Kinetics of the Reduction of Ni^{2+} Ions in an X-type Zeolite and in a Silica-Magnesia Gel

By M. KERMAREC,* M. BRIEND-FAURE, and D. DELAFOSSE

(*E. R. No.* 133, *Cinétique des réactions superficielles, Université Pierre et Marie Curie,* 4 *Place Jussieu,* 75230 *Paris Cedex* 05)

Summary The reduction of Ni^{2+} ions in a three-dimensional matrix suggests a diffusion mechanism, whereas when the ions are contained in the lattice of an amorphous gel a germination process is involved.

THE problems of the storage of hydrogen have stimulated interest in obtaining very highly dispersed metal atoms on supports of high surface area[1] or on 2- or 3-dimensional matrices[2] but few kinetic studies have been undertaken.[3] We now report preliminary results on the reduction of Ni^{2+} ions introduced as an exchangeable cation in an X-type zeolite and replacing Mg^{2+} in a silica–magnesia gel.

The composition of the Ni^{2+} X zeolite is $Na_{24}Ni_{31}(SiO_2)_{106}$, $(AlO_2)_{86}$, 264 H_2O. The particle size is homogeneous and the diameter of the particles, considered as spheres, is close to 1 μm. The very slow cation–proton exchange shown in equation 1 occurs without any modification of the zeolite

$$Na^+Ni^{2+}X + H_2 \longrightarrow Na^+2H^+X + Ni^0 \qquad (1)$$

structure. The ranges studied are from 448—573 K and 1·3—13 kN m^{-2}. The formation of Ni^0 was demonstrated by e.s.r. spectroscopy and the dispersion of the metal particles obtained can be determined qualitatively from ferromagnetic resonance curves.[4] The reactivity of Ni^0 particles with O_2 is related to their size which increases with increasing reduction temperature. Thus it is possible to reoxidize at 473 K the Ni^0 particles obtained at temperatures below 503 K whereas at higher reduction temperatures only partial re-oxidation can be effected.

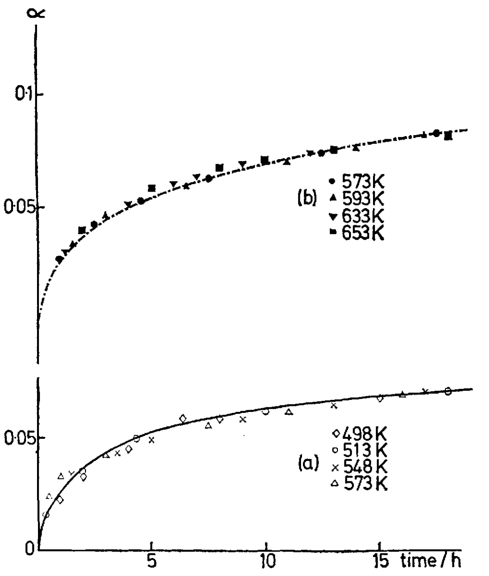

FIGURE. Superimposition of the $\alpha(t)$ reduction curves after a $[\alpha(t) \rightarrow k\alpha(t)]$ transformation for (a) Ni^{2+} zeolite; (b) Ni^{2+} substituted silica–magnesia gel.

The $\alpha = f(t)$ curves which express the extent of the reduction in terms of time are superimposable after a $[\alpha(t) \rightarrow k\alpha(t)]$ transformation (where k is a constant) (Figure). It can therefore be considered that, in this temperature and pressure range, there is only one rate-limiting process.[5] The activation energy is 117 ± 13 kJ mol^{-1} and the rate no longer depends on the hydrogen pressure above 6·5 kN m^{-2}. The $\alpha(t)$ curves can be transformed into straight lines of the form $F_D = kt$ [where $F_D = \frac{3}{(1-\alpha)^{1/3}} + \log(1-\alpha) - 3$]. F_D describes a mechanism of diffusion in a sphere in which the steady state approximation for Ni^{2+} and H^+ ions is made and a variable diffusion coefficient $D = D_0(1-\alpha)$ is assumed.[6]

The Ni^{2+} substituted silica–magnesia gel was prepared as described previously[7] and the overall composition corresponds to the formula $(SiO_2)_1\,(MgO)_{0\cdot16}\,(NiO)_{0\cdot14}\,(OH)_n$. Electron microscopic inspection shows it to consist of ill-defined clusters.

The gel reduction was studied in the ranges 523—653 K and 1·3—13 kN m^{-2}. The reaction is slow and the $\alpha = f(t)$ curves are superimposable after a $[\alpha(t) \rightarrow k\alpha(t)]$ transformation (Figure). The activation energy is 172 ± 20 kJ mole^{-1} and the rate varies with hydrogen pressure up to 13 kN m^{-2}. The $\alpha(t)$ curves can be transformed into almost parallel lines by a logarithmic equation (2). In the

$$\log[-\log(1-\alpha)] = f(\log t) \qquad (2)$$

absence of a well-defined geometry for the hydrogel it is not possible to determine precisely the regulating process; it is nevertheless highly probable that the rate is limited by germination. The formation of metal particles from such a solid requires a high energy and the presence of the very electropositive Mg^{2+} cation is likely to inhibit the reduction of neighbouring Ni^{2+} ions.[8]

These results indicate that the mechanism of Ni^{2+} reduction depends greatly on the environment of the cation and on the way in which it is bonded to the host lattice.

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