Cleavage of Water Over Zeolites

By PETER A. JACOBS, and JAN B. UYTTERHOEVEN
(Centrum voor Oppervlakteschiekunde en Colloïdale Scheikunde, Katholieke Universiteit Leuven, De Croylaan 42, B-3030 Heverlee, Belgium)

and HERMANN K. BEYER
(Central Research Institute of Chemistry, Hungarian Academy of Sciences, 11 Pustaszeri, út 57–69, Budapest, Hungary)

Summary Evidence is provided that silver zeolites can be used for the decomposition of water into hydrogen and oxygen; the process consists of a photochemically induced reduction of the zeolite, followed by an oxidative thermal desorption of hydrogen.

METHODS for solar energy conversion currently form an active area of research, and recently, the possibility of decomposing water into hydrogen and oxygen using photochemical energy has been reported. Sprintschnik *et al.*[1] have shown that ruthenium(II)–2,2′-bipyridine complexes immobilized on a glass surface catalyse the photochemical decomposition of water into hydrogen and oxygen. Kutal *et al.*[2] used sunlight in the presence of a sensitizing agent to convert norbornadiene into its high energy isomer quadricyclene. The stored energy can be released using a catalyst for conversion back into norbornadiene. Stevenson and Davis[3] used solar energy to reduce protons to hydrogen gas in an aqueous solution containing copper(I) ions. We now report on the use of silver zeolites in the cleavage of water into oxygen and hydrogen. Water is first decomposed using photochemical energy, the zeolite containing Ag^+

ions is reduced, and oxygen is generated. Heating the zeolite containing silver metal then releases hydrogen, while the solid is oxidized back to its initial state.

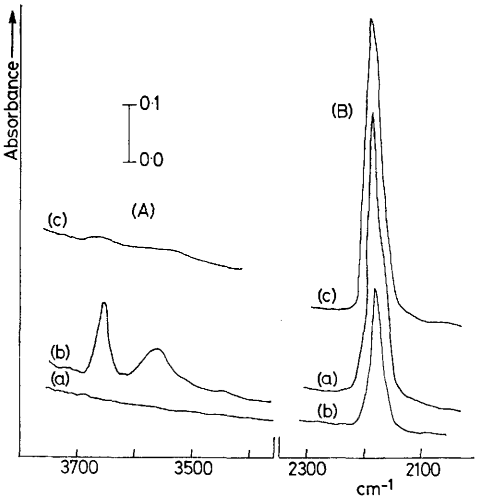

FIGURE. I.r. spectra of (A) OH and (B) CO adsorbed at room temperature on AgY zeolite: (a) original sample evacuated at 573 K; (b) water sorption followed by irradiation with sunlight and evacuation at 573 K; (c) degassing at 873 K.

It is well known that the colour of a Y zeolite containing Ag^+ ions darkens upon ageing.[4] At the same time hydroxy i.r. absorptions (*ca.* 3650 and 3550 cm^{-1}) appear, while the specific stretching vibration at 2174 cm^{-1} of carbon monoxide interacting with Ag^+ ions is weakened. In order to intensify this process 1 g of AgY zeolite was loaded in a U shaped quartz tube, evacuated at 1·33 mN m^{-2}, saturated with water vapour, and exposed to sunlight for 2 h. Mass spectrometry showed an increase in the pressure of oxygen in the vessel during irradiation and the sample turned grey. The Figure shows that upon irradiation hydroxy-groups appear at the usual frequencies and the concentration of Ag^+ ions in the supercages decreases as revealed by the relative importance of the $Ag^+ \cdots CO$ interaction. These observations indicate that the reduction upon irradiation with sunlight can be written as in reaction (1), where ZO^- represents the zeolite lattice.

$$2\,Ag^+ + 2\,ZO^- + H_2O \xrightarrow{h\nu} 2\,Ag^\circ + 2\,ZOH + \tfrac{1}{2}O_2 \qquad (1)$$

The Figure shows that upon thermal treatment of the reduced silver zeolite at 873 K the hydroxy-groups disappear and Ag^+ ions reappear in the supercages. Mass spectrometry shows that hydrogen gas is desorbed; the zeolite becomes white again. This suggests that reaction (2) occurs. The oxidative desorption of hydrogen occurs only when the silver metal is highly dispersed in the zeolite. Evidence for this will be reported later.

$$Ag^\circ + ZOH \xrightarrow{873\ K} Ag^+ + ZO^- + \tfrac{1}{2}\,H_2 \qquad (2)$$

The amount of hydrogen desorbed in the particular case described was 0·14 mmol per g of AgY zeolite. The cycle consisting of reactions (1) and (2) could be repeated several times with almost the same efficiency. The efficiency of the first step, all other factors remaining the same, could be improved using a purge of nitrogen gas saturated with water vapour during the irradiation. Using our experience and knowledge of transition-metal zeolites, the amount of Ag^+ ions and their reducibility was optimized using an X zeolite where the hexagonal prisms were filled partially with Mg^{2+} ions. In this way it has been possible to desorb as much as 0·47 mmol of hydrogen per g of zeolite during one cycle.

The system loses its reversible behaviour when hydroxy-groups are removed during the heating step as water *via* the dehydroxylation (3) or when Ag° metal is sintered out

$$2\,ZOH \longrightarrow ZO^- + Z^+ + H_2O \qquad (3)$$

of the zeolite during the heating or irradiation period.

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[1] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1976, **98**, 2337; C. Murray, *Chem. Eng. News*, 1976, May 31, 17.

[2] C. Kutal, R. R. Hautala, and R. B. King, *Chem. Eng. News*, 1976, September 13, 17.

[3] K. L. Stevenson and D. D. Davis, *Chem. Eng. News*, 1976, September 13, 17.

[4] H. Beyer, P. A. Jacobs, and J. B. Uytterhoeven, *J.C.S. Faraday I*, 1976, **72**, 674.