Reduction of Silver Cations in Silver Zeolites by Carbon Monoxide

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At room temperature silver oxide and silver carbonate react with CO much faster than do Ag-A zeolites, the kinetics of the latter reaction showing a pronounced dependence on water content and a significant dependence on the exchange conditions; no reaction takes place in the absence of water, and immersion of the stable dry Ag^+–CO zeolite complex in an alkaline aqueous environment results in immediate reduction of Ag^+.

A number of investigations on interactions of silver zeolites with carbon monoxide have appeared in the literature.[1,2] An elegant experiment studied the appearance and disappearance of OH, OD, and CO stretching vibrations on reduction and reoxidation of Ag-Y zeolite with hydrogen and upon exposure to CO.[3] We extended these investigations to Ag-A zeolites and to the far-IR region and found that the kinetics of the CO sorption depends on the degree of Ag exchange, becoming faster with increasing Ag content. The amount of adsorbed CO also increases with higher Ag content. Zeolite Na_{12}-A (Linde 4 A) does not interact with CO at room temperature.[4] These results are consistent with the finding of Förster and co-workers, who observed sodium zeolite–CO interactions at low temperature only.[5]

Remarkably, room temperature reduction of Ag^+ by CO was not reported in these experiments, although it has long been known that Ag_2O can be reduced easily by CO while AgCl does not react with CO.[6] It would therefore be interesting to know the conditions for reduction of silver zeolites by CO and to compare their reactivity with that of silver oxide and silver carbonate. We know that in Ag-Y, Ag-X,[2,3] and Ag-A zeolites[4] fairly stable Ag^+–(CO) complexes are formed; to determine whether these complexes are the precursors of the Ag^+-reduction with CO, we have studied the reactions (1) and (2) with Ag_2O, Ag_2CO_3, and with Ag-A zeolites. Preliminary experiments show that the reactivity of Ag-A zeolites depends strongly on the amount of water, and on the pH, but less on the degree of Ag exchange. From the stoicheiometric equation (2) a significant dependence of the redox kinetics on water content should be observed. If, however, Ag^+–CO complexes formed on dried Ag zeolites[4] are the precursors in the reduction, competition between Ag^+–CO complex formation, equation (3), and hydration of Ag^+ cations, equation (4), will play an important role.

$$Ag_2O + CO \rightarrow 2Ag + CO_2 \quad (1)$$

$$2Ag^+ + CO + 3H_2O \rightarrow 2Ag + CO_2 + 2H_3O^+ \quad (2)$$

$$[Zeol]^-Ag^+ + CO \rightleftarrows [Zeol]^-Ag^+\text{–}CO \quad (3)$$

$$[Zeol]^-Ag^+ + H_2O \rightleftarrows [Zeol]^-Ag^+\text{–}OH_2 \quad (4)$$

$$[Zeol]^-Ag^+\text{–}OH_2 + H_2O \rightleftarrows [Zeol]^-Ag^+\text{–}OH^- + OH_3^+ \quad (4a)$$

Samples of Ag_2O, Ag_2CO_3, and Ag-A zeolites were exposed to a CO atmosphere for a certain time. Before adding the CO, the 1 dm^3 stainless steel reaction chamber containing 100—160 mg of the samples in glass tubes, corresponding to 25—40 mg Ag, was evacuated and filled with argon several times to eliminate any oxygen. The humidity was controlled by putting sufficient water, oversaturated $NaCl/H_2O$, over-

Table 1. Percentage reduced silver after 16 h reaction time.

		Dried at 180 °C		Untreated	
	a_w[a]	Ag-A-pH 5.5	Ag-A-pH 9.5	Ag-A-pH 5.5	Ag-A-pH 9.5
H_2O	100	<1	9	0	3
$NaCl/H_2O$	75	5	18	5	14
$MgCl_2/H_2O$	31	12	20	11	21
$LiCl/H_2O$	12	8	14	6	26
P_2O_5	0	<1	3	<1	5

[a] a_w = % relative humidity.

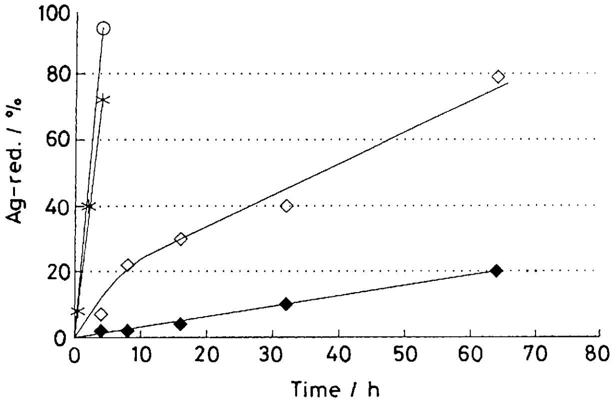

Figure 1. Reactivity of different Ag^+ compounds with CO at room temperature. (○) Ag_2O, (×) Ag_2CO_3, (◇) Ag-A-pH 9.5, 12% rel. humidity, (◆) Ag-A-pH 5.5, 12% rel. humidity.

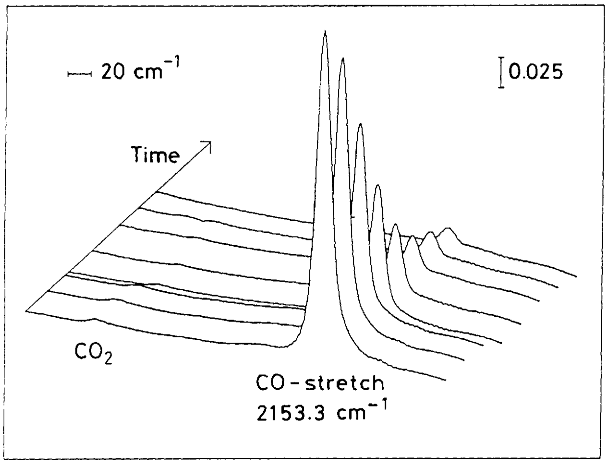

Figure 2. IR absorption spectra in the region 2400—2050 cm^{-1} for the Ag-A-pH 9.5 water rich sample. The plotted spectra were taken after 6, 22, and 40 min then 1, 2, 6, 10.75, and 18 h.

saturated $MgCl_2/H_2O$, oversaturated $LiCl/H_2O$, and P_2O_5 in the reaction chamber. After 4 h of preconditioning in this atmosphere the argon was replaced by 720 Torr CO. After the chosen reaction time the samples were immediately dissolved in 3 ml 1 M sulphuric acid to eliminate the remaining adsorbed CO, stopping the reduction. Unreacted Ag^+ is thus dissolved without affecting the reduced Ag. Following dilution with 70 ml water, 20 ml of 25% ammonia, 600 mg of solid NaOH, and 100 mg of $Na_2S_2O_3 \cdot 5H_2O$ were added and after 5 min the system was titrated with a 0.01 M thiourea solution (sensitivity ±0.2 mg Ag^+).

Self-supporting wafers of 15—20 μm thickness and ~ 6 mm diameter were prepared and analysed by FTIR transmission spectroscopy as described elsewhere.[4] The samples were pretreated in our transmission cell (a) by evacuation for 15 min to a pressure of about 7.5×10^{-4} mbar and (b) by overnight evacuation to a pressure lower than 10^{-6} Torr. Then 100 Torr of CO was added and the kinetics of CO sorption and oxidation measured by FTIR spectroscopy.

To prepare the silver zeolites $Na_{12}(SiO_2)_{12}(AlO_2)_{12}(H_2O)_{24}$ (Linde 4 A) was used as purchased from Union Carbide and Bayer. The two samples show some differences, but the main results are the same. 10 g Linde 4 A were suspended in 100 ml doubly distilled water containing 4.78 g $AgNO_3$. Stirring for 1 h resulted in Na_6Ag_6-A zeolite. After Ag^+ exchange the samples were washed with doubly distilled water and dried at 70 °C in air overnight. For reproducible results, the samples were conditioned for 1 day at 22 °C in air of 75% humidity. We call the samples obtained Ag-A-pH 9.5 because an aqueous suspension of them has a pH of 9.5. Ag-A-pH 5.5 samples were obtained by adding 10 M HNO_3 to an aqueous suspension of Linde 4 A to pH 6 prior to Ag^+ exchange as before. While the Ag-A-pH 5.5 samples have the same white colour as the original sodium zeolite, the Ag-A-pH 9.5 samples are sometimes slightly grey. Daylight was excluded in the experiments reported in this communication.

$$Na_{12}(SiO_2)_{12}(AlO_2)_{12} + H_2O \rightleftarrows Na_{11}H(SiO_2)_{12}(AlO_2)_{12} + Na^+ + OH^- \quad (5)$$

$$Na_{12}(SiO_2)_{12}(AlO_2)_{12} + H_2O \rightleftarrows [Na_{11}(SiO_2)_{12}(AlO_2)_{12}]^- + Na^+ + H_2O \quad (5a)$$

$$Na_nAg_mH_l(SiO_2)_{12}(AlO_2)_{12} + H_2O \rightleftarrows [Na_nAg_mH_{l-1}(SiO_2)_{12}(AlO_2)_{12}]^- + H_3O^+ \quad (5b)$$

Equilibria (5) govern the behaviour of the zeolites when dispersed in water. Figure 1 demonstrates that the reactivity of the Ag^+ towards CO depends very much on the type of compound and the reaction conditions. If only slightly humid, Ag_2O and Ag_2CO_3 are reduced completely after a few hours of exposure to 720 Torr CO while the Ag-A zeolites react much slower. Table 1 shows that both dried and water-containing Ag-A-pH 5.5 zeolites do not react significantly with CO within 16 h. Equation (2) explains why dried zeolites do not react. In the case of the wet samples, we assume that the Ag^+–CO complex is the precursor in the reduction as described by equation (3) and that reaction (4) competes with formation of the silver carbonyl. The condition for reaction is that CO and H_2O are available simultaneously. We must then ask why the dried and the wet Ag-A-pH 9.5 zeolites do show some reactivity. A straightforward explanation is that the Ag-A-pH 9.5 zeolite contains some Ag_2O, formed during the alkaline ion exchange, which reacts as in the case of Ag_2O.

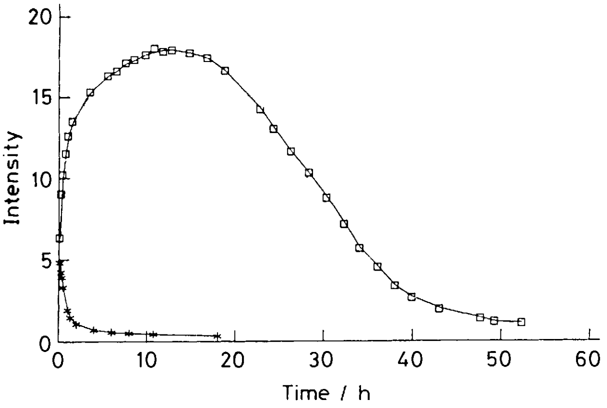

Figure 3. Time dependence of the intensity of the CO stretching vibration for (□) the water poor Ag-A-pH 9.5 and (×) the same water rich Ag-A-pH 9.5 sample as in Figure 2.

This explanation is supported by the observation that the samples show a fast initial reaction rate, becoming much slower after a few minutes; this behaviour can probably be used to determine the amount of Ag_2O on a zeolite. Colour changes from yellow to green, brown, and grey accompany the reaction, and it would be interesting to follow them quantitatively.

Table 1 shows that the reduction is enhanced by the presence of OH^-. This is supported by the observation that a zeolite which has been exposed to CO for a certain time is reduced immediately if immersed in an alkaline aqueous environment.

FTIR experiments demonstrate the effect of catalyst pretreatment on reactivity. We refer to the Ag zeolites which were evacuated for a short time, 'water rich' samples, in contrast to 'water poor' samples which were evacuated for several hours. The water rich Ag zeolites show rapid CO adsorption. Reduction commences with the beginning of the adsorption, which can be followed by the steadily decreasing CO band. Figure 2 shows the changes in the CO stretching vibration of the Ag^+–CO complex in the water rich Ag-A-pH 9.5 sample at different times. A small amount of adsorbed CO_2 produced in the first few minutes is indicated by the small absorption band at 2345 cm^{-1} due to the asymmetric stretching mode. Afterwards gaseous CO_2 is formed. In Ag-A-pH 5.5 samples no initial CO_2 formation is observed. We interpret this reaction as reduction of the small amount of Ag_2O formed during the alkaline ion exchange of Ag-A-pH 9.5.

Figure 3 shows CO adsorption and oxidation kinetics of a water poor (□) AgA-pH 9.5, time of evacuation 16 h, and the same water rich Ag-A-pH 9.5 sample (×) as described in Figure 2. The experimental points correspond to the integral of the CO stretching vibration at 2153.3 cm^{-1}. There is a pronounced difference in reactivity between the two samples. The water rich sample shows a fast initial decrease in intensity of the CO stretching vibration band which slows down after about 2 h. Other experiments have confirmed that this decrease correlates with the amount of CO_2 formed. The water poor Ag zeolite has a greater ability to adsorb CO. As observed under different conditions, the adsorption of CO obeys interesting kinetics. Fast- and slow-adsorbing species can be distinguished.[4] The latter are more stable and therefore rearrangement to these species occurs. The maximum of the CO band is reached within about 10 h, depending on the pretreatment. After about 18 h significant reduction of Ag^+ can be observed, as the CO stretching vibration intensity starts to decrease. We assume that this long time behaviour is caused by traces of water, not eliminated during the pretreatment, migrating slowly to the reaction centres. The spectroscopic data indicate that at the same time the primary physisorbed CO_2 becomes chemisorbed.[4]

The reaction scheme of equations (6) and (7) is consistent with all experimental observations. The only species in this reaction scheme not characterized till now is the $[Zeol]^-Ag^+$–$[CO(OH)]^-$ radical. Hence it is to be considered as a hypothetical intermediate which may be tested by spectroscopic methods.

$$[\mathrm{Zeol}]^-\mathrm{Ag}^+ + \mathrm{CO} \rightleftarrows [\mathrm{Zeol}]^-\mathrm{Ag}^+\text{–}\mathrm{CO} \qquad (6)$$

$$[\mathrm{Zeol}]^-\mathrm{Ag}^+\text{–}\mathrm{CO} + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Zeol}]^-\mathrm{Ag}^+\text{–}[\mathrm{CO(OH)}]^- + \mathrm{H_3O}^+ \qquad (6a)$$

$$[\mathrm{Zeol}]^-\mathrm{Ag}^+\text{–}[\mathrm{CO(OH)}]^- + [\mathrm{Zeol}]^-\mathrm{Ag}^+ + \mathrm{H_2O} \rightarrow 2[\mathrm{Zeol}]^-\mathrm{Ag}^0 + \mathrm{CO_2} + \mathrm{H_3O}^+ \qquad (6b)$$

$$[\mathrm{Zeol}]^-\mathrm{Ag}^+\text{–}\mathrm{CO} + [\mathrm{Zeol}]^-\mathrm{Ag}^+ + 3\mathrm{H_2O} \rightleftarrows 2[\mathrm{Zeol}]^-\mathrm{Ag}^0 + \mathrm{CO_2} + 2\mathrm{H_3O}^+ \qquad (7)$$

Hydrogen and CO have similar reduction capabilities. Therefore it is interesting that photochemically reduced Ag^+ on TiO_2 produces H_2 when irradiated in alkaline aqueous dispersions.[7] In both ground and excited state oxidation/reduction reactions the stability of intermediate Ag^+X and Ag^0X species appears to play a crucial role. Further experiments are needed to test this and to find out whether self-sensitization processes of these photoreactions occur, as observed on illumination of Ag zeolites in aqueous dispersion, when Ag^+ are reduced and O_2 is evolved.[8] Catalysed CO oxidation has been observed in the presence of oxygen and alkaline or alkaline earth forms of zeolite A.[5] CO interacts with these zeolites only at low temperatures. The fast and stable co-ordination of CO on Ag^+-A zeolites[4] together with the potential to oxidize completely the CO to CO_2 by adding an optimized amount of water could be used for the purification of gases from CO as well as for catalytic CO oxidation in the presence of oxygen.

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