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HYDROGEN SPILLOVER EFFECTS IN THE REDUCTION OF IRON OXIDE

R. P. VISWANATH, B. VISWANATHAN and M. V. C. SASTRI

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

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Freshly formed metal accelerates the rate of reduction of ferric oxide in the presence of water vapour. This effect is explained on the basis of the spillover of hydrogen from the metal sites to the oxide phase through "portholes" of water.

Свеже образующийся металл увеличивает скорость восстановления окиси железа в присутствии водяного пара. Этот эффект объясняется на основе вытечки водорода с металла на окисную фазу через ,,проходные дырки'' воды.

INTRODUCTION

The mechanism of the reduction of iron oxide by gaseous reductants, like hydrogen and carbon monoxide, has been the subject of numerous investigations in recent years /1, 2/. Interestingly enough, it has been reported by several authors that the products of this reduction, namely, metallic iron and water vapour or carbon dioxide, have an accelerating influence on the rate of reduction, contrary to expectations based on thermodynamic considerations. For example, Pokhvisnev and Abdelrassul /3/ have reported the catalytic action of metallic iron in the reduction of iron oxide by hydrogen. Benson et al. /4/ have shown that in the presence of platinum black, water vapour lowers the threshold reduction temperatures of metallic oxides. Sancier and Inami /5/ have also recorded similar observations in the case of the reduction of iron oxide.

As part of a wider study on the kinetics and mechanism of the reduction of iron oxide by hydrogen, the factors influencing the catalytic effects of water vapour and metals on the reduction of iron oxides have been investigated.

The essence of the results obtained is reported in the present communication.

EXPERIMENTAL

Essentially, four forms of iron oxide have been used in the present study:

1. Pure α-Fe_2O_3 prepared by thermal decomposition of pure (Baker Analysed) ferric nitrate,
2. α-Fe_2O_3 doped with 1% Li_2O or MgO prepared by heating the mixed oxides at 850 °C for 5 hrs,
3. Haematite ore, and
4. Magnetite ore.

Ultrapure hydrogen from an electrolytic generator provided with a Pd–Ag alloy diffuser cathode ("Elhygen" Milton Roy Co., St. Petersburg, Fla., USA) was used for the reduction of these oxides. The mixing of water vapour with the hydrogen stream was controlled by means of a constant pressure feeding system based on the regulated displacement of water by mercury.

The oxide ($\sim$200 mg) was placed in a quartz bucket suspended from a sensitive, calibrated quartz spring (sensitivity = 2 mg/mm), inside a Pyrex tube with a diameter of 25 mm. First, the oxide was heated slowly in a flow of nitrogen to the selected reduction temperature (465, 485, 505 °C) and, after temperature stabilization, the gas was changed to hydrogen (either pure or with added water vapour).

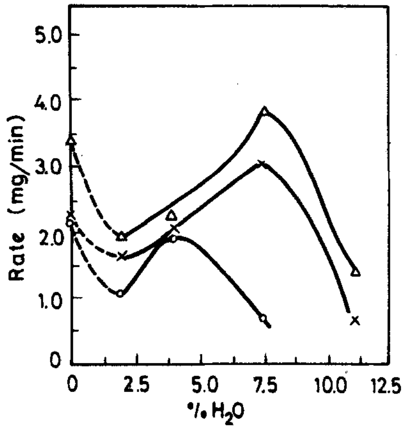

Fig. 1. Effect of water vapour on the rate of reduction of pure α-Fe_2O_3: ○ – 465 °C, × – 485 °C and △ – 505 °C.

RESULTS AND DISCUSSION

The variation of the rate of reduction of pure α-Fe_2O_3 with water vapour in the hydrogen feed is shown in Fig. 1, The corresponding data for the reduction of Li- and Mg-doped ferric oxide, and of haematite and magnetite ores at 505 °C are shown in Fig. 2. The marked difference between the trends for the two sets of rate curves is self-evident. The curves for the reduction of the doped Fe_2O_3 samples and of the ores show a monotonous decrease in the rate with increasing water content, in conformity with the thermodynamic expectations. In the case of pure ferric oxide, however, the rate increases between 2 and 7.5 v/v% of water vapour, but shows the normal decrease in rate with further increase in water content.

In order to elucidate the effect of water vapour, the reduction of pure Fe_2O_3 in the presence and absence of freshly reduced metal has been studied at 255 °C

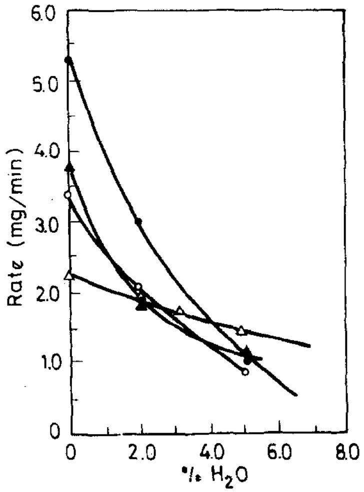

Fig. 2. Effect of water vapour on the rate of reduction of iron oxides at 505 °C: ○ - Fe_2O_3 ore, △ - Fe_3O_4 ore, ● - Fe_2O_3 doped with 1% MgO and ▲ - Fe_2O_3 doped with 1% Li_2O

with and without a liquid nitrogen trap attached to the system. The results obtained are shown in Fig. 3. It is seen that the reduction does not proceed beyond the stage of Fe_3O_4 when all the water vapour is removed in a liquid nitrogen trap, while in the presence of metal powder and water vapour (i.e. experiments without the liquid nitrogen trap) the reduction goes to completion. This indicates that for complete reduction of Fe_2O_3 at low temperatures, both the metal and water vapour are necessary. It can be seen from Fig. 4 that "fresh" iron and nickel powders are nearly equally effective catalysts for the reduction of ferric oxide, however, both metals lose this activity almost completely upon "aging".

The relative lowering of the reduction temperature in the presence of pure metal powder and water vapour, and the increased rate of reduction in the

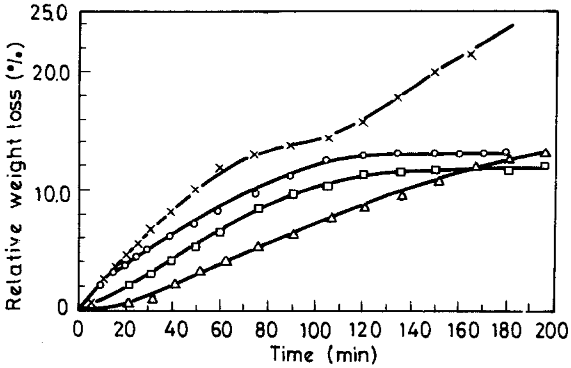

Fig. 3. Reduction of pure Fe_2O_3 with dry hydrogen (in the feed) at 255 °C: without a liquid nitrogen trap, ○ – pure Fe_2O_3, × – Fe_2O_3 in the presence of fresh iron powder, with a liquid nitrogen trap, □ – pure Fe_2O_3 and △ – Fe_2O_3 in the presence of fresh iron powder

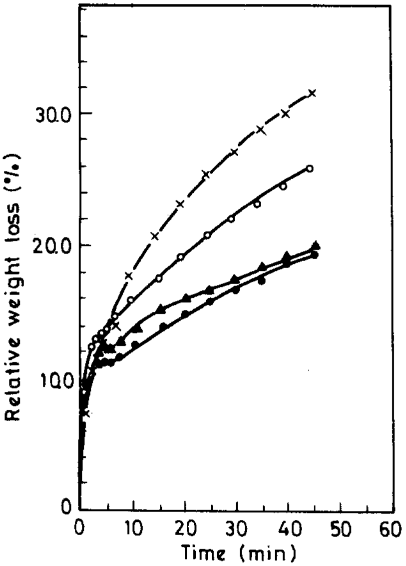

Fig. 4. Reduction of pure Fe_2O_3 in the presence of metals, with humid hydrogen at 395 °C: ● – pure Fe_2O_3, ▲ – Fe_2O_3 in the presence of aged iron powder, ○ – Fe_2O_3 in the presence of fresh nickel powder and × – Fe_2O_3 in the presence of fresh iron powder.

presence of freshly reduced metal powders, show that hydrogen is efficiently transported to the oxide phase in a reactive form when both metal and water vapour are present.

Boudart et al. /6/ have made a similar observation with tungstic oxide, which could be easily reduced in the presence of platinum black and water vapour. According to the authors, water vapour is inserted between the metal and the oxide and serves as a "porthole" for the transport of the active hydrogen species available on the metal surface owing to dissociative adsorption. This type of hydrogen spillover could account for a higher rate of reduction. The observation that the presence of reshly reduced iron or nickel accelerates the reduction at high temperatures as well as increases the extent of reduction at lower temperatures (255 °C) in the presence of water lends support to the hydrogen spillover mechanism.

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