

Non-isothermal reduction behavior of NiO in undiluted Ar and CH₄ atmospheres

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ABSTRACT

The present study aims to understand non-isothermal reduction behavior of nanocrystalline NiO powder in undiluted CH₄ and Ar atmospheres by thermal analysis, mass measurement and XRD techniques. Low Ni content observed in the oxide powder was attributed to the moisture and OH groups which were removed upon heating to 625 K above which reduction of NiO to Ni took place in both atmospheres. Under Ar flow, the oxide powder was slightly reduced to Ni as temperature increased to 1300 K. In CH₄ atmosphere, the oxide reduction was followed by C deposition with increasing temperature. Complete reduction of NiO to Ni was attained at ~1000 K owing to H₂ formed by CH₄ pyrolysis. It was observed that nickel particles were sintered into pellets with a size of ~2 μm at 1100 K under CH₄ flow. At 1200 and 1300 K, Ni had finer particles with sizes <200 nm and gained mass in consequence of C deposition.

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1. Introduction

NiO is an intermediate product extracted from nickel ores (e.g. lateritic ore) by various hydro/pyrometallurgical processes. It has been used for producing metallic Ni, which is an alloying element in metallurgical products (Evans and Koo, 1979). In addition, NiO has been exploited as a catalyst precursor for steam reforming of hydrocarbons to produce hydrogen, ammonia and methanol (Richardson et al., 1994) and for the synthesis of carbon nanotubes (CNTs) from hydrocarbons (Kukovec et al., 2000).

A comprehensive review on the reduction of NiO by gaseous agents (H₂, CO) is provided by Evans and Koo (1979). They reported that reduction of NiO by hydrogen or carbon monoxide can be considered irreversible on the thermodynamic ground. For example reduction by hydrogen is slightly exothermic (−3.14 kcal/g·mol at 1000 K) and reduction by carbon monoxide is more exothermic (−11.5 kcal/g·mol at 1000 K). On the kinetic basis, it was reported that extent of NiO reduction by hydrogen decreased with increasing temperature from 644 K to 1198 K owing to sintering of the Ni shell product (which is impervious to hydrogen) surrounding the remaining oxide (Szekely and Evans, 1971). Recently, methane (a main component of natural gas) has been used as alternative reducing agent for metal oxides because it is relatively cheap and abundant. Isothermal reduction of NiO was studied in the temperature range of 873–1023 K using methane diluted by helium

(Alizadeh et al., 2007) or Ar (Rashidi et al., 2013). The methane-oxide reduction reaction was described as follows: the reaction starts with the methane adsorption on the active site of the oxide surface and then proceeds with methane decomposition (Alizadeh et al., 2007). They reported no carbon formation on the reduced pellets.

The present work was carried out because little is known about non-isothermal behavior of NiO powder in undiluted CH₄ and Ar atmospheres. It should be emphasized that non-isothermal condition is usually encountered in metallurgical industry such as in moving bed reactor. Furthermore, neutral gases such as Ar are often allowed to flow through the reactor systems for purging air prior to introducing reactive gas. Hence, investigation of non-isothermal response of NiO in undiluted CH₄ and Ar atmospheres is of practical importance. The present study reports and discusses findings on this issue at temperatures up to 1300 K.

2. Experimental procedures

The experimental synthesis set-up used for the present study consists of a hot-wall furnace with SiC heating elements, a quartz tube (20 mm in diameter, 500 mm in length) and gas flowmeters. The chemicals used were NiO powder purchased from Sigma-Aldrich (Cat. No 637130, 99.8% purity based on trace metals analysis), argon (99.999%), methane (99.5%), hydrogen (99.99%) and air. Particle size of the NiO powder used was reported by the producer to be 10–20 nm. An alumina boat was used as a holder for the powder. Its gas entrance side was cut to allow smooth gas flow.

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The oxide powder (~0.3728 g) was heated non-isothermally at a rate of ~25 K/min in flowing undiluted-CH₄ (13.4 cm³/min) and Ar (42.5 cm³/min) atmospheres. The final temperatures were varied up to 1300 K. When the desired temperatures were reached, the products were cooled to the room temperature in Ar (42.5 cm³/min). Stagnant air and H₂ (111 cm³/min) were also used at temperatures in the range of 300–625 K to help characterize the starting oxide powder. Mass measurements before and after the experiments were carried out at room temperature by a calibrated electronic balance (Sartorius BP110S) with a sensitivity of $\pm 10^{-4}$ g in order to determine the extent of the reactions.

DSC, TGA and DTA analyses of the NiO powder used (0.06268 g) were simultaneously done using TA Instruments SDT Q600 equipment with a reference material of α -Al₂O₃ in Ar flow (100 cm³/min) at a heating rate of 10 K/min. Morphologies of the products were examined by a Field Emission Gun Scanning Electron Microscope (FEG-SEM) (JOEL 6335 F). The oxide powder was coated with gold to prevent sample charging. Phase analyses of the powders were carried out by a parafocusing X-ray diffractometer equipped with a Cu radiation tube and a monochromator (Rigaku D/Max-2200/PC). The crystallite size t of the oxide powder was calculated from the (111) diffraction peak using the Scherrer equation $t = 0.9 \lambda / (\beta \cos \theta)$ where λ is the wavelength of Cu K α radiation (0.15418 nm), θ is the diffraction angle and β is the full breadth of the peak at half-maximum intensity which was corrected for the instrumental broadening (~0.2°). Fourier Transform Infrared Spectroscopy (FTIR) (Bruker IFS 66/S) and Transmission Electron Microscopy (TEM) (JEOL 2100) were also used for further characterization of the oxide powder. For FTIR analysis, the NiO powder was placed on the diamond crystal of the ATR-FTIR spectrometer. Particle sizes of some powders were determined from the areas of particles using TEM and FEG-SEM images. Equivalent circular diameters of the measured areas were calculated to describe the mean particle size.

3. Results and discussion

3.1. Non-isothermal behavior

Fig. 1 shows variations of the NiO powder mass with temperature in CH₄ and Ar atmospheres. The results obtained in H₂ and stagnant air atmospheres were also included to better characterize the oxide powder. As can be seen from the figure, mass loss occurs in all atmospheres and at the temperatures studied (except 1200 and 1300 K for CH₄). When H₂

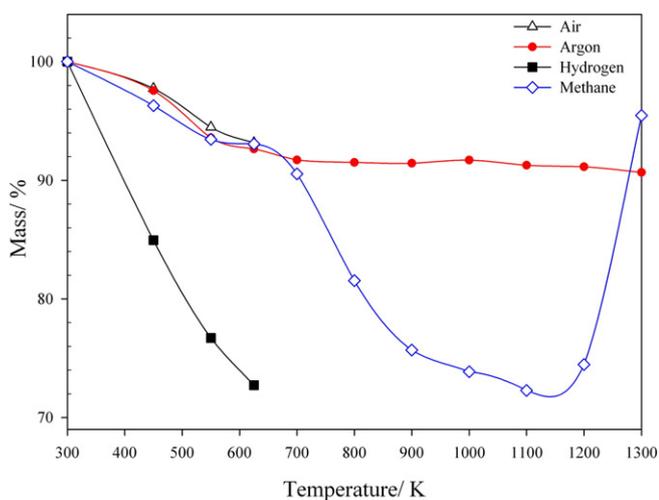


Fig. 1. Effect of temperature on the mass of the starting nickel oxide powder heated in argon and undiluted CH₄ atmospheres. The results obtained under H₂ and stagnant air atmospheres were also included.

is used, mass loss is rapid and NiO is fully reduced to Ni at ~625 K as revealed by XRD pattern (not shown here). The final mass of the powder in H₂ was measured to be ~70.5% which is much lower than the theoretical value 78.6% calculated for the conversion of stoichiometric NiO to Ni. This discrepancy indicates that the starting oxide powder contains moisture.

Mass of the oxide powder heated to 625 K in the other atmospheres (CH₄, Ar and air) was observed to be ~90%. This result indicates that moisture was removed from the oxide powder during heating to ~625 K. It was noted that its color changed from black to green (typical color of NiO). Drying of the starting powder at 373 K indicated that 3% mass loss was due to moisture. The remaining mass is attributable to minor phases which are not detectable by XRD. FTIR analysis of the starting powder was carried out because it may give information about possible minor phases. Fig. 2 shows middle- and far-FTIR spectra of the nickel oxide powder used. The peak at 3535 cm⁻¹ in mid-infrared FTIR spectrum (Fig. 2a) is assigned to the stretching vibration of hydroxyl group (Grgicak et al., 2005). The small sharp bands at ~2160 and 1978 cm⁻¹ are attributed to ATR crystal (diamond) (Zhao et al., 2004) used for the analysis. It is estimated that the band at 1614 cm⁻¹ is ascribed to O–H bending mode of H₂O and Ni(OH)₂ (Pecharrómán and Iglesias, 1994). The bands observed at 1444 and 1367 cm⁻¹ are also attributed to Ni(OH)₂ (Grgicak et al., 2005; Luo et al., 2006). The broad band at 392 cm⁻¹ in the far-infrared spectrum (Fig. 2b) is ascribed to the Ni–O stretching mode (Pecharrómán and Iglesias, 1994). These results may indicate the presence of minor Ni(OH)₂ phase in the NiO powder.

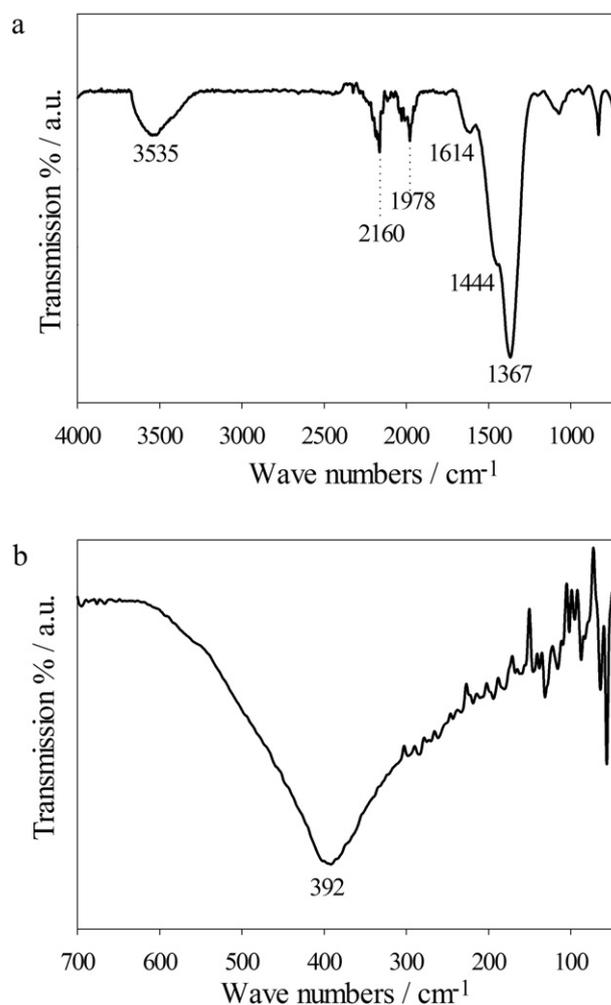


Fig. 2. FTIR spectra of the NiO powder used at a) middle and b) far-IR regions.

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