

TOWARDS ARTIFICIAL PHOTOSYNTHESIS

Experiments with Silver Zeolites, Part 2

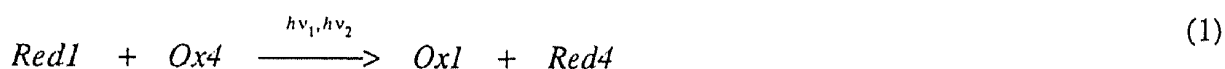
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Abstract. We discuss a photochemical energy storage system split in three parts: the oxidation of water to oxygen, the reduction of water to hydrogen and the coupling of the two processes. Coupling has to be accomplished by means of a membrane that allows the transport of electrons and protons from the oxidative to the reductive side and prevents recombination reactions. We discuss several specific possibilities to link the two half-reactions. One of them leads to an interesting coupling scheme between LMCT and MLCT states.

1. Introduction

Water splitting, carbon dioxide reduction and nitrogen reduction are the most desirable processes for chemical transformation and storage of solar energy. Today none of these reactions can be carried out under solar irradiation with a significant quantum efficiency by means of an artificial molecular system, but there is little doubt that chemists will succeed in designing efficient molecular solar energy storage devices. The net process in such a device is an endergonic oxidation-reduction reaction.



As shown in Figure 1, we split this reaction in three parts: the oxidation of water to oxygen in reaction 1, the reduction of water to hydrogen in reaction 3 and the coupling of 1 and 3.¹ The energy is added to the system by photons $h\nu_1$ and $h\nu_2$ which excite Ox2 and Red3 respectively. Reaction 2 has to fulfill the condition that the two electrons from Red2 are quantitatively transferred to Ox3. At the same time protons must move from 1 to 3 to satisfy electroneutrality. A membrane is needed to separate the oxidative and reductive reactions spatially. It has to prevent energy and material consumption caused by side reactions between redox systems on the reductive side 2 and redox systems on the oxidative side 1.

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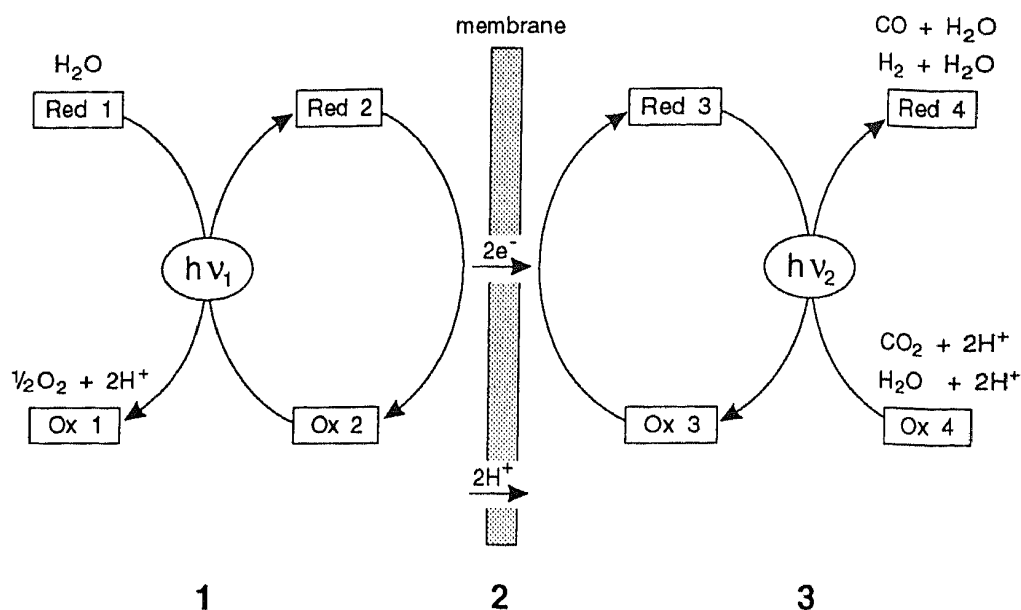
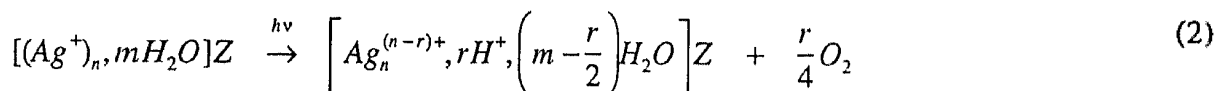


Figure 1. Schematic device for the water splitting or carbon dioxide reduction.

2. Oxidative part

On illumination of silver zeolites in aqueous dispersion under appropriate conditions, the Ag^+ ions are reduced and molecular oxygen is evolved. Z represents the negatively charged zeolite lattice.



Investigation of the spectral sensitivity of reaction (2) has led to the surprising result that a self-sensitization takes place: the further the reaction proceeds, the more the sensitivity shifts from initially near UV to visible wavelengths out into the red.^{2a,b}

To explain this photoreaction, we must learn why silver zeolite, unexposed to light and dispersed in water, absorbs light at about 370 nm for reaction (2) to start. Quantumchemical calculations of the Extended Hückel type of silver ions in zeolitic environment³ have led to the idea that the lowest energy transition is a ligand to metal charge transfer (LMCT), exciting an oxygen lone-pair electron to the silver species coordinated by the zeolite. Before accepting this interpretation, however, we have to understand why such an oxygen lone pair to $5s(\text{Ag}^+)$ transition in a silver zeolite can occur at this wavelength, while for Ag^+ ions solved in pure water it is observed only at about 225 nm. The energy ΔE_{CT} for this transition is equal to the difference of the ionization potential $\text{Ip}_{(\text{O} \leftarrow)}$ of the oxygen lone pair $n(\text{O} \leftarrow)$, and the ionization potential Ip_{Ag} of the $5s$ electron of the silver atom plus a small correction Δ which stands for the interaction of the empty $5s$ level with the environment; Figure 2, left.

$$\Delta E_{\text{CT}} (\text{Ag}^+ \leftarrow \text{O} \leftarrow) = \text{Ip}_{(\text{O} \leftarrow)} - \text{Ip}_{\text{Ag}} + \Delta \quad (3)$$

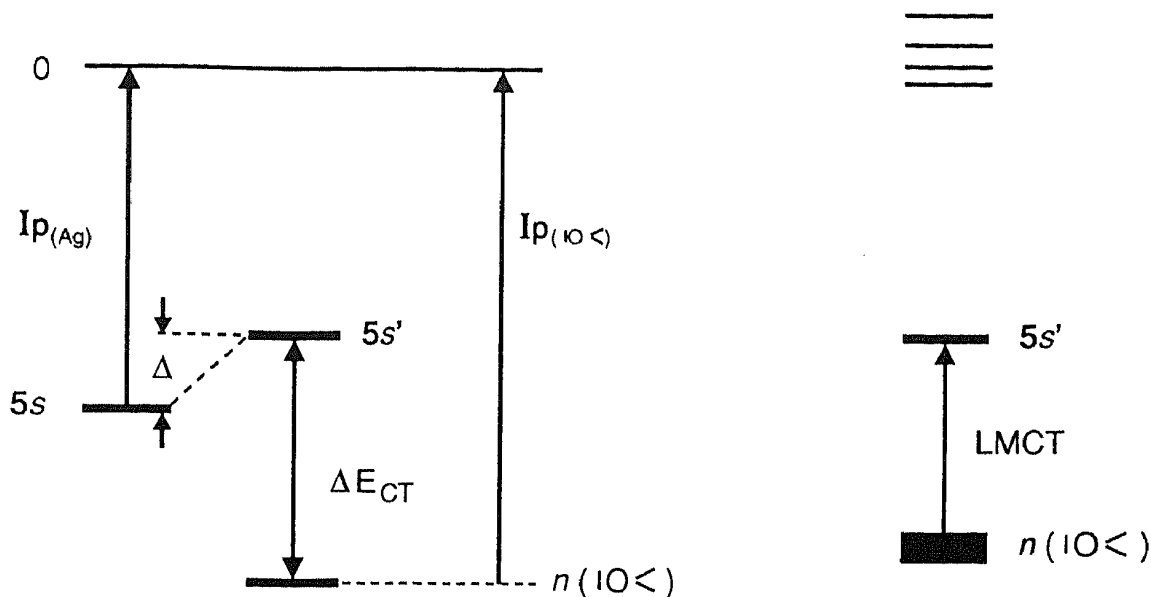


Figure 2. Oxygen lone pair to $5s(Ag^+)$ charge transfer transition. *Left:* energy balance. *Right:* a silver ion in zeolitic environment.

The first ionization potential of silver atoms is equal to $7.6 eV$. The first ionization potential of the water molecule is $12.6 eV$ and attributed to the energy of the oxygen lone pair $n(IO<)$ of the water molecule.⁴ This leads to

$$\Delta E_{CT}(Ag^+ \leftarrow IOH_2) = 12.6 eV - 7.6 eV + \Delta = 5 eV + \Delta \cong 246 \text{ nm} - |\Delta\lambda|$$

This result is in good agreement with the experimentally observed value of about 225 nm . It explains why aqueous solutions of Ag^+ ions are photoactive only in the far UV.

We have to know $I_{p(OZ)}$ to apply equation (3) to silver cations in a zeolite. EHMO calculations show that substitution of some silicon atoms by aluminium shifts the oxygen lone pairs to higher energies. As a consequence, $\Delta E_{CT}(Ag^+ \leftarrow IOZ)$ is expected to shift to longer wavelengths with increasing aluminium content of the zeolite. A small but realistic model for studying the energy of oxygen lone pairs of a zeolite is the spherosiloxane $H_8Si_8O_{12}$. The electronic structure of this molecule has been investigated in detail.⁵ The region of the highest occupied molecular orbitals starts at $-10.75 eV$ with a pure oxygen lone pair and extends to about $-11.7 eV$ with 23 other orbitals, all of them possessing at least 98% oxygen lone pair character. This theoretical finding is in full agreement with the experimentally observed photoelectron spectrum of $H_8Si_8O_{12}$. Furthermore, this low experimental ionization potential of $10.7 eV$ corresponds to the valence band photoelectron spectrum of silicon dioxide.⁶ As a result we get

$$\Delta E_{CT}(Ag^+ \leftarrow IOZ) = 10.7 eV - 7.6 eV + \Delta = 3.1 eV + \Delta \cong 400 \text{ nm} - |\Delta\lambda|$$

This charge transfer transition is illustrated on the right side of Figure 2.

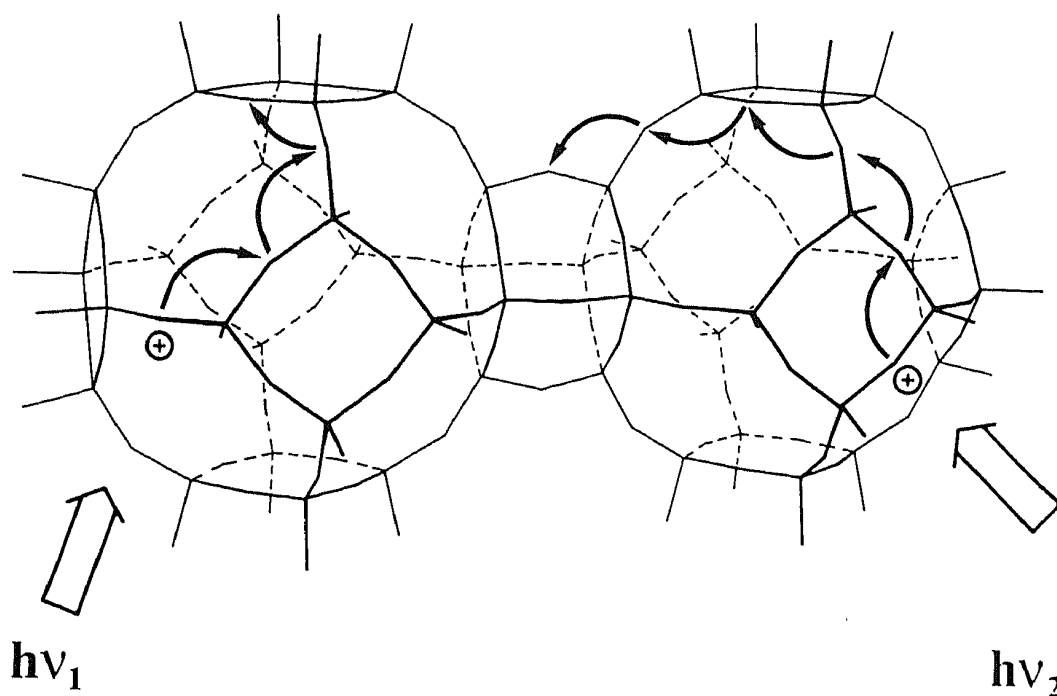


Figure 3. Accumulation of the photogenerated holes within the zeolite. Hopping from oxygen to oxygen of the zeolite framework is imagined to describe the movement of the holes.

The self-sensitization in the process of the photoreaction leads to new chromophores with bathochromically shifted absorption. They are able to drive the photoreaction themselves if excited. The self-sensitization phenomenon can be rationalized by the photoinduced formation of partially reduced silver clusters which absorb at longer wavelengths and then transfer their energy to reactive sites. To explain the oxygen release, we imagine that the lifetime of the holes generated in the oxygen lone pairs is sufficiently long so that they can accumulate and then react with the water, see Figure 3. Silver zeolites are also capable of photo-producing Cl_2 if dispersed in a 0.2 M aqueous KCl solution of low pH. Self-sensitization occurs^{2c,d,e} similarly to the water oxidation. Having two reactions at our disposal for the oxidative part **1** in Figure 1, we consider some thermodynamic arguments on the energy stored in the corresponding reactions.

The electrochemical potential of silver clusters in aqueous environment is a pronounced function of cluster size.^{7,8} Henglein^{7a} stresses the occurrence of two different potentials for the silver system, the

metal-electrode potential: $\text{Ag}^+ + \text{Ag}_{n-1} + e^- \rightarrow \text{Ag}_n$; $E_{\text{Ag}^+(\text{aq})/\text{Ag}_n}^0$, and the

ionization redox potential: $\text{Ag}_n^+ + e^- \rightarrow \text{Ag}_n$; $E_{\text{Ag}_n^+(\text{aq})/\text{Ag}_n}^0$.

The limit of the metal-electrode potential of bulk silver is equal to 0.8 V and that of the corresponding ionization redox potential is equal to 0.0 V. The metal-electrode reduction potential and the ionization redox potential of silver clusters can be calculated from thermodynamic cycles and expressed as follows:¹

$$E_{Ag^+(aq)\gamma Ag_n}^0 = Ip_{Ag} + \Delta G_h(Ag^+) + \varepsilon - \Delta G_b(n) = -1.8 \text{ eV} - \Delta G_b(n) \quad (4)$$

$$E_{Ag_n^+(aq)\gamma Ag_n}^0 = Ip_{Ag_n} + \Delta G_h(Ag_n^+) + \varepsilon \quad (5)$$

The metal electrode potential (4) depends on the ionization energy of silver atoms in the gas phase $Ip_{Ag} = 7.6 \text{ eV}$, on the energy $\varepsilon = -4.5 \text{ eV}$ involved in bringing an electron from the vacuum (infinity) to the level of the standard hydrogen electrode, on the energy of hydration $\Delta G_h(Ag^+) = -4.9 \text{ eV}$ of the silver cation and on the binding energy $\Delta G_b(n)$ of a silver atom to the silver cluster Ag_{n-1} . The binding free enthalpy $\Delta G_b(n)$ has been measured for $n = 1, 2, 3$.⁹

The ionization redox potential (5) depends on the ionization energy of the Ag_n cluster and on the free enthalpy of hydration of the cluster ion. Experimental values for Ip_{Ag_n} , $n = 1, 2, 3, 4$ have been published¹⁰ and the free enthalpy of hydration $\Delta G_h(Ag_n^+)$ can be calculated from the Born equation.⁸

The binding free enthalpy for larger clusters can be calculated from the free energy change associated with the change in surface area in the transference of one mole bulk metal to the dispersed form.¹¹ Equation (4) can therefore be modified to¹

$$E_{Ag^+(aq)\gamma Ag_n}^0 = 0.8 \text{ eV} + 3.176 \text{ eV} \cdot [(n-1)^{2/3} - n^{2/3}] \quad (6)$$

Table 1. Redoxpotential of silver clusters as calculated from equations (4 - 6)

n	$Ip_{Ag_n}^a)$	$\Delta G_h(Ag_n^+)^b)$	$E_{Ag_n^+(aq)\gamma Ag_n}^0$	$\Delta G_b(n)$	$E_{Ag^+(aq)\gamma Ag_n}^0$
1	7.6	-4.9	-1.8	(0.0) ^{c)}	-1.8 (-2.4) ^{d)}
2	7.3	-3.9	-1.1	-1.27 ^{c)}	-0.5 (-1.06)
3	6.2	-3.4	-1.7	-0.6 ^{c)}	-1.2 (-0.76)
4	6.3	-3.1	-1.3		(-0.6)
10					(-0.2)
100					(0.34)
∞	4.5	(0.0)	(0.0)	-2.6	+0.8

a)¹⁰, b)⁸, c)⁹, d) values in parentheses have been calculated from eq. (6).

From the numerical values in Table 1 we conclude that it is reasonable to assume the silver species produced in the photoredox reaction (2) being stronger reductants than bulk silver. We still have poor information of the photochemically produced silver species regarding their size, their geometry, their electronic structure, and the influence of the zeolite environment

on their redox potentials and redox kinetics. It is highly desirable to design experiments that give us directly access to these properties in the appropriate environment, since reactions such as $(Ag_n^+)_{solv} \rightleftharpoons (Ag_{n-1})_{solv} + (Ag^+)_{solv}$ can also be important.

3. Reductive part

The reductive half reaction **3** in Figure 1 has been studied by many groups under a variety of conditions. Two main fields can be distinguished. One is based on semiconductor particles and the other on transition metal complexes. Both of them having their advantages and disadvantages, it is too early to judge which approach will be more successful. Some possibilities with semiconductor particles have comprehensively been reviewed by Memming,¹² and many other systems for H₂ evolution have been described in the literature.¹³ Regarding the approach via transition metal complexes, we mention investigations carried out by Lehn et al.¹⁴ With the photocatalyst {Re(bipy)(CO)₃X, X=Cl,Br} they found a system that selectively reduces CO₂ to CO. Interesting complexes can also be obtained with p-phenyl-terpyridine (ptpy) as a ligand.¹

4. Coupling oxidation/reduction

Having the oxidation reaction **1** and the reduction reaction **3** in Figure 1 at our disposal, we discuss the coupling **2** that has to be realized by means of a membrane. Studies on the reactivity of Ag⁺ zeolites with CO¹⁵ do support our opinion that the whole system can only work with a membrane that prevents material exchange between the two parts, but enables the transfer of electrons and protons.

At this time we are not concerned about proton transport, a problem that might become important at a later stage. Sufficient electron conductivity across the zeolite is necessary to bring electrons from **1** to **3**. Experimental studies have led to the result that the resistance of even very thin silver zeolite pellets is by orders of magnitudes too high to guarantee the necessary electron conductivity. The cause of the far too high resistance lies in the interphase of the grain boundaries. We have therefore developed a simple and fast technique for preparing a monograin zeolite layer by covalently linking 1 μm sized zeolite A, 0.2 μm sized zeolite Y, and also zeolite L particles as a dense sheet onto an electrode. The silver reduction and oxidation steps in the so prepared zeolite electrodes are quasi reversible.¹⁶ Our technique can be extended to many different substrates. Up to now we have applied it to Pt, graphite, glassy carbon, glass, quartz and tin dioxide. The surface-functionalized zeolite was tested for its integrity by X-ray powder diffraction and by FTIR transmission spectroscopy. The overall shape of the IR spectrum is comparable to nonmodified zeolite A¹⁷ with additional bands in the olefinic and aliphatic range of carbon-hydrogen vibrations.

An appealing possibility to combine the oxidative and reductive half-reactions is shown in Figure 4. A membrane is coupling a silver zeolite monolayer on the oxidative side to a zeolite monolayer, loaded with semiconductor particles, on the reductive side. The semiconductor particles are located inside the zeolite cavities and therefore limited in size. Excitation of the semiconductor particles delivers the electrons necessary to reduce water. The holes produced in this process recombine with the electrons of the reduced silver zeolite. A problem demanding careful consideration is the junction between the two half reactions.

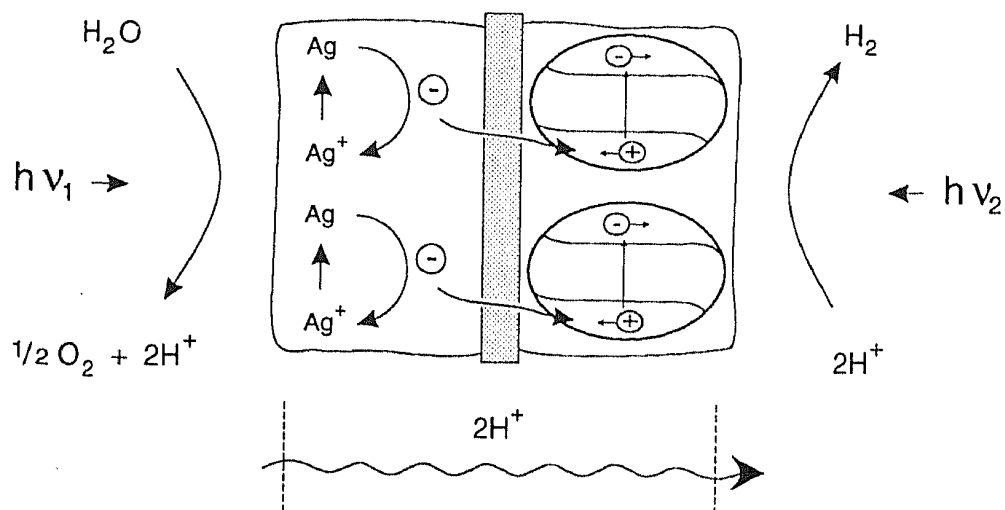


Figure 4. Arrangement to couple the oxidative and reductive half-reactions. We use a zeolite system on both sides. A silver zeolite drives the water oxidation. The water reduction is achieved by semiconductor particles encapsulated in a zeolite matrix.

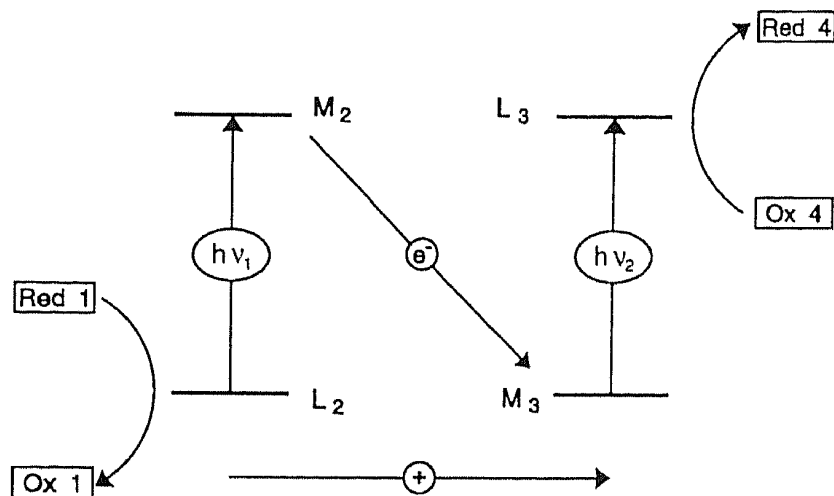


Figure 5. Coupling of a LMCT state in the oxidative reaction, *left*, to a MLCT state in the reductive reaction, *right*.

The arrangement illustrated in Figure 5 combines the silver zeolite with an appropriate transition metal complex. In this case a metal to ligand charge transfer transition MLCT leads to the reduction of water or CO₂ and an oxidized central metal atom. The metal atom is then reduced by capturing an electron from the reduced silver zeolite. It is interesting to realize that this type of system is based on the coupling of a LMCT state in the oxidative reaction 1 (oxygen lone pair to silver cation, or chlorine anion to silver cation) to a MLCT state in the reductive reaction 3 (metal to ligands such as ptpy, bpy and others). Positive charges have to be transported from 1 to 3 to keep electroneutrality.

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5. References

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