Catalysis Letters 20 (1993) 299–303

Reduction of nickel oxide on alpha alumina: coalescence of nickel to metallic crystallites

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Received 15 March 1993; accepted 3 May 1993

Reduction of alpha-alumina-supported nickel oxide was studied with hydrogen consumption, magnetization and XRD measurements. Rupture of Ni–O bonds at 270–350°C is much faster than nucleation of metallic nickel and precedes growth into crystallites. Water vapor and low hydrogen flows retard both processes. At higher temperatures, growth is more rapid than Ni–O bond rupture.

Keywords: Nickel catalysts; reduction; water inhibition

1. Introduction

Reduction of metal oxides to finely divided metallic crystallites is the final activation step for many catalysts. It is usually achieved by reaction with hydrogen at moderately elevated temperatures, either in situ or prior to loading into the operating plant. The process involves reduction of metal cations and loss of water vapor, followed by nucleation of the metal atoms into clusters and coalescence to crystallites of comparable size to those of the original oxide. Reduction kinetics are usually measured by following hydrogen consumption, production of water, or sample weight loss, and the growth of metallic crystallites has not been separated from chemical reduction.

It is necessary with some oxides to limit reduction exothermicity to prevent thermal runaway. Although reduction can be inhibited by water vapor, the reaction is

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not controlled by using excess steam but rather with low hydrogen concentrations in a high flow of inert gas to remove the heat of reaction. Concomitantly, a low level of water is achieved, which is desirable since water vapor is believed to cause metal crystallites to sinter, leading to low metal surface areas and low catalyst activities. For example, considerable attention is given to controlling water levels during reduction of copper-based catalysts, which are particularly sensitive to water-induced sintering during reduction [1]. Similar care is taken when reducing iron ammonia synthesis catalysts to ensure sintering is minimized [2,3].

In the light of the normally accepted behavior of metal oxide-based catalysts during reduction, we were surprised to discover that under some conditions it is possible to separate the chemical reduction of nickel oxide supported on alpha alumina and the growth of metallic crystallites. We also obtained tentative evidence that the early stage of nickel coalescence is inhibited by water vapor. We report our preliminary observations in this letter, and detailed results of our on-going experimental work will be given in a subsequent full paper [4].

2. Experimental

A sample of nickel oxide (15.6 wt%) on alpha alumina (1.0 $m^2 g^{-1}$) was prepared by multiple impregnation of nickel nitrate solution and calcination at 650°C. X-ray diffraction line broadening (Siemens 5000) indicated the nickel oxide crystallites were about 30 nm (cube edge) in size. Chemical reduction of the Ni–O bond was monitored for 0.1 g samples by measuring hydrogen consumed from the reducing gas stream (20% hydrogen in argon) using a thermal conductivity cell. Magnetization measurements of the amount of superparamagnetic nickel crystallites generated were made with a magnetometer previously described [5]. These data were supplemented by X-ray diffraction to determine the amount and size of nickel oxide and metallic nickel in the catalyst at different degrees of reduction. The effect of water was determined by passing the reducing gas through a saturator at a controlled temperature.

3. Results and discussion

Preliminary temperature programmed reduction experiments showed stoichiometric reduction of nickel oxide on alpha alumina occurred between 300 and 460°C rather than 285 to 366°C for a bulk nickel oxide with the same thermal history. This increase in temperature for reduction is believed due to incorporation of aluminium ions from the support into the surface of the nickel oxide during impregnation, as suggested by Mieth and Schwarz [6]. Richardson et al. have shown that coprecipitation of small amounts of aluminium ions with bulk NiO results in more difficult reduction [5].

Isothermal hydrogen consumption with both samples followed a shrinking core model [7] with a first order dependence on hydrogen. Magnetic measurements showed an induction period, where presumably nickel atoms liberated by reduction nucleate into small clusters, followed by a region where these clusters coalesce into larger crystallites. Fig. 1 compares the results of these two types of measurement on the supported NiO at 270°C, and shows chemical reduction is complete before crystallite growth begins. The curve for hydrogen consumption fits best the shrinking core model and implies chemical reduction is limited to about 39% of the NiO. This number increases with both increasing flow rate and temperature. For example, reduction for one hour at 270°C and 200 cm^3 min^{-1} resulted in 65% NiO reduction. However, X-ray diffraction could only account for 32% of NiO converted to nickel crystallites large enough to be detected by this technique (i.e. >1 nm). Presumably, the remaining 33% of reduced NiO exists as nickel clusters that are too small for X-ray diffraction, yet large enough (i.e. >20 atoms) for magnetic detection. The size of the nickel crystallites from X-ray diffraction line broadening was 20 nm.

Higher hydrogen flows also increased crystallite growth. We agree with earlier researchers who believed this flow effect is due to retention of water molecules on the surface [8,9]. However, our measurements with 3.2×10^{-2} atm of added water indicate the inhibiting effect of water on chemical reduction is not as significant as the effect on nucleation, a fact not previously appreciated.

Experiments with bulk nickel oxide show similar results. These are demonstrated in fig. 2 for chemical reduction of bulk NiO at different flow rates and crystallite growth at 220°C under "dry" and "wet" conditions. Chemical reduction is complete at 100% for all flow rates. Comparing curves (c) and (d), both at high flow rates but with added water in (d), the effect on the induction period during which nucleation occurs is apparent. Curve (b) for chemical reduction corresponds to an average "internal" water vapor pressure of 2.7×10^{-2} atm, emphasizing that the principal effect of water is to retard nucleation. It was not possible to check this

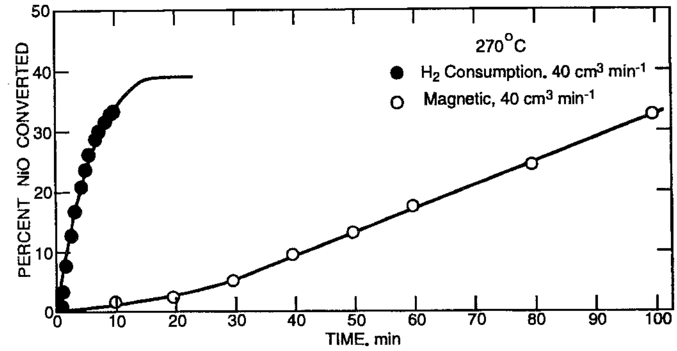

Fig. 1. Comparison of hydrogen consumption and nickel growth of alpha-alumina-supported nickel oxide during reduction at 270°C and 40 cm^3 min^{-1}.

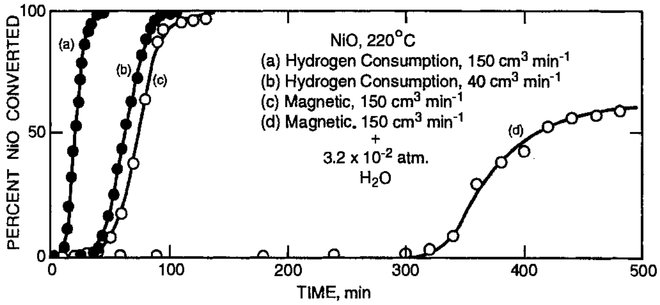

Fig. 2. Effect of flow rate and water on the chemical reduction, nickel nucleation and crystallite growth for bulk NiO reduction at 220°C.

with added water because of decreased sensitivity of the thermal conductivity detector. Magnetic measurements at 40 cm^3 min^{-1} show no detectable metallic nickel over the same time period. Once started, crystallite growth is fairly rapid, although not as fast as in curve (c) without water. It is not clear whether this slight decrease in growth rate results from inhibition of coalescence by water or merely the absence of sufficient precursor clusters.

At higher temperatures, the differences between the rates of chemical reduction, nucleation and growth become less. Chemical reduction dominates the process above about 350°C, since our measurements indicate the temperature dependence of chemical reduction is less than for nucleation and growth. For reforming catalysts consisting of nickel oxide on alpha alumina, normal industrial temperature conditions for reduction are above 450°C, sufficiently high that water has no retarding effect. However, this may not be true for catalysts containing promoters that may also enhance the adsorption of water.

4. Conclusions

In summary, our results indicate chemical reduction of NiO bonds is a rapid process for nickel oxide supported on alpha alumina, and subsequent coalescence into nickel crystallites is much slower at lower temperatures. Water inhibits both chemical reduction and nucleation of nickel clusters but appears to have a limited effect on crystallite growth. These effects could be important in the reduction of some steam reforming catalysts and other nickel catalyst systems, and they may well be general and apply to other catalysts.

Acknowledgement

We are grateful to ICI Katalco (Billingham, UK) for financial support to J. Kennerley and W.M. Sengelow for catalyst preparations, and to M. Lei, B. Turk, K. Forster and M. Coello for experimental measurements.

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