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Change of Hydrogenation Activity of Zinc Oxide by X-Ray Irradiation

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In preceding work (*1–3*) we have studied the influence of high-energy corpuscular irradiation on the hydrogenation activity of copper, nickel, and palladium and on the ortho–para hydrogen conversion by alumina. In all these cases a decrease of catalytic activity by preceding irradiation and a regeneration by hydrogen treatment have been found. It was concluded that in the case of metals, hydride hydrogen in covalent bonds and in the case of alumina, paramagnetic metal atoms are the active centers. In the present investigation a new example is added, the hydrogenation on zinc oxide and its modification by X-rays.

The apparatus is very similar to that described by Ritz, Schwab, and Sizmann (*2*). A hydrogen-ethylene mixture is circulated over the catalyst by a pump and the progress of reaction is followed manometrically. An aluminum disk (thickness 0.05 mm) bearing the catalyst (500 mg of ZnO powder in a layer of 0.23 mm) is situated on the bottom (thickness 1.4 mm) of the glass reaction vessel. It is irradiated between the measurements from below by a tungsten therapy tube with a voltage of 90 kV.

Special measurements showed that with an average absorption coefficient of 43 cm^{-1} (7.5 $\text{cm}^2\ \text{g}^{-1}$) a dose of 4235 R/hr is absorbed by ZnO, corresponding to 0.185×10^6 erg/hr. With an average frequency of $10^{19}\ \text{sec}^{-1}$ one formula unit of ZnO absorbs only about 7×10^{-10} einstein/hr. In the experiments a stoichiometric mixture of hydrogen purified over Cr^{II} and chromatographically pure ethylene of an initial total presure of 96 torr was used. Mercury vapor was excluded. The catalyst was a powder prepared from precipitated zinc oxalate at 400°. Since the deactivation–regeneration cycles are not fully reversible the catalyst had to be changed frequently.

The kinetics of the reaction is, in good approximation, of first order. From the general kinetic equation

$$\frac{dx}{dt} = k \frac{b_h b_e [H_2][C_2H_4]}{1 + b_h[H_2] + b_e[C_2H_4]}$$

this order follows under the condition fulfilled at not too high temperatures

$$1 + b_h[H_2] \ll b_e[C_2H_4]$$

Therefore it is sufficient to indicate only half-life times, as is done in Table 1.

At both the temperatures of the experiment with irradiation of 75 hr, i.e., with 5×10^{-8} einstein per formula unit, the half-life time has been increased by 70% and the catalytic activity has been decreased to 60%. The activation energy has remained practically identical.

In order to achieve activity the unirradiated catalysts must be preheated several hours to 400° in high vacuum (10^{-5} torr) or in hydrogen. It is interesting to note that the same treatment is also able to restore the part of the activity destroyed by irradiation, as shown in Table 2.

It is remarkable in this table that also a treatment with oxygen results in a considerable regeneration.

TABLE 1

Activation Energies and Irradiation Influence

Irradiation (hr)	Temperature (°C)	Half-life time (min)	Activation energy (kcal/mole)
0	105°	42	14
0	120°	21	
75	105°	70	13
75	120°	36	

TABLE 2

Regeneration

Temperature (°C)	Irradiation (hr)	Activation	Half-life time (min)
105°	0	400°, H_2	41.3
105°	75	—	70.2
105°	75	400°, O_2	45.3
105°	75	400°, H_2, 16 hr	50.0
105°	75	400°, vac	43.8

Discussion

The decrease of activity by X-ray irradiation with constant activation energy shows that the number but not the specific activity of the active centers is diminished by irradiation. The fact that this effect already occurs at doses as low as the applied ones proves that the effect is one of ionization by secondary electrons rather than a primary quantum effect. Finally, the fact that heating in vacuum or in hydrogen regenerates the activity suggests that the active centers are to be identified with interlattice zinc, which normally exists as Zn^+ and which increases in abundance by thermal dissociation in vacuum or by reduction in hydrogen (*4*). By ionizing impacts these will be converted to Zn^{2+} and thus become inactive. This is, however, in contradiction to the regeneration effect of oxygen. It is, however, to be taken into account that this effect might be an apparent one since after the oxygen activation the sample must be evacuated and the reducing reaction mixture must be added.

References

1. Schwab, G.-M., Sizmann, R., and Todo, N., *Z. Naturforsch.* **16a**, 985 (1961).

2. Ritz, J., Schwab, G.-M., and Sizmann, R., *Z. Phys. Chem.* **39**, 45 (1963).

3. Schwab, G.-M., and Konrad, A., *J. Catalysis* **3**, 274 (1964).

4. Eischens, R. P., Pliskin, W. A., and Low, M. J. D., *J. Catalysis* **1**, 180 (1962).