was also clarified.

Introduction

It is well-known that the copper ions deposited on supports exhibit catalytic activity as well as adsorption activity in various systems. Examples are the hydrocracking catalyst,¹ the catalyst for the synthesis of methanol from H_2 and CO,^{2,3} and the catalyst for the low-temperature water-gas shift reaction,⁴ and so on. Among such catalysts, the copper ion-exchanged zeolite, in particular, ZSM-5-type zeolite (CuZSM-5), exhibits high and

sustained activities in NO_x decomposition^{5–8} and also in specific N₂ adsorption at room temperature.^{9–12} A large number of studies have so far been made on the catalytic activities of this material, intending to develop new practical catalysts, and have made it clear that the copper ion (Cu⁺) is in the core of the active site. Little is known about the electronic and structural environment of the exchanged copper ion, though such information could help to rationalize the catalytic behavior exhibited by the monovalent copper ion. If we draw our attention on the outer shell orbitals, it is clear that Ag⁺ takes the isoelectronic

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structure with Cu⁺. To examine the state of Ag⁺ is helpful for getting the information on the specificity of the copper ion in zeolite. Relating to the silver ion, the photocatalytic decomposition of NO_x has been trying on the silver ion-exchanged ZSM-5 sample.^{13–17} Actually, the development of the effective photocatalysis is the everlasting dream of humans in reducing global air and water pollution.

In the present paper, a thorough study of ZSM-5, aluminosilicate, and SiO₂ that were modified by silver ion is presented to reveal the properties of Ag^+ and also to clarify the specificity of the electronic state of Cu⁺ in CuZSM-5. In particular, IR spectroscopy was applied in combination with adsorption microcalorimetry to picture the bonding nature of the silver ion supported on solid materials by utilizing CO as a probe molecule. The effect of supports on the properties of exchanged silver ion was also examined in this study.

Experimental Section

Materials. A sodium type of ZSM-5 zeolite (NaZSM-5: Si/ Al = 11.9) and silica sample (Aerosil 200) were kindly provided by Tosoh Co. and by Japan Aerogel Co., respectively. An aluminosilicate sample (SiO₂·Al₂O₃) was prepared in the following manner.¹⁸ A mixed solution including 0.93 g of aluminum isopropoxide and 11.3 g of tetraethyl orthosilicate in 25 mL of isopropyl alcohol was added to an aqueous solution of NaOH (0.33 g in 100 mL). The solution thus prepared was kept stirred at 318 K, then kept at 343 K for 24 h. The precipitate was thoroughly washed with distilled water and then dried in air. The sample was finally calcined at 873 K for 6 h.

Silver-ion exchanged ZSM-5-type zeolite (AgZSM-5) and $SiO_2 \cdot Al_2O_3$ (Ag/SiO_2 $\cdot Al_2O_3$) samples were prepared by a conventional ion-exchange method with an aqueous solution of silver nitrate. The ion-exchange was repeated several times to obtain the sample with a desired ion-exchange capacity. The ion-exchange capacity was determined by the chelatometric method; the silver ion liberated by treating the sample with a solution of HClO₄ was titrated. It was assumed that one monovalent sodium ion can be exchanged with one monovalent silver ion. The samples, hereafter, are abbreviated as AgZSM-5-X and Ag/SiO_2 \cdot Al_2O_3 - Y, where X and Y mean the ion exchange capacity in % and in wt % for the respective samples. The sample was pretreated at 473 K under a reduced pressure of 1 mPa for 4 h prior to all the measurements of adsorption heats, isotherms, IR, and XAFS.

The silver-ion supported SiO₂ sample (Ag/SiO₂) was prepared by impregnating silica (Aerosil 200) with an aqueous solution of silver nitrate. This sample is designated as Ag/SiO₂-Z, where Z represents the amount of deposited silver ion in wt %.

The Ag₂O sample used as a reference sample was prepared by mixing a 0.5 mol dm⁻³ AgNO₃ solution and a 0.5 mol dm⁻³ NaOH solution at room temperature. The precipitate was washed thoroughly with distilled water and then dried in a vacuum cell to avoid an easy adsorption of CO₂ gas.

The metal silver (Ag) was presented from Vacuum Metallurgicals Co. and K[Ag(CN)₂] was purchased from Aldrich Chemicals. Carbon monoxide (CO) gas used as an adsorbate was purchased from GL Science Co. and was purified by passing through a cold trap (at liquid N₂ temperature) before every measurement. Dinitrogen (N₂) gas was obtained by vaporizing a liquid N₂.

Measurements of Adsorption Heat and Isotherm. The measurement of adsorption heats was carried out by using the adiabatic-type calorimeter that was made in our laboratory. The procedure for the measurement was as follows; first, simulta-

neous measurements of the adsorption heat and the adsorption isotherm of CO were performed at 301 K for the sample evacuated at 473 K under a pressure of 1.3 mPa. After these measurements, the sample was degassed at 301 K to remove weakly physisorbed CO molecules. Then, the second adsorption measurement was performed again at 301 K. The equilibrium pressure of CO gas was measured with a capacitance pressure sensor, MKS 310 BH.

IR Spectra. IR spectra were measured by a Mattson 3020 FT-IR spectrophotometer with a TGS detector at a nominal resolution of 2 cm^{-1} . Sixty-four scans were collected to obtain each spectrum. The sample was pressed into the self-supporting disk and was placed in an in-situ IR cell. IR spectrum of the sample was recorded after evacuation at 473 K, and it was used as a reference spectrum. To analyze the surface state of the sample, CO gas was adsorbed at 300 K.

XAFS Spectra. X-ray absorption fine-structure spectra were recorded at the beam line BL-10B at KEK–PF of Tsukuba. The electron storage ring was operated at energy of 3.0 GeV and 300 mA. A Si(311) double-crystal monochromator was used. Photon energy was calibrated by measuring the absorption of Cu foil and was taken to be 8.9788 keV. Changes in the energies of XANES and of EXAFS features were detectable to an accuracy of 0.5 eV and of 2-3 eV, respectively. The EXAFS data were analyzed using a program developed by Maeda.¹⁹ In these measurements, all samples were treated in-situ.

Calculation Method. The gradient corrected density functional (DF) and the hybrid functional methods, so-called, the Becke-three-parameter Lee-Yang-Parr functional²⁰ (B3LYP) were employed in the present calculation. It was composed of the Slater²¹ and Becke²² exchange functionals as well as the "exact" Hatree-Fock exchange and the Voslo-Wilk-Nusair²³ and Lee-Yang-Parr²⁴ correlation functionals. The Gaussian 94/98 programs were used throughout the work.²⁵ Both calculations using the Los Alamos model core potentials (MCP)²⁶ and the 6-31G(D) all-electron were carried out. We found that the optimized structures were close to each other but the harmonic frequencies calculated with all-electron basis for the adsorbed CO molecule were more close to the experimental values. Hereafter we will refer to the mixed basis results where the 6-31G(D) basis is used for the CO moiety and the MCP basis for the zeolite moiety.

We used two types of clusters to model the CO adsorption sites on AgZSM-5. One is so-called the pentameric model, $Ag^+/Al(OSi(OH)_3)_4$ and the other is $Ag^+/Al(OH)_4$ (see in the text). The latter is constructed by replacing the Si(OH)_3 unit with the H atom. For the pentameric model, only the central Ag^+/AlO_4 moiety was optimized, and the peripheral (Si(OH)_3)_4 moiety was fixed to the crystalline structure. For $Ag^+/Al(OH)_4$, the whole cluster as well as the adsorbed CO molecule was optimized.

Results and Discussion

Adsorption Heats and Isotherms of CO. Adsorption microcalorimetry permits an accurate determination of the energetic strength of adsorption site by using a suitable probe molecule.²⁷ In the present study the calorimetric study of CO adsorption was carried out in order to evaluate the adsorption properties of the AgZSM-5 sample. The relevant energies of CO adsorption, differential heats of adsorption (q_{diff}), are represented in Figure 1, together with the adsorption isotherms. Corresponding to the drastic increase in the adsorbed amount along ordinate axis in the first adsorption, q_{diff} for the 473 K-treated sample gives a large and constant value of 90 kJ mol⁻¹ after passing a



Figure 1. The differential heats of adsorption (a) and adsorption isotherms (b) of CO at 301 K for the AgZSM-5–93 sample evacuated at 473 K. Filled and open circles represent the first and second adsorption processes, respectively.

 TABLE 1: Ratios of the Number of Adsorbed CO

 Molecules to That of Silver Ions

sample	$CO_{\text{first}}\!/Ag^+$	$CO_{\text{second}}\!/Ag^+$	CO_{chem}/Ag^+
AgZSM-5-93	1.13	0.63	0.50
Ag/SiO ₂ •Al ₂ O ₃	0.54	0.37	0.17
Ag/SiO ₂	0.28	0.28	

high energy region of 100 kJ mol⁻¹ at the initial adsorption stage, followed by descending values from 90 to 75 kJ mol⁻¹ with increasing adsorbed amount from 8 to 12 cm³ g⁻¹. After passing this region, the adsorption heat decreases from 75 to 40 kJ mol⁻¹ as the adsorbed amount increases from 12 to 25 cm³ g⁻¹, coinciding with a departure from the ordinate axis in the isotherm. It may be reasonable to assume that the q_{diff} data, corresponding to the values of more than ca. 90 kJ mol⁻¹ and those of descending from 90 to 75 kJ mol⁻¹ with increasing coverage, suggest a presence of two types of sites for strong adsorption, i.e., chemisorption. The almost constant value of ca. 90 kJ mol⁻¹ is in fairly good agreement with the data reported by Meyer et al.28 who examined the gaseous carbonyl complexes of the silver ion. The second adsorption restores the part of latter half in the first adsorption, which indicates that the latter part (75-40 kJ mol⁻¹) of the first adsorption corresponds to physisorption. Therefore, the chemisorbed and physisorbed amounts can be estimated to be 12.0 and 14.0 cm³ g^{-1} , respectively. By combining the number of the exchanged silver ions with the adsorbed amounts, the CO/Ag⁺ ratios are calculated to be 0.50 and 0.63 for the chemisorption and physisorption, respectively (Table 1).

IR study gives information on the state and bonding characteristics of silver ions when CO is used as an adsorbate because of its high IR absorbance intensity and weak basic nature.²⁹ The spectra of CO adsorbed on AgZSM-5 are shown in Figure 2. At the initial adsorption stage, a distinct and sharp IR band is observed at 2193 cm⁻¹. With increasing coverage, an additional broad band is observed with a slight tailing toward lower frequency side, and the 2193 cm⁻¹ band finally shifts to 2185 cm⁻¹.³⁰ By the succeeding evacuation of the sample at 300 K the strong band centered at 2193 cm⁻¹ recovers (spectrum



Figure 2. Infrared spectra for the AgZSM-5–93 sample treated in the following manner: (1) evacuated at 473 K; equilibrated at 300 K with CO gas of increasing pressure of (2) 0.266 Pa, (3) 0.533 Pa, (4) 57.6 Pa, (5) 403 Pa, (6) 1.05 kPa, (7) 2.99 kPa, (8) 5.27 kPa, and (9) 13.8 kPa; followed by reevacuation at (10) 300, (11) 373, and (12) 473 K. Broken lines in spectrum 10 represent two component spectra separated from the experimental spectrum.

10), which indicates the existence of a strong adsorption site on AgZSM-5, being very consistent with high q_{diff} values of 100-75 kJ mol⁻¹. This absorption band disappears completely after the evacuation at 473 K (spectrum 12). Spectrum 10 can be resolved into two components, though the second component centered at 2184 cm⁻¹ is extremely weak. In this deconvolution procedure we assumed that the spectrum for the 373 K-treated sample consists of one component (spectrum 11), and then the analysis of the spectrum for the 300 K-treated sample was performed by using both resultant peak position and fwhm of single band for the 373 K-treated sample. The observed band for the 300 K-treated sample was successfully recovered by these procedures; there are two bands consisting of a major and a minor components. The former band vanished by the heat treatment at 473 K and the latter band easily disappeared through the evacuation at 373 K. For the CuZSM-5-CO system a broad IR band (ν_{CO}) due to Cu⁺-CO species was observed at around 2155 cm⁻¹; in this case the band could be resolved into three components, that is, two dominant components which are resistant to the heat treatment up to 573 K and one minor component.12,31-33

It is meaningful to examine the factors affecting the bonding nature observed for AgZSM-5, and hence we compared the adsorption data for Ag/SiO₂·Al₂O₃ and Ag/SiO₂ with the results obtained for the AgZSM-5 system. Figure 3 shows the adsorption isotherms and the adsorption heats of CO for these samples. The heat of adsorption of CO on Ag/SiO₂·Al₂O₃ is about 100 kJ mol⁻¹ at the initial stage, and then it decreases to 80 kJ mol⁻¹ at an adsorption of ca. 2 cm³ g⁻¹, followed by a continuous decrease to about 40 kJ mol⁻¹ with increasing coverage. Corresponding to the fact that the adsorption isotherm is of Langmuir type, the adsorption heats are relatively larger, probably due to chemisorption of CO on Ag⁺ species. On the other hand, CO adsorption on Ag/SiO₂ gives the value of 70 kJ



Figure 3. The differential heats of adsorption (a, c) and adsorption isotherms (b, d) of CO at 301 K for the Ag/SiO_2 - Al_2O_3 -6 (a, b) and Ag/SiO_2 -12 (c, d) samples that were pretreated at 473 K in vacuo, respectively. Filled and open circles represent the first and second adsorption processes, respectively.

 mol^{-1} at the initial stage and then reveals descending values, 50–30 kJ mol⁻¹, with a slight increase in the adsorbed amount. This feature is distinctly different from those observed for the AgZSM-5 and Ag/SiO₂·Al₂O₃ systems. Furthermore, an extremely small amount of adsorption is also characteristic of the Ag/SiO₂–CO system; in other words, there are few sites interacting strongly with CO molecules. These are reflected in the small differences in the adsorbed amounts and in the adsorption heats between the first adsorption and the second adsorption. Comparison of CO adsorption on these three samples is given in Table 1.

Figure 4 represents the FTIR spectra obtained after dosing CO sequentially onto Ag/SiO₂•Al₂O₃ and Ag/SiO₂ at 300 K. For the Ag/SiO₂•Al₂O₃ sample, the center of the band shifts from 2191 to 2183 cm⁻¹ with increasing pressure or coverage. This band is obviously due to the CO species adsorbed on the



Figure 4. (a) Infrared spectra for the Ag/SiO₂·Al₂O₃-6 sample treated in the following manner: (1) evacuated at 473 K; equilibrated at 300 K with CO gas of increasing pressure of (2) 10.5 Pa, (3) 147 Pa, (4) 744 Pa, (5) 1.42 kPa, (6) 4.52 kPa, and (7) 14.3 kPa; succeedingly evacuated at (8) 300 K and (9) 373 K. (b) Infrared spectra for the Ag/ SiO₂-12 sample treated in the following manner: (1) evacuated at 473 K; equilibrated at 300 K with CO gas of increasing pressure of (2) 8.40 Pa, (3) 22.5 Pa, (4) 98.9 Pa, (5) 463 Pa, (6) 919 Pa, (7) 2.90 kPa, (8) 5.05 kPa, and (9) 16.3 kPa; succeedingly evacuated at (10) 300 K.

silver ions, and it remains even after evacuation at 300 K, being indicative of chemisorption on Ag/SiO₂·Al₂O₃ (Figure 4a). In the case of CO adsorption on Ag/SiO₂ a band at 2177 cm⁻¹ becomes distinct when CO pressure is increased considerably, and at the same its center shifts to 2175 cm⁻¹ (Figure 4b). Furthermore, it is found that this band disappears after evacuation at 300 K, corresponding to a weak interaction of CO



Figure 5. Variation of the wavenumber of stretching vibration of adsorbed CO (ν_{CO}) with equilibrium pressure of CO for AgZSM-5–93 (**•**), Ag/SiO₂·Al₂O₃-6 (\bigcirc), and Ag/SiO₂-12 (\bigcirc), respectively.



Figure 6. Fourier transform of the EXAFS oscillations at Ag K-edge of the respective samples: (a) AgZSM-5–93, (b) Ag/SiO₂+Al₂O₃-6, and (c) Ag/SiO₂-12. These samples were treated under various conditions; (a) evacuated at increasing temperature: (1) 300 K; (2) 373 K; (3) 473 K; (4) followed by CO adsorption at 300 K; (5) reevacuated at 300 K after CO adsorption.

molecule with the silver-ion deposited on SiO_2 . These IR data are consistent with the results shown in Figure 3.

Increasing of equilibrium pressure from nearly zero to 16 kPa causes band shifts from 2193 to 2185 cm⁻¹ for AgZSM-5 and from 2191 to 2183 cm⁻¹ for Ag/SiO₂·Al₂O₃, and from 2177 to 2175 cm⁻¹ for Ag/SiO₂. The wavenumber of the bands, which are obviously assigned to the C–O stretching vibration of adsorbed CO molecules, are plotted in Figure 5 as a function of equilibrium pressure. The differences in position and extent of shift of these bands mean the difference in the bonding nature between the silver ion and CO molecule; for the larger band shift the heat of adsorption of CO is higher. Since the silver ion exchanged with proton acting as the Brønsted acid is responsible for the generation of higher heat of CO adsorption,³⁰ the concept of acidity of solid as well as its electronic feature will be of benefit to the discussion on the state of exchanged silver ions.

Structural Information on Exchanged Silver Ion. The EXAFS spectra of the AgZSM-5, Ag/SiO₂·Al₂O₃, and Ag/SiO₂ samples are shown in Figure 6. Prior to the measurement the sample was evacuated at increasing temperature from 300 to 473 K, followed by the adsorption of CO at a pressure of 13.3 kPa and at 300 K, and finally reevacuated at 300 K. The EXAFS spectra of the reference samples are represented in Figure 7. Fourier transformed spectra for the samples treated in vacuo (spectra 1–3) exhibit a strong band at around 1.85 Å (no phase-shift correction) that can be ascribed to a backscattering from the first nearest lattice oxygen atoms or water molecules.^{14,17,34,35} A new finding for the AgZSM-5 sample is the appearance of a band at around 2.6 Å, which is observable after evacuation at



Figure 7. Fourier transform of the EXAFS oscillations at Ag K-edge of the reference samples: (1) Ag metal; (2) Ag_2O ; (3) $K[Ag(CN)_2]$.

 TABLE 2: Results of EXAFS Analysis for AgZSM-5–93

 Sample Treated under Various Conditions

pretreatment	contribution	Ν	<i>r</i> /Å	σ^2	<i>R</i> /%
evacuated at 300 K	first shell $A\sigma^+ - O(L)$	3.6	2.21	0.022	8.4
evacuated at 473 K	first shell $Ag^+ - O(L)$	2.6	2.14	0.013	2.8
	second shell $\Delta q^+ - \Delta q^+$	0.9	2.86	0.014	8.1
after CO adsorption	first shell $Aa^+ - C$	1.1	1.99	0.040	14.0
	second shell $A\sigma^+ - O(L)$	1.9	2.31	0.025	
	second shell $\Delta \sigma^+ - \Delta \sigma^+$	0.8	2.85	0.017	17.7
	second shell $Ag^+-O(CO)$	1.3	3.12	0.014	

373 K and becomes more obvious after evacuation at 473 K. Analysis of the EXAFS spectra collected for the AgZSM-5 sample evacuated at 473 K gives the parameters: N = 2.6 and r = 2.14 Å for the first shell and N = 0.9 and r = 2.86 Å for the second shell, respectively (Table 2). These values are interpreted as follows; the silver ion takes a distorted two- or three-coordination structure with the lattice oxygen atoms (in the first shell), being concomitant with an existence of another silver ion (in the second shell). When CO was adsorbed on the 473 K-treated sample, the band at around 2.50 Å (no phaseshift correction) became stronger (spectrum 4), accompanying a slight shift of the band from 1.85 Å (no phase-shift correction) to 1.95 Å. After evacuating this CO-treated sample at 300 K, the 1.95 Å-band (no phase-shift correction) recovered at its original position, keeping the distinctive band at around 2.5 Å (spectrum 5). The spectra collected in the presence of CO was analyzed using one-shell and three-shell fittings for the first and the second bands: the former fitting due to the carbon atoms of the adsorbed CO molecules and the latter one due to the lattice oxygen atoms, the silver ion, and oxygen of the CO molecule. In the first shell around the silver ion on which CO was adsorbed, the radial distribution was inverse-Fourier transformed in the range 1.06-2.16 Å (Figure 8). The best fit was obtained in the range of k (wave vector) from 3.92 to 10.76 Å⁻¹. In this analysis, the λ -value, i.e., the photoelectron mean free-path for the Ag-C pair, of the $[Ag(CN)_2]^-$ sample was used as the backscattering contribution from the Ag-C pair that is assumed to be transferable as a reference. A similar



Figure 8. The transform of the data $(k^3\chi(k) \text{ vs } k)$ into real space is performed over a range of $3.00-12.00 \text{ Å}^{-1}$. The best-fit spectra (broken line) for the AgZSM-5–93 sample evacuated at 473 K (a, b) and succeedingly treated with CO (c, d) were obtained by using parameters of Ag–O in Ag₂O and of Ag–C in K[Ag(CN)₂]. Inverse transforms (solid line) of the sample treated at 473 K were taken over the range of *R* (a) from 1.16 to 2.12 for the first band, and (b) from 2.32 to 2.96 Å for the second band. The same procedure was performed for the sample on which CO had been adsorbed in the region (c) from 1.60 to 2.16 for the first band, and (d) from 1.98 to 3.07 for the second band.

procedure was applied to the second shell around the silver ion, taking account of the backscattering from the species, Ag^+-O , Ag^+-Ag^+ , and $Ag^+-(C)-O$ by use of parameters for Ag_2O . The resultant best-fit data are also shown in Figure 8 and Table 2. The change of Ag-O distance from 2.14 Å (before CO adsorption) to 2.31 Å (after CO adsorption) is obviously due to the interaction of the silver ion with CO molecule. This may be the first example concerning the structure of the Ag-COspecies formed in zeolite. However, as for the detailed coordination structures around the silver ion, we were not able to separate the band into two components suggested from the IR data. The coordination environment of the silver ion that has a low adsorbablity for CO molecules is not clear at the present stage.

Similar tendencies were observed for the EXAFS spectra of the $Ag/SiO_2 \cdot Al_2O_3$ sample, though the feature of the second band is not so distinct as in the case of AgZSM-5. The band assignment was also similar to the latter case. The Ag/SiO_2 sample also exhibited a similar band feature to those of other two samples, though the change of spectra was far less pronounced owing to both the small surface area and the small content of silver ions of this sample.

The XANES spectra of AgZSM-5, Ag/SiO₂·Al₂O₃, and Ag/ SiO₂ samples that were treated under different conditions are shown in Figure 9, and those of reference samples are represented in Figure 10. The spectral pattern of the 300 K-evacuated sample (spectrum 1) is found to be different from those of reference samples (Ag metal and Ag₂O), which implies that the silver ion takes the isolated state: coordination to lattice oxygen atoms and/or adsorbed water molecules. Evacuation of the sample at 473 K yields a slightly different pattern from that observed for the 300 K-treated sample. In this sample, the silver ions take a bridging structure between two lattice oxygen atoms or a distorted three-coordination structure, corresponding to the models proposed below. An important point should be added when the change in XANES spectra is looked at carefully; for the AgZSM-5 sample the lower energy side of the first strong band decreases in intensity upon CO adsorption. The differences



Figure 9. Ag K-edge XANES spectra of the (a) AgZSM-5–93, (b) Ag/SiO₂·Al₂O₃–6, and (c) Ag/SiO₂–12 samples. These samples were treated under various conditions; (a) evacuated at increasing temperature: (1) 300 K; (2) 373 K; (3) 473 K; (4) followed by CO adsorption at 300 K; (5) reevacuated at 300 K after CO adsorption.

spectra between respective processes and the 473-K treated one are depicted in Figure 11. The most striking feature observed after CO adsorption is that the intensity of the band at 25.49 keV decreases, and that at 25.50 keV increases. These data indicate that the electronic configuration of the silver ion is strongly affected by the formation of $[Ag(CO)]^+$ species. However, the quantitative analysis of the spectral pattern is difficult for the silver ion system, because of a broadening nature of these bands. The original pattern for the 473 K-treated sample could not be completely recovered by the reevacuation at 300 K after CO adsorption. This implies that the strong CO adsorption takes place on the monovalent silver ions.

Force Being Operative in the Interaction between Silver Ion and Coming Molecules. It is expected that the nature of bonding between metal ions and CO affects both values of q_{diff} and ν_{CO} as well as their relationship.^{36,37} We have so far emphasized that the IR technique in combination with microcalorimetry is useful to picture the bonding nature between metal-ion exchanged in the zeolite sample and CO molecule.



Figure 10. Ag K-edge XANES spectra of the reference samples: (1) Ag metal; (2) Ag_2O ; (3) $K[Ag(CN)_2]$.



Figure 11. (a) Normalized XANES spectra of the AgZSM-5–93 sample under various conditions. (b) Difference XANES spectra between respective spectra and the spectrum of 473 K-treated sample. The sample was treated under various conditions; (a) evacuated at increasing temperature: (solid line) 300 K; (dotted line) 373 K; (short-dashed line) 473 K; (long-dashed line) followed by CO adsorption at 300 K; (dashed-and-dotted line) reevacuated at 300 K after CO adsorption.

We applied this technique to the present study to examine the state of silver-ion exchanged or supported on the solid materials. The relationships between $q_{\rm dif}$ and $\nu_{\rm CO}$ for the respective adsorption stages are represented in Figure 12a. Analogous relationships have been found in the CuZSM-5–, Cu/SiO₂·Al₂O₃–, and Cu/SiO₂–CO systems,^{12,33,36} though the absolute values are different from those for the AgZSM-5–CO system. The data obtained for the M-ZSM-5–CO (M = alkali-metal ions) system^{38–41} are also shown in this figure for comparison.

The nature of the bonding between metal ions (M) and CO molecules can be evaluated on the basis of both covalent bond and electrostatic force.⁴² Through the discussion on the bonding nature between Ag^+ or Cu^+ and CO, it makes it possible to interpret the differences in electronic feature and in reactivity between Ag^+ and Cu^+ species. When the former type of



Figure 12. (a) Relationship between differential heats of adsorption of CO (q_{diff}) and observed CO stretching vibration (ν_{CO}) for different samples: (**●**), AgZSM-5–93; (**○**), Ag/SiO₂·Al₂O₃-6; (**○**), Ag/SiO₂-12; (**♦**), CuZSM-5; (**◇**), Cu/SiO₂·Al₂O₃; (**■**), LiZSM-5; (**□**), NaZSM-5; (**⊞**), KZSM-5. (b) Plots of $\Delta\nu_{\text{CO}}$ values versus $1/(R_{\text{M+}}+R_{\text{CO}})^2$. The number in the parentheses represents the coordination numbers of the respective metal ions in the samples: (**●**), AgZSM-5–93; (**♦**), CuZSM-5; (**■**), LiZSM-5; (**□**), NaZSM-5; (**⊞**), KZSM-5; (**□**), RbZSM-5; (**□**), CsZSM-5.

bonding, i.e., covalent bonding, is predominantly operative, it consists of two parts: one based on the withdrawal of an electron from the 5σ orbital of CO molecule, and the other depending on the back-donation of an electron from the metal to the π^* antibonding orbital.^{42,43} The 5σ orbital of CO molecule is assumed to possess some C-O antibonding character. Consequently, M–C σ -bond formation should lead to the removal of an electron from this orbital to result in raising $\nu_{\rm CO}$, whereas π -bonding due to a back-donation clearly induces a decrease in $\nu_{\rm CO}$ owing to the flowing electron into the π^* orbital of CO. As for the case where the electrostatic attractive force is operative, it is also expected that ν_{CO} of the adsorbed species becomes higher than that of the gas molecule due to the induction of dipole moment in CO by electric fields. It seems, therefore, that the increases in the ligand-to-metal σ -donation and in strength of the electrostatic force are expected to give a positive contribution to $\nu_{\rm CO}$, and that the increase in π^* backdonation from metal ions exhibits a reverse tendency, though these bond formations enhance the bonding energy between metal ions and CO molecules. We can recognize that q_{diff} means a formation energy of the Ag-CO bond and v_{CO} corresponds to strength of the bond AgC–O. In the case of σ -bonding and electrostatic force being operative, it is expected that as for the bonding strength between metal ion and carbon atom both values of $q_{\rm diff}$ and $v_{\rm CO}$ increase, whereas the simultaneous raising of the $q_{\rm diff}$ and $\nu_{\rm CO}$ values is not expected in view of the π backdonation, because it contributes to lowering of the ν_{CO} value. By taking account of the observed value of 2193 cm⁻¹ for $\nu_{\rm CO}$, which is higher than the value for a free molecule, the concept of π^* back-donation is clearly excluded in the present system. As a result, it is found that the M–C σ -bonding or electrostatic interaction plays a major role in raising both values of q_{diff} and $\nu_{\rm CO}$ and in the present AgZSM-5–CO system. On the other hand, the similar phenomenon observed for the Cu⁺–CO system may be explainable through the ligand-to-metal σ -donation, as pointed out for zeolite by us^{12,33} and for complexes by Strauss's group.^{44,45} In Figure 12a, it is clearly seen that the plots for the AgZSM-5–CO system closely locate at the position where the alkaline-ions exchanged ZSM-5–CO systems are plotted, whereas the plots for the CuZSM-5- and also Cu/SiO₂·Al₂O₃– CO systems are situated at different positions.

On the basis of IR data of CO adsorbed on various alkaline metal ion-exchanged zeolites, Zecchina et al. have proposed that the relationship between $\Delta v_{\rm CO}$ (= $v_{\rm obsd} - v_{\rm gas}$) for CO molecule and $1/(R_{\rm M} + R_{\rm CO})^2$ reflects the bonding nature between the metal and CO, where $R_{\rm M}$ and $R_{\rm CO}$ are the radii of the exchanged cation and the CO molecule, respectively. For some kinds of alkali ion-exchanged ZSM-5 samples the linear relationship was established between $\Delta \nu_{\rm CO}$ and $1/(R_{\rm M} + R_{\rm CO})^2$, which indicates the electrostatic force being dominant in these systems.³⁹ Figure 12b shows such data for the AgZSM-5-CO system, together with the data obtained for other systems.^{39,41} Here, the ionic radius of silver ion was estimated from the EXAFS data of the first nearest distance due to the backscattering from the lattice oxygen atoms by assuming the ionic radius of oxygen ion being 1.21 Å.46 As can be seen from Figure 12b, the datum for the AgZSM-5-CO system is virtually placed on the same line as that was drawn by the data of other alkali ion-exchanged ZSM-5-CO systems. This makes us confirm that the nature of bonding is substantially governed by the electrostatic force, as is different from the case of CuZSM-5-CO system in which σ -bonding is operative.^{12,36} However, we should also point out the experimental facts as mentioned above: the larger adsorption heat and the irreversible behavior of the IR band upon degassing of CO at room temperature. Therefore, it may be reasonable to consider that in the present AgZSM-5-CO system the bonding nature between ion-exchanged Ag⁺ species and CO molecule is mainly due to the electrostatic force with some contribution of covalent nature. Similar consideration will be given to the other systems of Ag/SiO₂·Al₂O₃-CO and Ag/SiO₂-CO.

Figure 13a shows the IR spectra measured before and after the adsorption of dinitrogen (N₂) at 300 K on 473 K-evacuated AgZSM-5. A weak and distinct band at 2328 cm⁻¹ is observed at a pressure of 13.3 kPa. This band is close to the stretching vibrational band of free N₂ molecule (in the Raman spectrum) and is found to be higher in wavenumber, as compared with the band (2295 cm⁻¹) observed for the CuZSM-5–N₂ system.¹² In addition, the band intensity is extremely weak, which indicates that the adsorbed amount and the interaction energy are much smaller than those for the CuZSM-5–N₂ system.

The relationship similar to Figure 12b is obtained for the AgZSM-5-N₂ and some kinds of metal ion-exchanged ZSM- $5-N_2$ systems, as shown in Figure 13b. Here, $\Delta v_{N=N}$ is the extent of shift in wavenumber from the N≡N stretching vibration of gaseous N₂ molecule, and the ionic radius of Ag⁺ was obtained from the present XAFS data and other radii were taken from Zecchina's report.³⁹ The plots can be classified into two groups, i.e., the group of nearly zero or small positive shift and the group of large negative shift. The foregoing considerations are helpful in evaluating the interaction between the exchanged metal-ion and N2 molecule. It is expected that a purely electrostatic interaction should bring about a blue shift of $v_{N\equiv N}$ due to an induced polarization. In fact, alkali metal ions exchanged in zeolite belong to such a group that gives a positive shift. On the other hand, a covalent nature (both σ and π -bonds) induces a red shift, because the electron in the



Figure 13. (a) IR spectra of N₂ adsorbed on the AgZSM5–93 sample: (1) after evacuation at 873 K; (2) succeedingly treated with N₂ gas under an equilibrium pressure of 13.3 kPa and at 300 K. The difference spectrum is also shown in the figure. (b) Plots of $\Delta \nu_{N_2}$ values versus $1/(R_{M^+} + R_{N_2})^2$ for the various samples: (\bullet), AgZSM-5–93; (\bullet), CuZSM-5; (\blacksquare), LiZSM-5; (\square), NaZSM-5; (\boxplus), KZSM-5; (\square), RbZSM-5; (\square), CsZSM-5.

 5σ -bonding orbital of an N₂ molecule has a bonding nature, different from the case of a CO molecule, and the π backdonation undoubtedly causes an electron penetration into antibonding orbital of N₂ molecule from the metal center. In the AgZSM-5-N₂ system, the adsorbed N₂ species brings about a slight red-shift effectively, and hence it seems reasonable to suppose that the dominant force being operative in this system is the electrostatic force.

Calculation Based on the Density Functional Theory (DFT). The quantum chemical calculation method allows us to verify the model of the monovalent silver ion exchanged in ZSM-5. We also intended to compare the bonding nature of silver ion and of copper ion in zeolite. Furthermore, the hybridtype density functional approach is helpful to determine the vibrational frequency of the adsorbed CO species, ν_{CO} , the bonding energy of the Ag⁺-CO structure, and the optimized structures. In this process, the harmonic frequency was evaluated by the analytical second-derivative method. Taking account of both data of the emission spectra and of IR spectra using CO molecule as a probe, we have proposed that there are at least two types of metal ions exchanged in ZSM-5 (i.e., two- and three-coordination sites with regard to lattice oxygen atoms in CuZSM-5).³² The presence of two types of exchangeable site was also proposed for NaZSM-5, through the dielectric measurement and NMR spectroscopy.⁴⁷⁻⁴⁹ In recent years, some interesting papers on this subject were published by Dedecek and Wichterlová,⁵⁰ by Sauer's group,⁵¹⁻⁵³ and by Zecchina's



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group.^{54,55} They independently proposed a model of copper ions exchanged in ZSM-5. The first group inferred a model for ionexchangeable sites from the emission data, and the second group justified the model by the density functional quantum calculation method. Moreover, the third group argued on the basis of EXAFS data that there exist two types of exchangeable site in ZSM-5. With respect to our proposed model for the copper ion in ZSM-5,³² the most interesting point is that there are twoand three-coordination sites in many exchangeable sites. Here, we propose, as the first approximation, two types of neutral pentameric cluster model (Scheme 1) similar to the case of CuZSM-5;32 the silver ion is anchored by two- or threecoordination to lattice oxygen atoms near aluminum atoms in the zeolite framework. In these models, the formal charge assigned to the monovalent silver ion compensates the excess negative charge of each cluster. In calculation, it was assumed that an aluminum atom with four lattice oxygen atoms is mobile and the position of four Si(OH)3 units is fixed. The resultant optimized structures are shown in Figure 14. The two-coordination site exists as an energetically stable site, and the threecoordination site changes its geometrical arrangement through the movement of a silver ion, as shown in Figure 14b; the latter type of site is relatively unstable and is different from the case of copper-ion exchanged in zeolite.³² It may be due to the fact that the ionic radius of a silver ion is larger, compared with that of monovalent copper ion, as is deduced from the EXAFS results. Recently, on the basis of computational results Silhan et al. have proposed the model of ion-exchanging structure of Ag⁺ in ZSM-5, and they described that the two-coordination site is most stable site, though the bond distance is about 0.1 Å longer, compared with our result.56

For the present, we shall confine our attention to the analysis of the state of adsorbed CO on the respective sites. Unfortunately, when we used the pentameric model, we have failed to get a stable structure of the adsorbed CO species on the threecoordination site, probably because of its extremely unstable nature (liable to move to the two-coordination site). Therefore, we adopted, as the first approximation, the following two small and simple neutral-cluster models in order to get information on the IR frequencies for the adsorbed CO species. Here, we utilized four hydrogen atoms instead of four Si(OH)₃ units, and tried to examine which site would be responsible for higher (or lower) IR absorption band when CO molecule is adsorbed. The stretching vibrational frequency of the adsorbed CO and the binding energy of the Ag⁺–CO bond were also estimated by the hybrid type density functional approach. The resultant



Figure 14. Results of DF calculation for two dominant types of the silver-ion exchanged in ZSM-5 (pentameric model): (a) two-coordination silver ion; (b) three-coordination silver ion.

optimized structures are shown in Figure 15. It is clearly seen that the CO molecule chemisorbed on the two-coordination and three-coordinated silver-ions gives adsorption heats of 93 and 79 kJ mol⁻¹, respectively. This finding is consistent with previous description and also with the results of CuZSM-5 sample.³² Furthermore, the chemisorbed CO molecules give the IR bands at 2212 and 2207 cm⁻¹ when they are bound to the two-coordination Ag⁺ site (species I) and three-coordination Ag⁺ site (species I), respectively. These wavenumbers may be regarded as those shifted to a slightly higher side from the observed ones (2193 and 2184 cm⁻¹). The value for the free



Figure 15. Results of DF calculation for the adsorbed CO species on the respective sites: (a) two-coordination silver ion; (b) three-coordination silver ion. In the calculation, the simplest model was used as a zeolite.

CO molecule in such field was evaluated to be 2209 cm⁻¹. This result is well explained by considering that the interaction between Ag⁺ and CO molecule is dominantly electrostatic, as described in the previous section. Such interaction is stronger for the species I than species II, which is consistent with the following facts: (1) the higher wavenumber for the adsorbed CO on the Ag⁺ site in the bridged structure, compared with the value for the gaseous CO molecule, indicates that the electrostatic interaction is dominantly operative; and (2) the bond length of Ag⁺–CO is slightly shorter for the two-coordination site than for the three-coordination site, as shown in Figure 15.

We have tried to compare the bond distances of Ag^+-O (lattice) and Ag^+-C (relating to the CO species adsorbed on the silver ion) obtained by the EXAFS analysis with those by the present DFT calculation method. As a result, the computed value of Ag^+-O in the two-coordination site is about 0.1 Å shorter than the experimental value from the EXAFS data, and for Ag^+-C the computed value is 0.06 Å longer than the experimental one. These findings support the above-mentioned idea that the site in the two-coordination environment exclusively acts as the adsorption site for CO molecule by the electrostatic force.

In the previous section we showed that the ratios of CO/Ag⁺ are 0.50 for the chemisorption and 1.13 for the total adsorption including chemisorption and physisorption (Table 1). These values clearly indicate that half of the silver ions act as the strong adsorption sites (two-coordination sites) and the remaining half as the physisorption or weak chemisorption sites (threecoordination sites). Furthermore, we revealed that respective IR bands at 2193 and 2184 cm⁻¹, which were obtained by deconvolution of the band due to the CO species adsorbed on the sample evacuated at 300 K, correspond to chemisorption and weak adsorption of CO molecules. These findings also support the model proposed above; CO molecules were adsorbed on the two-coordination silver-ion sites can be stabilized and those on the three-coordination sites are less stable, in other words, only weak adsorption occurs on the latter sites. In addition, the fact that no dicarbonyl species on the silver-ion sites was observed in the present system gives a reasonable interpretation of the ratio CO/Ag⁺.

SCHEME 2



Feature of the Interaction between Silver Ion and CO Molecule. Recently, revision of the bonding nature between metals or metal ions and CO molecules has been performed for the classical or nonclassical classification of M-CO bondtype.^{42,43,56} It is meaningful, therefore, to discuss the bonding nature between the silver ion and CO molecule, in comparison with the case of the copper ion-CO system. Since π backdonation involves a transfer of electron from the filled metal d-orbital to the empty CO orbital, it is related to the tendency of a removal of electron from the metal, i.e., ionization potential. In this stage, it is worthy to describe two points. First, Rack and Strauss reported that the 4d95s1(1D) state of Ag+ lies at 473 kJ mol⁻¹ above the ground state $4d^{10}5s^{0}(^{1}A)$, which is compared with 261 kJ mol⁻¹ for the corresponding state in Cu⁺.^{42,44,45,57} Their datum was also substantiated by the photoemission spectra which give the larger energy separation between 5s and 4d levels of the silver ion, ^{13,15,17} compared with that between 4s and 3d levels of the copper ion (Scheme 2).49 Second, the second ionization potential of silver metal is larger than that of copper metal.^{42,45,57} Taking account of the data given above, the contribution of π back-donation can be ruled out in the copper ion-CO system and also in the silver ion-CO system. In the case of the latter system, another covalent nature, namely, σ -bonding, may be considered similarly to the former system. It has been demonstrated that the extent of σ -donation from the 5σ MO of CO molecule, i.e., the lone-paired electron of carbon atom, to the empty levels of the monovalent silver ion is not such to allow the classification of the Ag⁺-CO bonding as a σ -dative surface complex in the present system. The interaction of silver ions with CO molecules can be of entirely electrostatic nature; the large energy difference between 5s and 4d levels for the silver ion reflects in the larger d-population and smaller s-population of AgCO⁺, in contrast to the case of CuCO⁺, which indicates less 5s4d σ -hybridization and more σ -repulsion. In this connection we must recall here that the adsorption energies for the AgZSM-5-CO system are in the range of 100-80 kJ mol⁻¹; these values for bond energy of Ag^+-C in an $(O_L)_2Ag^+-CO$ species are smaller than those for Cu⁺-C in (O_L)₂Cu⁺-CO (i.e., 140-110 kJ mol⁻¹).^{31,36} Barnes et al. estimated the bond energies of metal-carbonyl to be 138 and 79 kJ mol⁻¹ for $[Cu(CO)]^+$ and $[Ag(CO)]^+$, respectively, and found that the bond distance (M-C) is much greater for AgCO⁺ than for CuCO⁺.58 It is worth noting that the initial adsorption heat of 100 kJ mol⁻¹ is in fairly good agreement with the data reported by Meyer et al. for the gaseous monocarbonyl silver-ion complex.²⁸ A few groups also reported the bond energies of M–CO in $[Cu(CO)]^+$ and $[Ag(CO)]^+$.^{28,58,59} They also pointed out that the complex $[Ag(CO)_2]^+$ is energetically more stable than $[Ag(CO)]^+$, as is quite different from the present case. In addition, Strauss described that the π -bonding type of interaction is operative in the copper carbonylcomplexes and σ -bonding in the silver carbonyl-complexes,⁵⁷ which are also different from our cases.³⁶ On the other hand, Veldkamp and Frenking pointed out the contribution of electrostatic interaction even in the silver carbonyl-complex system, $[Ag(CO)]^+$.⁶⁰ In the present stage, we have interpreted that the difference in interaction type between these carbonyl complexes and zeolite systems may be explained by taking account of the Wall effect (Pauli's repulsion).^{61,62} As a result, it is reasonable to conclude that the operating force between the silver ion and CO molecule in the AgZSM-5-CO system is dominantly the electrostatic force. The difference in bonding nature between Ag^+ -CO and Cu^+ -CO has become apparent in this study; in other words, the copper ion in zeolite has a specificity.

Conclusions

In this study we have examined the properties of silver ionexchanged zeolite by IR technique in combination with microcalorimetry and tried to picture the bonding nature between Ag⁺ and CO, as well as to get some information on the prominent feature (specificity) of the electronic state of the copper ion exchanged in ZSM-type zeolite. Some useful information obtained is as follows:

1. The Brønsted-acid type sites play an important role in determining the electronic state of the silver-ion exchanged or deposited on ZSM-5, SiO₂·Al₂O₃, and SiO₂.

2. From the relationship between $q_{\rm diff}$ and $\nu_{\rm CO}$, the position of the IR band due to the adsorbed CO species is well explained on the basis of the concept of electrostatic attraction, as is different from the case of CuZSM-5–CO system in which σ -bonding is dominantly operative.

3. We assumed two types of models for the silver-ion exchanged in ZSM-5: two coordination- and three-coordination sites relating to the Br ϕ nsted acid center. The former sites are responsible for larger heat values and higher-frequency IR band when CO molecules are adsorbed. On the other hand, the latter type of sites acts as weak chemisorption or physisorption sites to yield smaller adsorption heat and lower IR-band frequency, corresponding well to the results evaluated by the DFT calculation.

4. The energy separation between 4d and 5s levels of Ag^+ is expected to be large, as suggested from the larger absorption energy between $4d^{10}$ level and the first excitation $4d^95s^1$ level, as well as the larger second ionization energy, which is compared with the case of copper ion (between 3d and 4s). As a result, it is concluded that the mixing of orbitals of 5s and 4d levels encounters a great difficulty for the silver ion in ZSM-5 zeolite, resulting in the greater σ -repulsion.

Acknowledgment. This work was supported in part by foundation from Wesco Co. A part of this work has been performed under the proposal (No. 2001G128) of the Photon Factory Program Advisory Committee. Thanks are also due to Profs. M. Nomura, A. Koyama, and N. Usami of the Photon Factory (KEK) in Tsukuba for their kind assistance in measuring the XAFS spectra. We also thank the glassblowing workshop of Osaka University for technical assistance in making the in situ glass cell for IR and XAFS measurements.

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