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The effect of water on the reduction of nickel/alumina catalysts

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The crucial role of water in the reduction of calcined nickel/alumina catalysts is demonstrated. A fraction of nickel oxide in the catalysts is reduced as NiO powder in the absence of water vapour, and as a nickel aluminate in the presence of water. A much higher dispersion of nickel is attained when the reduction is carried out at low concentration of water vapour.

Keywords: Effect of water; reduction; nickel/alumina catalysts

1. Introduction

The reduction of NiO/Al_2O_3 precursors to Ni/Al_2O_3 catalysts with hydrogen has been the subject of numerous studies, and significant results have been obtained with the aid of the temperature-programmed reduction (TPR) method [1–4]. The TPR profiles recorded for the precursors consist of two hydrogen consumption peaks centered at about 500 and 700 K. The peaks were ascribed to reduction of "free" and "fixed" forms of nickel oxide, respectively; the appearance of the fixed form of the oxide was connected with the formation of nonstoichiometric nickel aluminate [1].

The reduction of NiO/Al_2O_3 precursors is suppressed by water; thus it was found that the TPR peaks of the free and fixed nickel oxide shifted to higher temperatures by 60 and 30 K, respectively, when the reduction was performed with a hydrogen stream saturated at 273 K with water vapour [1]. In this communication further TPR studies of the effect of water on the reduction of the specimens are presented. These demonstrate the crucial role of water vapour in the reaction and provide a new insight into the morphology of NiO/Al_2O_3 precursors.

2. Experimental

The examinations were carried out in a flow system [1] equipped with a gradientless microreactor [5]. Prior to TPR measurement the samples were dried in flowing helium (40 cm^3/min, 623 K, 0.5 h). The reduction was carried out in an 80% $H_2 + Ar$ mixture (40 cm^3/min) under a linearly increasing temperature (8.3 K/min) from 293 to 973 K. The gas leaving the reactor was dried in a 195 K trap, and the change in H_2 concentration in the mixture was measured by means of thermal conductivity.

The reduction of 12% and 88% NiO/Al_2O_3 precursors, prepared from chemically pure reactants, was examined. The low loaded specimen was obtained by impregnation of alumina (calcined at 973 K, surface area 111 m^2/g, and grain size 0.15–0.38 mm) with aqueous solution of $Ni(NO_3)_2$. After the impregnation the material was dried and calcined (673 K, 2 h) in air.

The high loaded precursor was prepared by coprecipitation from $Ni(NO_3)_2$ and $NaAlO_2$ aqueous solutions. The precipitate was washed, then dried and calcined as with the low-NiO specimen. The material was in the form of a fine powder.

Examinations of NiO/Al_2O_3 precursors were complemented by parallel tests of NiO powder: the oxide was prepared by a precipitation method from ultra-pure $Ni(NO_3)_2$ and NH_4HCO_3 reactants. The precipitate was washed, dried, and calcined, as for the high-NiO specimen.

Two series of TPR experiments were carried out: (i) for NiO/Al_2O_3 precursors alone, at 10^3–10^4 ppm of water in the $H_2 + Ar$ stream, and (ii) for NiO/Al_2O_3-alumina mechanical mixtures, at a minimal concentration of water in the stream because the alumina sorbed water produced during the reduction, and thereby lowered the H_2O concentration below 1 ppm.

The NiO/Al_2O_3-alumina mixtures were prepared in-situ in the reactor. Weighed portions of NiO/Al_2O_3 and alumina (the material used for preparation of the low-NiO specimen) were placed in separate positions in the reactor, dried in a He stream (40 cm^3/min, 0.5 h; NiO/Al_2O_3 at 623 K, and alumina at 873 K) and, after cooling, were mixed by shaking the reactor.

3. Results and discussion

Fig. 1 shows the main results of this work. TPR profiles recorded for NiO/Al_2O_3 precursors alone (solid lines) consist of a single hydrogen consumption peak at a temperature much higher than that for NiO powder. According to the previous studies [1–4] this indicates that nickel oxide appears in the precursors in the fixed form only, i.e. as a nickel aluminate type compound and/or a solid covered by tight nickel aluminate layer. This interpretation, acceptable for the low-NiO specimen, seems dubious for the high-NiO specimen.

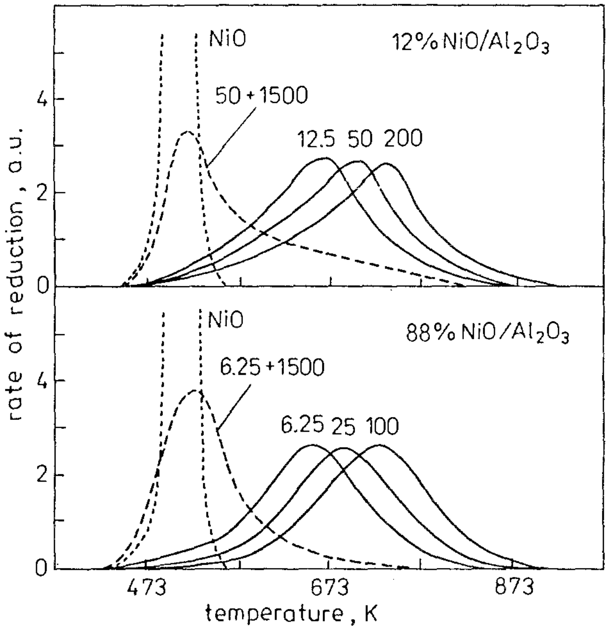

Fig. 1. TPR tests of NiO/Al_2O_3 precursors; - - - - - - NiO/Al_2O_3 alone. The numbers on the curves denote sample weight in mg; ——— NiO/Al_2O_3-alumina mixtures. Numbers on curves denote weight of NiO/Al_2O_3 and alumina portions in mg; ······ NiO powder, sample weight, 6 mg.

The profiles recorded for NiO/Al_2O_3 alone (fig. 1) steadily shift to lower temperatures when the sample weight is decreased, that is when the concentration of water in the gas phase decreases. This suggests that in the absence of water the reduction should proceed at still lower temperatures, and this prompted us to undertake TPR examinations of the NiO/Al_2O_3-alumina mixtures. The examinations were preceded by supplementary tests which showed that the alumina effectively sorbed water produced during the programmed reduction, and was inert to H_2 + Ar mixtures.

Preliminary TPR examination of the NiO/Al_2O_3-alumina mixtures revealed that admixed alumina considerably affects reduction of NiO/Al_2O_3: the TPR profile maximum appears at significantly lower temperature and its shape is different. Complementary examination showed that the effect gradually increases with the amount and the extent of grinding of the alumina. Fig. 1 presents the TPR profiles recorded in the experiments in which the largest amount of thoroughly ground alumina was admixed. The profiles consist of a peak centred at a temperature characteristic of the reduction of NiO powder, and a tail at higher temperatures. The appearance of the peak indicates that pure nickel oxide still exists in the precursors. The oxide is reduced as free nickel oxide in the absence of water, and as fixed nickel oxide in the presence of water. (Hereafter that oxide is referred to as "para-fixed" nickel oxide.) At the same time it is supposed that the tail is related to reduction of nickel oxide fixed with alumina, i.e. a nickel aluminate type compound and/or a solid covered by a coherent layer of nickel aluminate [1]. This oxide is reduced at higher temperatures both in the absence and in the presence of water, and its fraction is larger for the precursor of higher alumina content (fig. 1).

The effect of water on the reduction of para-fixed nickel oxide is large in comparison with the effect reported for NiO powder [1], implying that the effect is brought about by a collective action of alumina and water on the oxide.

Complementary TPR tests showed that ground mixture of NiO and Al_2O_3 powders, 12% NiO + Al_2O_3, is reduced just as NiO powder, indicating that the components hardly interact and produce the fixed form of nickel oxide when they are combined by a mechanical method. It also implies that para-fixed nickel oxide is in intimate contact with alumina in NiO/Al_2O_3 precursors which affords possibilities for their interaction during a TPR test. It seems that in the presence of water para-fixed nickel oxide and alumina interact producing a surface nickel aluminate that retards reduction of the oxide.

Under standard TPR examinations of NiO/Al_2O_3 precursors, that is carried out without an extra removal of water, the concentration of water vapour in the gas phase is about 10^3–10^4 ppm, and para-fixed nickel oxide interacts with nearby alumina. In view of this study, the following interpretation of the standard TPR tests of NiO/Al_2O_3 precursors seems justified:

(i) the peak at 500 K indicates the presence of nickel oxide not in contact with alumina, and

(ii) the peak at 700 K the presence of nickel aluminate type compounds and/or nickel oxide in intimate contact with alumina.

The crucial role of water in the reduction of NiO/Al_2O_3 precursors suggests a significant effect of water on the morphology of Ni/Al_2O_3 catalysts. Our preliminary examinations supported this hypothesis, e.g. it was found that the catalysts obtained from 12% NiO/Al_2O_3 precursor at the highest and at a minimal concentration of water vapour (see fig. 1) had nickel surface area 10.7 and 18.1 m^2/g_{cat}, respectively.

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