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Investigation of the Kinetics of Reduction of Nickel Oxide and Nickel Aluminate by Hydrogen

The reduction kinetics of NiO and NiAl₂O₄ in hydrogen have been studied by thermogravimetric measurements. In the case of NiO, the experiments were restricted to the temperature range 564 to 782 K due to the high rate of the reaction whereas, in the case of the aluminate, due to the sluggishness of the reduction, a higher temperature range of 1287 to 1537 K was employed. The activation energy for the reduction of NiO was evaluated to be 18 kJ/mol while the corresponding value for the aluminate was 134 kJ/mol. The difference in the activation energies is discussed in terms of the bond strengths. The morphology of the reduced specimens shows that the method is promising in the preparation of alumina-based nickel catalysts.

1 Introduction

In the production of metal-matrix composite materials, the reduction of complex oxides is an important process route. The Department of Theoretical Metallurgy is currently involved in a project concerning the investigation of the fundamentals of these processes. One of the reactions which is of interest in the production of alumina-impregnated Ni-based alloys is the reduction of the complex oxides of nickel and aluminum. The present work aims at a study of the kinetics of reduction of NiAl₂O₄ by hydrogen. These studies are relevant to the production of Ni-based catalysts as well. To the knowledge of the present authors, no previous work has been carried out on the hydrogen reduction of NiAl₂O₄, whereas the reduction of NiO by hydrogen has been investigated by several groups earlier [1 to 4]. From a theoretical point of view, these studies are interesting in the sense that the difference in the activation energies for the reduction of NiO and NiAl2O4 under identical experimental conditions would reveal the effect of the bond energies in the Al₂O₄-complex ion on the activation energy for the reduction of this oxide. In this respect, the present work is part of a series of reduction of metal oxide systems [5 to 7]. The reduction studies were carried out in the present work using a thermogravimetric method. The sample was held in thin shallow beds so that the reductant gas has access to all the particles in the sample and mass-transfer effects are kept to a minimum.

2 Experimental

2.1 Materials

Anhydrous aluminum oxide powder (chloride < 0.02 wt.%, sulphate < 0.05 wt.%, arsenic < 0.0005 wt.%, iron < 0.02 wt.%) and oxygen-rich nickel oxide powder (black, pro analysi) were obtained from E. Merck, Darmstadt, Germany. To remove excess oxygen in the nickel oxide, the powder was heated to 1273 K for 1 h and cooled in an argon atmosphere [8]. The alumina powder was calcined at 1273 K for 12 h before use. In order to prepare the nickel aluminate, equimolar amounts of NiO and Al₂O₃ powders were mixed thoroughly in an agate mortar. The mixture was held in an alumina crucible and sintered in air at 1873 K for 4 days. X-ray diffraction analysis showed that NiAl₂O₄ was the only oxide present in the sintered sample, indicating that the reaction was complete. The NiAl₂O₄ and NiO powders obtained were ground in an agate mortar and preserved in a desiccator before being used in the reduction experiments. The hydrogen gas (SR grade) used for reduction and the argon gas (maximum of 2 ppm impurity) used during the prereduction period were supplied by AGA Gas, Stockholm.

2.2 Apparatus and Procedure

The reduction studies of NiO as well as NiAl₂O₄ were carried out in a SETARAM, TGA 92 thermogravimetric unit, which has a detection limit of 1 µg and is fully controlled by an IBM PC through a CS92 controller. A detailed description of this apparatus has been given in an earlier publication [5].

A shallow alumina crucible of 8 mm inner diameter and 2 mm in height was employed as the container to hold the oxide powder bed. The crucible was hung by a Pt suspension wire in the thermobalance and introduced into the alumina reaction tube (16 mm inner diameter), which, in turn, was placed in a graphite furnace. The powder bed was positioned in the even temperature zone of the furnace. Before heating, the reaction tube was evacuated for 15 min down to a vacuum of 10 Pa. The tube was then filled with argon gas through the carrier gas inlet connected to the balance chamber. The sample was then heated up in a constant argon flow of 0.05 l/min up to the reaction temperature. No weight change was observed during the heating period. After the temperature was stabilized, the reaction was started by stopping the argon gas and introducing hydrogen gas through an auxiliary gas inlet on the upper part of the reaction tube. A constant hydrogen flow rate of 0.6 l/min was then maintained during the whole course of the reduction. Preliminary experiments with different flow rates of H₂ showed that this flow rate was high enough to

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