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## Volume 3

PHOTOCHEMICAL AND PHOTOELECTROCHEMICAL TRANSFORMATION AND  
STORAGE OF SOLAR ENERGY

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### ABSTRACT

Ag<sup>⊕</sup> exchanged zeolites evolve O<sub>2</sub> from water and Cl<sub>2</sub> from Cl<sup>⊖</sup> under irradiation. A photoelectrochemical cell with an open circuit potential of 1.1 V has been constructed, based on the photochemical decomposition of AgCl into Ag and  $\frac{1}{2}$ Cl<sub>2</sub>. Two cells in series can be used for the photodecomposition of water into O<sub>2</sub> and H<sub>2</sub>. Photochemically reduced silver clusters are promising candidates to achieve reduction of H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>. Molecular orbital calculations lead to the result that AgCO<sub>2</sub> and Ag<sub>2</sub>CO<sub>2</sub> are stable species which could probably undergo further reactions. Specific information about these systems can be obtained by IR spectroscopy. Therefore FTIR spectra of zeolites from 4000 to 40 cm<sup>-1</sup> are reported. Reduction of Ag<sup>⊕</sup> by H<sub>2</sub> is probed directly in the FAR-IR. We describe first results obtained with CO<sub>2</sub> on Ag<sup>⊕</sup> and Ag<sup>0</sup> zeolites.

### KEYWORDS

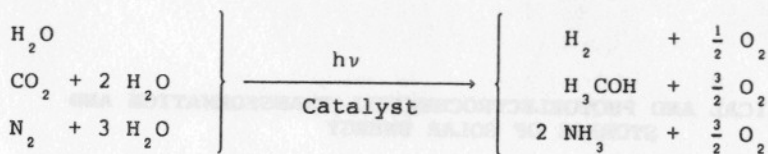
Silver zeolites; photoelectrochemical cell; photolysis of water; CO<sub>2</sub> reduction; FTIR in situ spectroscopy; solar energy.

Ag<sup>⊕</sup> exchanged zeolites are sensitive to light. In aqueous dispersions, under irradiation, they evolve O<sub>2</sub> from water and Cl<sub>2</sub> from Cl<sup>⊖</sup>, while Ag<sup>⊕</sup> is reduced to Ag<sup>0</sup> (Calzaferri, 1986b, 1984). When irradiated below 400 nm, an electrochemically deposited AgCl film on a silvergrid reacts at low pH according to:

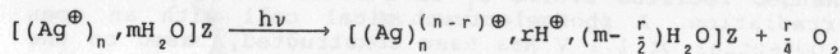


This reaction can be used to build a photoelectrochemical cell with an open circuit potential of more than 1 Volt. Its electromotive force [Ag;AgCl:HCl(1M):Cl<sup>-</sup>;  $\frac{1}{2}$ Cl<sub>2</sub>] is 1.14 Volt. The discharge reactions of the cell, the principle of which is shown in Fig. 1, are: Ag → Ag<sup>⊕</sup> + e and  $\frac{1}{2}$ Cl<sub>2</sub> + e → Cl<sup>⊖</sup>. Two cells in series have been demonstrated to be capable of photoelectrochemical decomposition of water into hydrogen and oxygen (Calzaferri, 1987b). They work with sunlight.

Although efficient photoelectrochemical cells are very interesting, the most challenging solar energy conversion processes are watersplitting, reduction of  $\text{CO}_2$  and reduction of  $\text{N}_2$ :

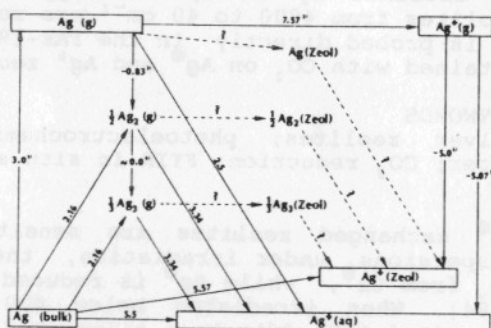
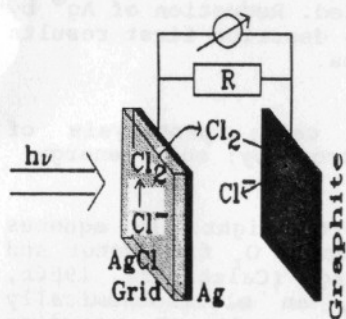
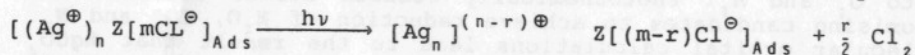


Oxygen must be produced in every case. In aqueous dispersions of  $\text{Ag}^\oplus$  zeolites one observes efficient photo-oxygen (Calzaferri 1984; Schumacher, 1978; Jacobs, 1977) and photo-chlorine evolution (Calzaferri, 1986, 1987), depending on the conditions. Both reactions show a self-sensitization, i.e. the further the reaction proceeds, the more the sensitivity shifts from the near UV to the visible, and both reactions depend on the pH. From molecular orbital calculations we deduce that the photo-oxygen evolution in absence of  $\text{Cl}^-$  is caused by oxygen-to-metal charge-transfer transitions (Calzaferri, 1987). The stoichiometry of the photo-oxygen generation in absence of  $\text{Cl}^-$  is:



Z = Zeolite framework

In the presence of  $\text{Cl}^-$  at pH 4 and below, the stoichiometry is



Energies  $\Delta H^\circ$  in eV

Fig. 2: Enthalpy diagram  
zeol=zeolite

Fig. 1: Schematic diagram of the photoelectrochemical cell  
[Ag; AgCl:HCl(1M):Cl<sup>-</sup>; 1/2Cl<sub>2</sub>]

From a thermodynamic point of view it seems possible that the photochemically produced silver clusters can be used to achieve reduction of  $\text{H}_2\text{O}^\oplus$  to  $\frac{1}{2}\text{H}_2 + \text{H}_2\text{O}$ . An enthalpy diagram giving interesting information about the reduction capabilities of silver clusters is shown in Fig. 2 (Calzaferri, 1982). The

enthalpy of formation  $\text{Ag}(\text{bulk}) \rightarrow \text{Ag}^\oplus(\text{aq})$  is related to the heat of hydration of the gaseous  $\text{Ag}^\oplus$  ion -5.07 eV (Lohmann, 1967). The values for  $(\text{Ag}_n)_g$  are taken from Hilpert and Gingerich (1980). A similar diagram can be constructed for  $\Delta G^\circ$ . It follows from the values given in Fig. 2 that, from a thermodynamic point of view, not only  $\text{Ag}(\text{g})$  but also  $\text{Ag}_2(\text{g})$ ,  $\text{Ag}_3(\text{g})$  and probably much larger clusters are able to reduce hydrated protons. The question is, how much energy is lost by the reaction  $\frac{1}{n}(\text{Ag}_n)_g \rightarrow \frac{1}{n}(\text{Ag}_n)_{\text{env}}$ . It can only be answered in reference to specific environmental conditions. Studies regarding this problem have been carried out (Henglein, 1977, 1981) or they are in progress (Belloni, 1987).

We are interested in the photochemical reduction of  $\text{CO}_2$ . The reaction  $\text{CO}_2 + \text{H} \rightarrow \text{HCOOH}$  is slightly exothermic, depending on the conditions. Considering the information given in Fig. 2, it should be possible to reduce  $\text{CO}_2$  with photochemically produced silverclusters. To get an idea how such a reaction could proceed, we have carried out quantumchemical calculations on silver carbondioxide systems. First we calculated the interaction of an Ag atom with a  $\text{CO}_2$  molecule. The results are shown in Fig. 3a and 3b. We found an energy minimum along the y-axis with an Ag-C distance of 2.8 Å and a O-C-O angle of  $123^\circ$ . The stabilization energy relative to free Ag and  $\text{CO}_2$  is -1.95 eV. This means that  $\text{AgCO}_2$  is predicted as a fairly stable molecule.

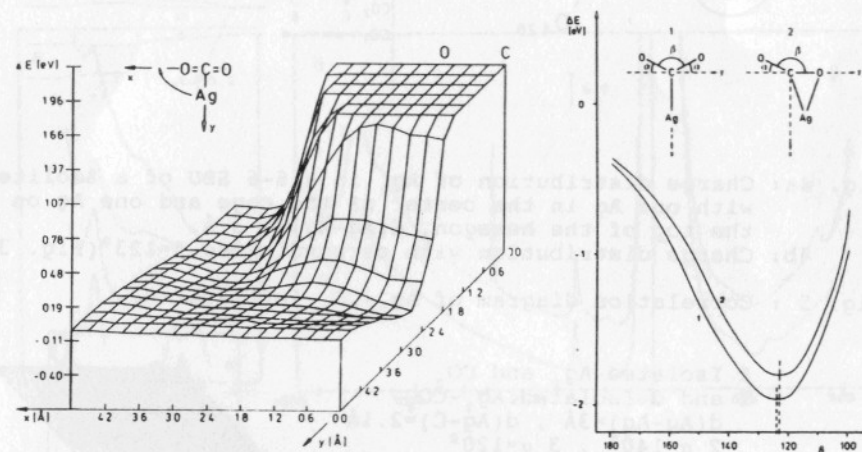


Fig 3a: Energy surface for a silver atom around a  $\text{CO}_2$  molecule. The minimum lies on the y-axis at 2.8 Å.

3b: Energy curve for the change of the O-C-O angle with a fixed silver-carbon distance of 2.8 Å. Minimum at  $123^\circ$ .

X-ray measurements of silverzeolite X show simultaneous silver occupation of the center SI of the 6-6 SBU and the site SI' outside the 6-ring (Eulenberger, 1967). We have therefore calculated the charge distribution of a silver in the center of the 6-6 SBU and one on the top of the hexagon (Calzaferri,

1986). Fig. 4a shows very pronounced polarization of the Ag—Ag bond with a negative charge on the atom outside of the cage. This polarized Ag<sub>2</sub> in a zeolite X should be a good electron donor. Let us try to find out what happens if a CO<sub>2</sub> molecule comes across the negatively charged silver atom. The calculations lead to the result that the negative charge is transferred to the CO<sub>2</sub> molecule i.e. the CO<sub>2</sub> is reduced by this system Fig. 4b.

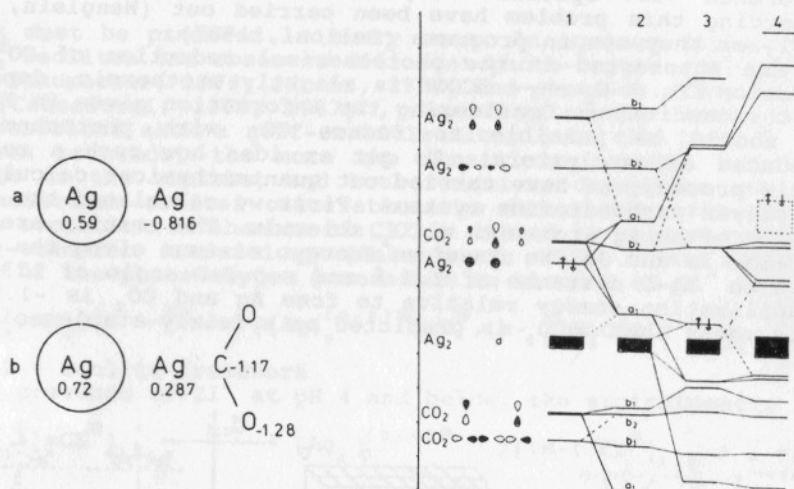
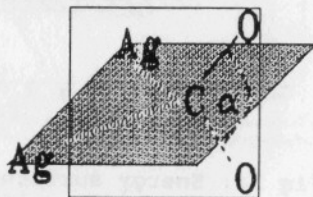


Fig. 4a: Charge distribution of Ag<sub>2</sub> in a 6-6 SBU of a Zeolite X with one Ag in the center of the cage and one Ag on the top of the hexagon, d(Ag-Ag) = 3 Å.

4b: Charge distribution with carbondioxide.  $\beta=123^\circ$  (Fig. 3b)

Fig. 5 : Correlation diagram of Ag<sub>2</sub>-CO<sub>2</sub> interaction.

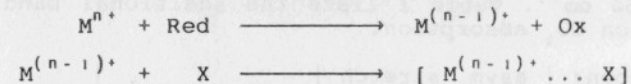
- 1 Isolated Ag<sub>2</sub> and CO<sub>2</sub>
- 2 and 3 Isolated Ag<sub>2</sub>-CO<sub>2</sub>  
d(Ag-Ag)=3Å, d(Ag-C)=2.1Å  
2  $\alpha=140^\circ$ , 3  $\alpha=120^\circ$



- 4 Ag<sub>2</sub>-CO<sub>2</sub> in the  $\beta$ -cage of a zeolite. The dashed box represents the HOMO of the zeolite, which consists of lone pairs on the oxygen atoms. The broad black bar in all cases represents the narrow spaced silver d-orbitals.

Based on this results it is reasonable to expect that infrared spectroscopy on silver exchanged zeolites under various conditions should lead to valuable information on the

interaction of CO<sub>2</sub> with reduced and unreduced silver centers. Our general interest in the FTIR spectroscopy of metal loaded zeolites is the detailed understanding of reactions such as:



with  $M^{n+} = \text{Cu}^{2+}, \text{Cu}^+, \text{Ag}^+$  and  $X = \text{N}_2, \text{H}_2\text{O}, \text{CO}, \text{CO}_2, \text{H}_2, \text{D}_2$

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  $\mu\text{m}$  thickness can be simultaneously evacuated to  $10^{-6}$  Torr, heated to  $500^\circ\text{C}$ , cooled below ambient temperature, exposed to gases and illuminated with visible or UV light for photochemical investigations. The metal cations within the zeolite can be directly probed by far infrared spectroscopy. A completely silver exchanged Zeolite A shows two bands at  $105$  and  $148 \text{ cm}^{-1}$  which can be attributed to vibrations of Ag<sup>+</sup> ions Fig. 6a. Upon reduction of the Zeolite with H<sub>2</sub> the intensity of these two bands decreases while a new absorption at  $195 \text{ cm}^{-1}$  appears. The addition of water vapor after the reduction induces a very intense and broad absorption. Fig. 6b shows the mid-IR spectrum of a partially Ag<sup>+</sup>-exchanged Zeolite A pressed into a self supporting wafer of  $15 \mu\text{m}$  thickness, before and during CO<sub>2</sub> adsorption.

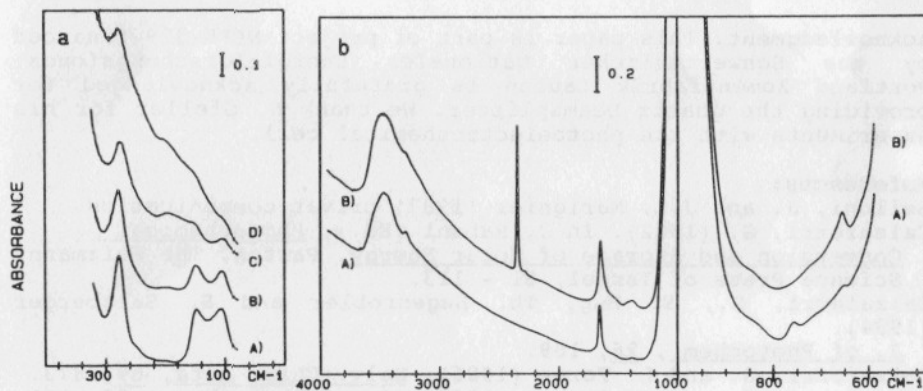


Fig. 6a: FAR-IR-spectra of Ag<sub>11.8</sub>Na<sub>0.2</sub> zeolite A.

A evacuated at RT to  $2 \cdot 10^{-6}$  Torr, B reduced with 200 Torr H<sub>2</sub> for 10' at  $100^\circ\text{C}$  followed by evacuation, C additional 10' reduction with H<sub>2</sub> followed by evacuation, D addition of 25 Torr H<sub>2</sub>O followed by evacuation.

Fig. 6b: Adsorption of CO<sub>2</sub> on Ag<sub>11.8</sub>Na<sub>0.2</sub> zeolite A at RT.

A evacuated at RT to  $2 \cdot 10^{-6}$  Torr, B loaded with 15 Torr CO<sub>2</sub> at RT and measured in CO<sub>2</sub> atmosphere. Absorptions of gaseous CO<sub>2</sub> are properly compensated.

The most intense spectral features of the unloaded substrate are the SiO<sub>4</sub>/AlO<sub>4</sub> asymmetric stretch band around  $1000 \text{ cm}^{-1}$  and

several other framework vibrations below  $600\text{ cm}^{-1}$ . Residual adsorbed water shows its bending mode at  $1650\text{ cm}^{-1}$  while the OH stretch vibrations produce the broad, partially structured band centered around  $3450\text{ cm}^{-1}$ . Table 1 lists the additional bands which are observed on  $\text{CO}_2$  adsorption.

	bend $\nu_2$	asym. stretch $\nu_3$		$\nu_3 + \nu_1$	
		$^{12}\text{CO}_2$	$^{13}\text{CO}_2$		
Gas phase	667	2349	2284	3716	—
on $\text{Ag}_{4.3}\text{Na}_{7.7}\text{A}$	657	2350	2285	3711	1382

Table 1: observed  $\text{CO}_2$  frequencies [ $\text{cm}^{-1}$ ] in gas phase and adsorbed on  $\text{Ag}_{4.3}\text{Na}_{7.7}\text{A}$ .

The bands listed in the table disappear when the zeolite is evacuated after  $\text{CO}_2$  adsorption except for the band at  $1382\text{ cm}^{-1}$  which remains even after complete removal of  $\text{CO}_2$ . We assign this band to a carbonate like species formed by chemisorption of  $\text{CO}_2$ . If the zeolite is reduced by  $\text{H}_2$  the adsorption capacity for  $\text{CO}_2$  increases up to a maximum and decreases at high reduction degree. Instead of the single  $\text{CO}_2$  stretch band at  $2350\text{ cm}^{-1}$ , several new bands close by are observed which indicate the existence of new adsorption sites which are created in the process of reduction.

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