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FTIR Characterization of Metal-Loaded Zeolites

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Abstract. FTIR transmission spectra of self-supporting zeolite wafers of $Na_{12}A$ (Linde 4A), $Na_{3.6}Ca_{4.2}A$ (Linde 5A) and $Ag_{11.8}Na_{0.2}A$ in the range of 20 to 13 500 cm^{-1} are reported. Reduction of Ag^+ by H_2 is probed directly in the FAR IR and indirectly by adsorption of CO and CO_2.

Key words: infrared spectroscopy, FAR IR, silver zeolites, photochemistry, carbon monoxide.

Infrared spectroscopy has been extensively used for characterizing clay minerals and zeolites [1]. Our interest in FTIR spectroscopy of metalloaded zeolites is the detailed understanding of reactions such as

$$M^{n+} + \text{Red} \xrightarrow{h\nu} M^{(n-1)+} + \text{Ox},$$

$$M^{(n-1)+} + X \rightarrow [M^{(n-1)+} \cdots X] \qquad [2]$$

with $M^{n+} = Cu^{2+}, Cu^+, Ag^+$ and $X = N_2, H_2O, CO, CO_2, H_2, D_2$.

A home-built high vacuum cell attached to the external port of a Bomem DA3 FTIR instrument is used for in-situ studies. Three self-supporting wafers of 15 to 20 μm thickness can be simultaneously evacuated to 10^{-4} Pa, heated to 500°C, cooled below ambient temperature, exposed to gases and illuminated with visible or UV light for photochemical investigations.

In Fig. 1 we show the transmission spectra of $Na_{12}A$ (Linde 4A), $Na_{3.6}Ca_{4.2}A$ (Linde 5A) and $Ag_{11.8}Na_{0.2}A$. Water is still present as is seen from the broad band around 3500 cm^{-1} and the sharp feature at 1640 cm^{-1}. Lattice vibrations appear between 250 and 1200 cm^{-1} while the regions from 1200 to 1600 and below 250 cm^{-1} [3] are clearly cation dependent. The near IR is included to demonstrate that transmission spectra can be obtained even in this region despite large scattering losses.

The Ag^+ ions in the zeolite can be reduced by H_2, thus generating finely dispersed Ag^0 atoms and clusters. We observed that upon admittance of D_2

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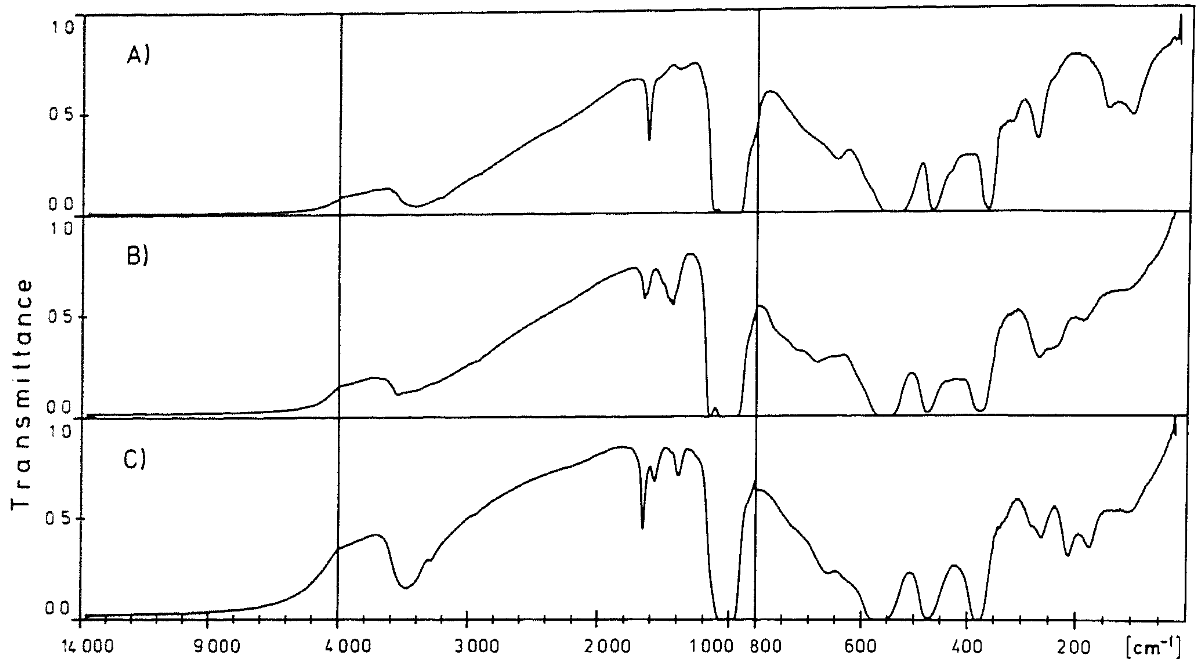

Fig. 1. Transmission spectra of self-supporting wafers of *A*: $Ag_{11.8}Na_{0.2}A$, *B*: $Na_{3.6}Ca_{4.2}A$ (Linde 5A) and *C*: $Na_{12}A$ (Linde 4A), evacuated to 2.6×10^{-4} Pa for 12 h at 25°C

the zeolitic water is slowly replaced by HDO and D_2O, but only if the zeolite contains Ag^+. D_2 and hence H_2 adsorption is therefore dissociative and occurs at Ag^+ ions in the zeolite. In the FAR IR at least one new absorption band at 196 cm^{-1} appears upon strongly reducing $Ag_{11.8}Na_{0.2}A$.

It is known from studies with Ag^+ zeolite Y that CO is a useful label to probe the oxidation state of the silver in the zeolite since it adsorbs selec-

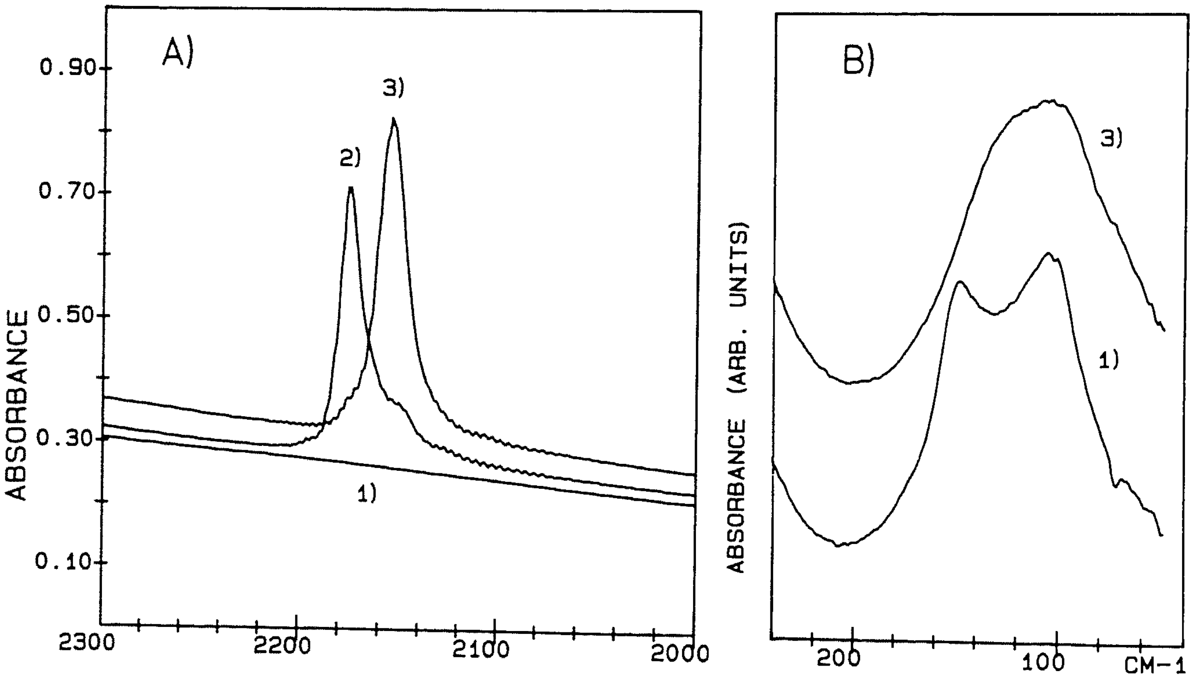

Fig. 2. Kinetics of CO adsorption on *A*: $Ag_{4.3}Na_{7.7}A$ and *B*: $Ag_{11.8}Na_{0.2}A$. Curves *2* and *3* were measured under $1.3 \cdot 10^4$ Pa CO atmosphere and absorptions due to gaseous CO are properly compensated; *1*: evacuation at 25°C; exposure to $1.3 \cdot 10^4$ Pa CO at 25°C for *2*: 25 min and *3*: 4 h

tively on Ag^+ [4]. This behaviour has been confirmed with Ag^+ zeolite A at different degrees of reduction. In addition, the CO absorption band which is located at 2174 cm^{-1} in the unreduced zeolite develops into a composite of several bands after H_2 treatment, indicating that reduction of the zeolite creates additional and distinguishable sites for CO adsorption. In Fig. 2*A* we present evidence that CO adsorption to equilibrium is a slow process, possibly involving diffusion of Ag^+ to new sites. Within 4 h of CO exposure a shift of the CO absorption frequency from 2174 to 2153 cm^{-1} is observed which is fully reversible on evacuation. Fig. 2*B* shows the change of the two Ag^+ specific bands at 148 and 105 cm^{-1} which merge into one broad band upon CO adsorption.

In contrast to CO, the adsorption capacity of silver zeolite A for CO_2 increases with reduction degree up to a maximum and falls off only at highly reduced samples.

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