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Photochemical/Thermal Cleavage of Water Over Silver-Zeolite*

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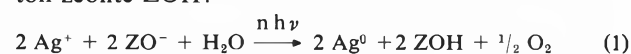
Abstract

Silver ion exchanged zeolites are sensitive to visible light similar to silver oxide. They release oxygen from adsorbed water while irradiated, and form molecularly dispersed silver. This is capable of thermal reduction of zeolite water to hydrogen ($> 600^\circ\text{C}$) under oxidation to Ag^+ . The process is promising but not yet practical for photochemical solar energy storage. Research topics for improvements are identified.

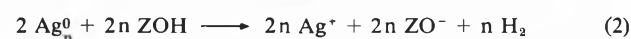
Introduction

It is well known that Ag^+ -containing silicates or aluminosilicates are light sensitive systems [1]. Ag^+ -exchanged molecular sieve zeolites coated as a thin layer on a glassplate and exposed imagewise can be developed in ordinary photographic developers and fixed. Depending on the particle size, images with reasonable granularity are obtained, which, however, do not offer any advantage over conventional silver photography [2]. The "latent" image or printout silver, if barely visible, are not stable. They are bleached especially in the presence of water.

These observations led to the following *hypothesis* [3] about the photochemical processes in the system Ag^+ZO^- , water (ZO^- represents the zeolite frame): During the exposure Ag^+ is reduced to some form of Ag^0 with evolution of oxygen and formation of a proton zeolite ZOH:



Ag^0 is interacting with the silver ions in the pores of the zeolite, forming particles Ag_n^{+m} ($m < n$) capable of spontaneous reduction of the proton zeolite if m has become small enough (≈ 0):



Hence the overall reaction would sum up to a photocatalytic cleavage of water into hydrogen and oxygen driven by visible light and thus converting solar radiation to chemical free enthalpy.

This hypothesis has experimentally been tested, among other objectives, almost five years ago [3]. Recently *Jacobs*, *Uytterhoeven* and *Beyer* [4] have published about the photochemical oxygen production from water by Ag^+ -zeolites. The reduced Ag^0 -zeolite was reoxidized under hydrogen evolution at 600°C . Their

experiments were explained by reactions (1) and (2). The formation of ZOH by (1) was followed by IR-spectra of the $-\text{OH}$ groups. They used Ag^+ -exchanged zeolite Y (Si: Al 2.51) or X, in which large Ag^0 -clusters can be readily obtained by wetting with aethanol and drying at 60°C [5]. *Beyer*, *Jacobs* and *Uytterhoeven* have recently studied the redox-behaviour of AgY and $\text{Cu}^{\text{II}}\text{Y}$ [6]; *Texter*, *Strome*, *Herman* and *Klier* communicated spectroscopic and photochemical information about CuY [7].

Experimental

Our experiments have been performed with Linde A molecular sieve (5\AA) with Si: Al = 1. 92.5 to 99.5% of the Ca^{2+} -ions in CaA have been exchanged for Ag^+ -ions.

Photochemical part: Two types of experimental set-ups were used:

1) A series of glass-ampoules with teflon gasket, silicon-septum, screw-cup, and glass-taper joint cup at one end were filled with a water suspension of 5 g AgA in 80 ml water and some glass-balls. The ampoules with the solutions were evacuated and filled with ultrapure nitrogen (three times) and then sealed under vacuum. They were exposed on a rocking table under two iodine quartz-lamps (250 W each, distance 40 cm from samples). A chemical actinometer [9] was included in every run of six samples. After 2–3 h exposure a part of the now gray suspensions was withdrawn by syringe through the septum in a nitrogen filled glove-bag, injected and measured with a calibrated Clark O_2 -electrode in a thermostated, stirred and closed volume. With the assumption of the validity of the Henry-Dalton gas absorption law, total oxygen production could be secured, and related to the total irradiation.

2) The nine Erlenmeyer flasks of a *Gilson* Differential Respirometer [8] were filled with a number of samples of 1 g AgA and 20 ml water each, and several samples of the same volume of the chemical actinometer *Reinecke*-salt [9] (precipitated as potassium salt, recrystallized in dark room and stocked in a dessicator; for each run, the solution was freshly prepared). At $25 \pm 0.1^\circ\text{C}$ each flask was irradiated by a 53 Watt Krypton lamp of calibrated spectral emissivity. In intervals of 20 min an aliquot from one actinometer flask was withdrawn and measured in the usual way based on a non-exposed blank treated identically. The photochemical gas evolution in every sample was measured as a function of time.

In both series of experiments the AgA samples were randomly placed and accompanied by suspensions of freshly prepared AgCl , TiO_2 , ZnO , and SnO_2 in water exposed under identical conditions.

Thermal part: The amount of reduced silver was determined 1) by acid decomposition of the zeolite, oxidation of the silver by excess Ce^{4+} and backtitration with standard As_2O_3 -solution; 2) by diffuse reflectance spectrometry on a Cary 17 spectrophotometer using untreated NaA powder as remission standard. The evaluation by Schuster-Kubelka-Munk theory was based on AgA-samples with definite Ag^0 content prepared by careful reduction at room temperature and 80°C with H_2 . 3) ESR-spectra

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This communication is a compact summary of the main results. Details will be published elsewhere.

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of photochemically and chemically produced $\text{Ag}_n^{(+m)}$ -clusters were obtained with a Varian E-9 spectrometer, X-band modulation, and determined as a function of temperature between liquid N_2 /room temp.

The thermal reaction of Ag_n^0 with ZOH was accomplished in a small quartz tube furnace equipped with thermocouple and thermostat; during the high temperature treatment ultrapure nitrogen loaded with a variable H_2O partial pressure was swept through the furnace. After freezing out the water in a liquid N_2 -trap (filled with pyrex wool) the N_2 -stream loaded with produced H_2 was led through a quartz tube furnace filled with dry NiCl_2 at 600°C . Hydrogen reacts with NiCl_2 to form reduced nickel and HCl [10]. This was collected in a second cold trap and at the end of the experiment determined by acid-base or argentometric titration.

All analytical steps have, of course, been checked by repeated blanks.

Results

Whereas untreated TiO_2 , ZnO , and SnO_2 did not give any significant gas evolution during irradiation, as expected since the UV-component was very low in both experiments, AgCl [11] and AgA produced oxygen. With AgCl we obtained a quantum yield of oxygen production of nearly 1 in both, with AgA 0.62 in the first and 0.67 in the second experiment. The gas evolution was a linear function of time at constant light intensity. With AgCl a spectral sensitization of oxygen-production could be observed [11]. Photographic and electrophotographic spectral sensitizers [12] were destroyed and without effect, whereas chlorophyll a (freshly prepared and of high purity) adsorbed on the AgCl microcrystals was effective ($8.7 \mu\text{mol Chl a/mol AgCl}$) without signs of photodegradation if a yellow or red filter was used preventing excitation of the Soret-band.

The first experimental set-up gives the oxygen-evolution as measured by the oxygen sensitive Clark electrode, while in the second only total gas evolution is registered with higher precision. The difference in quantum yield between the two measurements is statistically not significant. We assume, therefore, that the gas evolved in the second experiment is also oxygen.

The reduced silver is stoichiometrically equivalent to the photochemically evolved oxygen. During exposure of AgA to visible light the zeolite darkens and develops an ESR-signal proportional to the decrease in spectral reflectance and identical in shape to the signal obtained in AgA reduced by H_2 at 80°C . Hence eq. (1) is verified.

For the reductive step of water, eq. (2), the following information has been obtained: By high temperature treatment of the reduced Ag_n^0/ZOH system in the presence of water-vapour the zeolite is partially bleached (reflectance spectrometry), Ag^+ reappears (Ce^{4+} titration), and an equivalent amount of H_2 is evolved (HCl -titration). In 5 h the process reaches yields of 12% at 305° , 30% at 516° , and 69% at $> 700^\circ\text{C}$. Since at $> 700^\circ\text{C}$ the zeolite lattice is slowly transformed, the

photochemical/thermal redox cycle with AgA is not completely reversible.

No measurements of hydrogen evolution during irradiation at ambient temperature have so far been made. Hence, the mechanism mentioned for image fading remains hypothetical and eq. (2) has only partially been verified.

Discussion

Beyer et al. [4] have probably been more successful with high temperature hydrogen evolution from their photochemically reduced AgY and AgMgX zeolites than we. However, the only experimental quantity given in their paper is the mass-spectrometric determination of two H_2 -volumes. It is well known that H_2 -volumetry with a mass-spectrometer is unreliable unless performed under strictest precautions [13]. We therefore have refrained from this technique. The choice of AgY (and AgMgX) instead of AgA is recommendable because of better lattice stability of the SiO_2 -rich zeolites. On the other hand, the necessary electron transfer between zeolitematrix and Ag^+ is probably favoured in A-zeolites, as evidenced by the quenching of luminescence of Cu(I) in A- and not in Y-zeolites [7].

The non-complete recovery of Ag^+ and H_2 in our case against the asserted (almost) reversibility in ref. [4] may be due to the choice of AgA and the presence of water vapour during the reductive step. It has become known since that steam treatment of MA-zeolite at high temperature can lead to pore closure [14]. Furthermore, water vapour produced thermodynamically less favourable conditions for hydrogen release than vacuum or an inert gas atmosphere.

For utilization and storage of solar energy in chemical form Ag-zeolites seem to be promising but still far from a practical applicability. The endothermic conversion of the Ag_n^0/ZOH at 873 K and vacuum into H_2 and Ag^+ZO^- is an unacceptable step, even if the nonactinic radiation $\lambda > 720 \text{ nm}$ ($\sim 50\%$ of the solar power density) is captured by parabolic collectors and used for generating 600°C . The overall energy yield factor is probably close to zero or negative. On the other hand, by partition of water cleavage into two half cycles the tiny free enthalpy expenditure for O_2/H_2 -separation is already provided for. If successful, metals supported by zeolites and functioning as heterogeneous photocatalysts are among the most practical solutions for a photochemical solar energy reactor.

Our aim is the discovery and utilization of the mechanism of image forming and fading under illumination at ambient temperature in a silver- or possibly less noble metal-zeolite/water system. The argument at the start of our early experiments with Ag^+ -zeolites (February 1973) was as follows: Water cleavage with the photon energy available with sunlight at ground level is barely possible with one photochemical primary step ($n = 1$) at $\bar{\omega} \simeq 20 \text{ kK}$ ($\eta = 1$), since $\bar{\omega} \geq$

$\Delta G^0/n\eta$ [kK]; $\Delta G^0 = 237.2 \text{ kJ/Mol} = 19.9 \text{ kK}$ for $\text{H}_2\text{O} (l) \rightarrow \text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g)$ at 298 K, n number of Einsteins/Mol, η fraction of photon-energy at $\bar{\omega}_{\min}$ which is transformed into chemical free enthalpy. A realistic process has $\eta \simeq 0.7$, for which a single photon within the sun's surface radiation has not enough energy, so that two photochemical steps are required. Now $\bar{\omega}_{\min} \simeq 10 \text{ kK}$, $\lambda_{\max} \simeq 1000 \text{ nm}$. Since water does not absorb in the visible, nor at 1μ , sensitization is necessary with complex mechanisms and hence loss factors. An $\eta \gtrsim 0.4$ is reasonable and with $n = 2$ $\bar{\omega} \geq 12.4 \text{ kK}$, $\lambda_{\max} = 800 \text{ nm}$. Incidentally, this estimate is realistic, since the green plant photosynthesis needs an overall potential difference of $\Delta E^0 = 1.28 \text{ V}$ against $\Delta E^0 = 1.23 \text{ V}$ for water photolysis, hence both processes have similar boundary conditions. Nature uses two photochemical steps and spectral sensitization to make use of the best part of the sun's visible spectrum, thus corroborating our conclusion. Now, a two photon sensitized process requires a quantum storage device and a quantum transfer agent. In analogy to the latent image centre of silver photography, which is a quantum storage device [15], we chose silver zeolites. The neutral or positively charged silver clusters Ag_n^m ($m < n$) formed therein during light exposure are supposed to play three essential parts: 1) Oscillators for light absorption; 2) quantum storers by chemical reaction: $\text{Ag}_n^m \rightarrow \text{Ag}_n^{m-1}$ or $\text{Ag}_{n-1}^0 + \text{Ag}^+ \rightarrow \text{Ag}_n^+$; 3) spontaneous or light assisted reductants of the proton zeolite generated by light absorption.

AgA is yellow to ochre, depending on treatment. From the 12 Ag^+ -ions of the unit cell 8 Ag^+ are located in hydrated AgA near the centre of the O^{2-} -6-rings on the 3-fold axes inside the large α -cage, site I. The remaining 4 Ag^+ -ions are associated with water molecules and the O^{2-} near the 8-ring-openings of the α -cage, site II [16]. α - and β -cages contain 24 water molecules/unit cell if fully hydrated. Both types of silver ions are partly coordinated to frame-oxygens, partly to water molecules. This is not unlike wet Ag_2O ("AgOH") which is brown, light sensitive and performs the same photochemistry, i.e. O_2 -evolution and formation of Ag^0 -particles under irradiation. However, the silver formed in this system is not capable of H_2 -production, because the redox potential $\text{Ag}^+ (\text{aq})/\text{Ag} (s)$ is unfavourable for reoxidation of $\text{Ag} [0]$ and reduction of water. This process is, however, possible with molecularly dispersed silver Ag_n^m with n probably $\lesssim 6$, hence the choice of zeolitic " Ag_2O ", where the reduced silver is, hopefully, prevented from agglomeration by the rigid pore structure. The standard redox potential of $\text{Ag}^+ (\text{aq})/\text{Ag}^0 (\text{aq})$ between silver ion and hydrated silver atom is $E^0 = -1.8 \text{ V}$, if the free hydration enthalpy of Ag^0 is neglected [17]. For silver clusters $\text{Ag}_n^0 (\text{aq})$ we assume a more or less monotonous $E^0(n)$ -curve [18] which approaches asymptotically the bulk metal value $E^0(\infty) = +0.8 \text{ V}$ for $\text{Ag}^+ (\text{aq})/\text{Ag} (s)$. Unless the interactions of silver ions and silver clusters

with the zeolite lattice are very different from those with water, we expect spontaneous hydrogen evolution from ZOH at small n and ambient temperature. This is favoured by a large proton activity a_{H^+} . The hydrogen zeolite ZOH becomes strongly acidic at a temperature where a_{H^+} is no longer quenched by adsorbed water ($> 350^\circ\text{C}$).

Neither the experiments of ref. [4] nor our own seem to confirm these arguments except for the last remark (no measurements of H_2 -evolution at ambient temperature during irradiation has so far been made, however). H_2 -evolution becomes exergonic only at $T \gtrsim 873 \text{ K}$. Many speculations can be given for this "misbehaviour", e.g. the existence of an H_2 -"overvoltage" or the known fact of metal diffusion out of the pores and formation of macroscopic silver on the surface of the crystallites [19]. We believe that the experimental conditions have not yet created well matched redox pairs. It seems that the pure silver system is lopsided in favour of the oxydative half cycle, hence the difficulty in H_2 -recovery. A less noble metal is probably better suited.

In order to identify possible experimental degrees of freedom, the sequence of events for photocatalytic water-splitting over Ag-zeolites (to stick to this example) is sketched as follows: AgZ (Z stands for A, X or Y zeolites) if once dried at $\sim 100^\circ\text{C}$ becomes yellow-red to ochre. It absorbs a photon from the visible into a (collective) charge-transfer transition [20]. The photoelectron is trapped by Ag^+ forming Ag^0 and the hole by the cage anions (see below). Ag^0 is a short lived intermediate [17]. It is according to Slater's rules very large $r \simeq 3.5 \text{ \AA}$, and because of repulsion by the frame O^{2-} it moves out from site I into the α -cage where electronic interaction with nearby Ag^+ -ions leads to delocalization and stabilization against recombination [21]. This Ag_n^{n-1} ($n \leq 8$) serves as an improved resonant oscillator – the system darkens under illumination – for capturing a second photon at the same site, forming Ag_n^{n-2} a.s.o. Meanwhile the captured holes on the negatively charged cage wall form "Lewis-sites" which are short lived, because they are transformed by water into "Brønsted-sites" ZOH and perhaps peroxy-type ligands ZOOH [22]. After accumulation of 4 holes in the same or nearby cage, O_2 is released (dispersed silver is a catalyst for H_2O_2 decomposition). The growing electron population in the Ag_n^m -cluster does not prevent further charge transfer transitions but it leads to a bathochromic shift of the LUMO-HOMO difference of the cluster from the ultraviolet (for the ${}^3\text{D}_3 4d^9s \leftarrow {}^1\text{S}_0 4d^{10}$ transition of the free Ag^+ at 39 kK) into the visible. At some stage the cluster becomes, therefore, photochemically active as a reductant, forcing electrons from its excited state (LUMO) onto ZOH and forming H_2 . Gradually all the silver accessible to radiation will thus be converted into a photocatalyst. The silver clusters most probably form a system of two redox pairs $\text{Ag}_n^m/\text{Ag}_n^{m-1}$

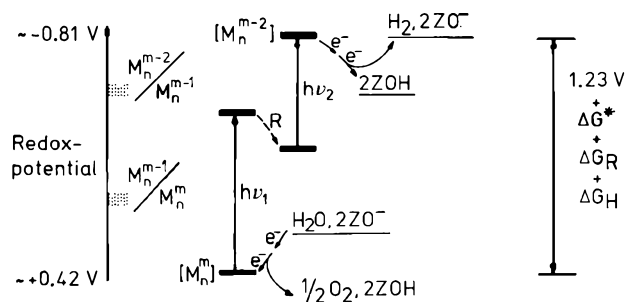


Fig. 1: Photocatalytic cleavage of water driven by two photons of visible light as proposed for metal zeolites M^+ZO^- . M_n^m are small metalatom-clusters with charge $m < n$. R is the relaxation (and ΔG_R the corresponding free enthalpy) of the excited M_n^{m-1} within the zeolite cage and electron transfer from the first to the second photosystem. ΔG^* is the sum of free enthalpy contributions caused by the change in standard states of $H_2O(l)$, $H_2(g)$, $O_2(g)$ to the adsorbed state on the zeolite (known). ΔG_H is the free enthalpy contribution for nucleation and desorption of O_2 and H_2 gas. The hypothetical redox pairs on the left would be matched pairs to the underlined redox-reactants and simultaneously oscillators for light absorption.

and Ag_n^{m-1}/Ag_n^{m-2} connected by several processes as depicted on fig. 1. They should match the H_2O , O_2 , H_2 system and its intermediates. This model realizes the postulates: There are two types of oscillators, the charge-transfer $Ag^+ \xleftarrow{e^-} O_2^-$ and the "homogeneous" $Ag_n^{m-1*} \xleftarrow{h\nu} Ag_n^{m-1}$ types, quantum storage by the two consecutive excitation steps and the spontaneous reductant $Ag_n^{m-2} + 2ZOH \rightarrow Ag_n^m + H_2 + 2ZO^-$. Matching the redox pairs, preventing the clusters from agglomeration to bulk metal, and improving the catalytic properties for O_2 - and H_2 -release (overtoltage reduction) are problems now under study in this laboratory.

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- 8 See *Umbreit, Burris, Stauffer and Burgess*: Manometric Techniques, Minneapolis 1957, p. 79-83. We should like to thank Prof. *K. Erismann*, Institute for Plant Physiology, Univ. of Bern, for allowing us to use his equipment and laboratory space.
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- 13 Most mass spectrometers have a high $m/e = 2$ background. Only measurements with internal standards are reliable, e. g. D_2 or He. A number of H_2/D_2 or H_2/He mixtures have to be used for calibration. The measured m/e ratios have to be extrapolated to zero time of the sample because of the large discrimination introduced by preferential pumping of H_2 under molecular flow. Already some solar energy work has been marred by mass-spectrometric H_2^- measurement, e. g. *Sprintschnik et al.*: J. Amer. Chem. Soc. 98 (1976) 2337, which is a non-reproducible experiment, see *Sprintschnik et al.*: ibid. 99 (1977) 4947.
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- 18 For Na_x clusters $x \leq 14$, K_x $x \leq 8$, see *A. Herrmann, E. Schumacher, and L. Wöste*: J. Chem. Phys., submitted.
- 19 E. g. *E. Czárán, K.-H. Schnabel and M. Selenina*: Z. anorg. allg. Chem. 410 (1974) 225; for Pt-supported on Y-zeolite, and ref. [6] for AgY.
- 20 The transitions responsible for the AgA colour are not well specified. Localized excitations of Ag^+ or O_2^- are far removed in the UV. Hence the colour must come from either some slightly delocalized nonstoichiometry caused by a small electron excess on the Ag^+ -content (caused by thermal reduction of the extremely active Ag^+ particles) or from the interaction of Ag^+ with the O_2^- -frame. In both variants the colour is a collective phenomenon as known in many oxides, sulfides etc.
- 21 compare the clusters Na_4^{3+} , Na_6^{5+} observed by ESR-spectra in partially reduced NaY by *J. A. Rabo, C. L. Angell, P. H. Kasai and V. Schomaker*: Disc. Farad. Soc. 41 (1966) 328; furthermore: *J. A. Rabo*: ed. Zeolite Chemistry and Catalysis, Am. Chem. Soc. 1976, chapt. 6 and chapt. 10.
- 22 We are intentionally vague about this point. Presently the acid-base properties of zeolites are much in debate and one school denies the clear-cut distinction between Lewis- and Brønsted-sites. There is, however, experimental proof, that "decationized" zeolites can be very strong electrophiles, so strong that they become oxidants. Decationized X-zeolite e. g. oxidizes ferrocen to ferrocenium-ion (unpublished experiments with *W. Heinzelmann* (1964) and *F. Berdat* (1973)). Whether peroxo-groups or free radical states of the frame are responsible has not been clarified. The literature is mystic about these points, because too much industrial know-how seems to be at stake; see: *J. J. Fripiat, A. Léonard and J. B. Uytterhoeven*: J. Phys. Chem. 69 (1965) 3274 and books ref. [14] and ref. [21].