3.1 Introduction

Metal oxides are used as catalysts for a wide range of reactions as selective oxidation, dehydrogenation and ammoxidation. In such reactions the oxidation-reduction properties of metal oxides are very important in controlling the activity and selectivity. Non stoichiometric oxides are more active than stoichiometric oxides because of the presence of mixed valence states. The metal oxides which can change their oxidation state easily are considered as good materials to be used as selective oxidation catalysts. In many of the applications where metal acts as catalyst, the metal oxide is converted to metal by hydrogen at elevated temperatures. It is highly essential that metal should be in its metallic state (without getting oxidized) to maintain the stability of catalytic reaction. Detailed study on oxidation-reduction properties would be helpful in developing efficient oxidation catalysts.
Oxidation-reduction properties of metal oxides are made use of in their application in chemical looping combustion (CLC) as solid oxygen carriers [1]. Unlike most of other energy generating technologies, CLC can separate the greenhouse gas, CO$_2$, more efficiently. In CLC a solid oxygen carrier is used to transfer the oxygen from air to fuel [2]. The CLC system (Figure 1) consists of two reactors connected together namely an air reactor and fuel reactor.

\[ \text{MO} + \text{fuel} \rightarrow \text{M} + \text{CO}_2 + \text{H}_2\text{O} \]

The exothermic energy of this reaction can be used for power generation. As the exit gas consists of only CO$_2$ and H$_2$O, CO$_2$ can be easily separated by condensation. The reduced metal oxide is transported and oxidized in the air reactor.

\[ \text{M} + \frac{1}{2} \text{O}_2 \rightarrow \text{MO} \]

The whole process can be operated continuously generating power. In CLC, as combustion takes place without flame in two steps, NOx formation is avoided.
The suitable selection of an oxygen carrier is very much important in CLC. Among transition metals, oxides of Fe, Cu and Ni are widely studied for this purpose [3-5]. Recently CaSO₄ was also studied for application in CLC [6]. Pure NiO, NiO/YSZ (yttria stabilized zirconia) and NiO/NiAl₂O₄ are the materials studied for application in CLC [7, 8]. In view of the importance of reduction of NiO, the reduction kinetics of nickel oxide was studied in detail by non isothermal gravimetry and the results are discussed in this chapter.

3.1.1 Reduction mechanism of NiO

Hydrogen reduction of nickel oxide is only slightly exothermic.

\[ \text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \]

The reaction is irreversible, as in the temperature range 0 to 1000 °C the equilibrium constant (Kₚ) has values in the range 10³ to 10². Unlike iron oxide, only two solid phases are involved. These facts make the reaction simple and easy to follow. Kinetics of nickel oxide reduction has always attracted the interest of researchers and technologists and is considered to be a model reaction for the reduction of transition metal oxides. In the first reported (1924) kinetic study of nickel oxide, Benton and Emmett [9] have pointed out the existence of a nucleation period, which depends on nature of sample, temperature of reduction, “autocatalytic effect” of nickel atoms and a reaction interface consisting of nickel oxide and previously reduced nickel. They monitored the reaction by following water formation as indication of extent of reaction. In 1932, Taylor and Starkweather studied NiO reduction by following hydrogen consumption and arrived at similar conclusions of existence of nucleation period and autocatalytic effect [10]. Koga and Harrison [11] suggested that the nucleation (induction) period is the time for generation of nickel atoms on surface of nickel oxide particles. These nickel atoms grow two dimensionally and coalesce. Recent studies by Jankovic et al. [12], also confirm the above mechanism consisting of induction period, autocatalytic effect and overlapping of growing nickel grains. The importance of hydrogen adsorption
sites on the stoichiometric surface of nickel oxide during reduction was pointed out by Fursteanu et al. [13]. The reaction is preceded by an induction period which is due to the scarcity of hydrogen adsorption sites on the stoichiometric surface. The hydrogen adsorption removes the surface oxygen and replacement of the depleted oxygen occurs through Fickian diffusion from the sub surface region. They proposed a mechanism based on the dissociation of hydrogen at a partially reduced nickel surface site, followed by hydroxylation of lattice oxygen and subsequent water condensation and desorption. Later Rodriguez et al. [14] confirmed the role of oxygen vacancies by in situ time-resolved XRD and NEXAFS/EXAFS studies. They also proposed an induction period in which surface defect sites are created which have high efficiency for dissociation of hydrogen. They observed a direct correlation between concentration of vacancies in NiO lattice and the rate of oxide reduction. Lee and Kim [15] reported the synthesis of nanocrystalline nickel by hydrogen reduction of nickel oxide and the related kinetics. Their studies showed that for nanoagglomerate of NiO, the reduction initially starts by the nucleation-growth process and then retards later due to the diffusion controlling process owing to porous structure of the nano agglomerate. No discussion about NiO reduction kinetics would be complete without mentioning the works of Richardson et al. [16]. In situ hot stage X-ray diffraction was used to measure the NiO depletion and Ni formation simultaneously during the reduction reaction. Their studies reveal that, after a small induction period, the kinetics is pseudo-frist-order up to conversion levels of 0.8. The remaining NiO crystallites are covered with the metallic nickel crystallites and the inaccessibility of NiO crystallites retards the rate. The retention of product, H$_2$O, on the surface also reduces the rate.

**Influence of grain size and crystallite size**

The two different models proposed for the reduction of metal oxides are i) nucleation model and the ii) interface controlled model. Grain size of the sample is of much important in the interface controlled model (also called as shrinking core model). As per this model, the Ni–NiO interface moves towards the center of the grain, leaving behind a porous metallic product layer through which H$_2$ diffuses in
and H$_2$O diffuses out. The rate equation will depend on the slowest process. When the chemical reaction at the interface is the slowest step the model is best described by the function

$$x_{\text{NiO}} = 1 - (1 - k_c t)^3$$

where $k_c = (kP_{\text{H}})/R_g$; ($R_g$ is the grain radius). Moriyama and Yamaguchi [17] found that reduction rate constants are inversely proportional to grain size above a diameter of about 10 μm.

In the nucleation model, the induction period is described as the generation of nickel atoms on the outer surface of NiO crystallites. After nucleation, the formed Ni clusters grow two-dimensionally across the surface. At this point the hydrogen dissociation is very fast and the interface proceeds quickly to the grain. This type of nucleation growth is best described by Avrami relationship [18] given as

$$x_{\text{NiO}} = 1 - \exp(-kt^m)$$

where $x_{\text{NiO}}$ is the fractional conversion at time $t$, $k$ an overall rate constant, and $m$ is an exponent whose value (0.5–4) depends on grain geometry and the limiting step (i.e. chemical nucleation or diffusion). Many sigmoidal reduction curves are best explained by the Avrami relationship. The reduction curve in the work of Benton and Emmet [9], was fitted with Avrami relation with an $m$ value of 1.34. This value suggests instantaneous nucleation and three dimensional growth, with the rate controlled by diffusion across the interface.

Influence of crystallite size was studied by Richardson et al. [19]. They found out that the crystallite size had no dependence on $T_{50}$ (temperature for 50 % reduction) and also inferred that NiO, from whatever source will exhibit the same type of reduction behaviour.
3.1.2 Solid state kinetics

The kinetics of solid state reactions is treated in a different way compared to kinetics of reactions in homogeneous solutions. In solid state reactions the reaction is considered to initiate and propagate at the interface of solids. Figure 2 shows the changes caused by the introduction of dimensionality to the rate equation.

![Figure 2. Introduction of dimensionality in solid state kinetics [From ref-20]](image-url)

The molar concentration of reactants in the homogeneous solution kinetics is replaced by degree of conversion, $\alpha$, which is usually defined as

$$\alpha_t = \frac{(C_t-C_0)}{(C_\infty-C_0)}$$

Where, $C$ is the concentration of reactants or any other physical property chosen to study the system. The subscripts in the above equation correspond to the value at initial time ($t = 0$) and final time ($t \rightarrow \infty$), respectively. The time dependence of $\alpha$ is obviously expressed in the form of a differential equation.
where \( k \) is the Arrhenius rate constant and \( f(\alpha) \) is the kinetic model, which is an algebraic function describing the mechanism of the process. There are various models for solid state kinetics and a few are listed in Table 1.

**Table 1.** Different models of solid state reactions and corresponding \( f(\alpha) \) functions

<table>
<thead>
<tr>
<th>Model name</th>
<th>( f(\alpha) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random nucleation</td>
<td>((1-\alpha))</td>
</tr>
<tr>
<td>Generalized ( n^{th} ) order</td>
<td>((1-\alpha)^n)</td>
</tr>
<tr>
<td>Generalized Avrami- Erofeyev</td>
<td>(n(1-\alpha)(-\ln(1-\alpha))^{(n-1)/n})</td>
</tr>
<tr>
<td>Contracting area</td>
<td>((1-\alpha)^{1/2})</td>
</tr>
<tr>
<td>Contracting volume</td>
<td>((1-\alpha)^{1/3})</td>
</tr>
<tr>
<td>Generalised model by Sestak</td>
<td>(\alpha^n(1-\alpha)^p(-\ln(1-\alpha))^p)</td>
</tr>
<tr>
<td>One dimensional diffusion</td>
<td>(1/2\alpha)</td>
</tr>
<tr>
<td>Two dimensional diffusion</td>
<td>(-\ln(1-\alpha) -1)</td>
</tr>
<tr>
<td>Three dimensional diffusion (Jander equation)</td>
<td>(3(1-\alpha)^{2/3}/2(1-(1-\alpha)^{1/3}))</td>
</tr>
<tr>
<td>Three dimensional diffusion (Ginstling-Brounshtein equation)</td>
<td>(3/2((1-\alpha)^{-1/3}-1))</td>
</tr>
</tbody>
</table>

**3.1.3 Methodology – non isothermal thermogravimetry**

Kinetics of nickel oxide reduction was followed by simple thermogravimetric experiments. There are several studies in literature, in which nickel oxide reduction was studied by thermogravimetry [21].
The fundamental rate equation for kinetics of solid state reactions is

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)
\]

where \(A\) is the pre exponential factor, \(T\) the absolute temperature, \(R\) the gas constant and \(f(\alpha)\) is a function of the reacted fraction \(\alpha\). Under non isothermal conditions, temperature varies with time at a constant heating rate \((\beta)\), where \(\beta = \frac{dT}{dt}\) and equation (1) changes to

\[
\beta \left(\frac{d\alpha}{dT}\right) = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)
\]

Though hydrogen reduction of nickel oxide is a gas solid reaction, under our experimental conditions the hydrogen concentration is a constant (large excess of hydrogen) and above equation is sufficient to describe the process. A complete kinetic analyses of solid state reaction should include determination of \(E_a\), \(\ln A\) and \(f(\alpha)\) which are generally termed as the kinetic triplet.

**Estimation of Activation energy \(E_a\)**

Model free isoconversional methods based on multiple heating curves are considered to be better to determine activation energy than methods based on model fitting, which are based on single heating curves [22]. The assumptions of isoconversional methods are that the reaction rate at a constant conversion is only a function of temperature, and the reaction model is independent of the heating rate. Variation of heating rate causes changes in the reaction processes. The material spends more time at low temperature with low heating rates. At higher heating rates the reaction rates are faster, as the material is quickly exposed to elevated temperatures. This varying reaction rates at different heating rates can be used to estimate the activation energy of the process. The isoconversional methods can estimate activation energy at different conversions. For a single-stage reaction the activation energy \((E_a)\) will be a constant throughout the conversion; but, for a reaction which consists of more than one stage, the activation energy varies with the
extent of reaction. This variation of $E_a$ with alpha ($\alpha$, extent of reaction) can be used to explain the reaction mechanism [23].

The Flynn-Wall-Osawa [24] method is an integral isoconversional method and the equation in its differential form is as below.

$$\frac{d \ln \beta}{d (1/T)} = \frac{1.052 * E_a}{R}$$

The method is based on measurement of temperatures for each degree of conversion, $\alpha$, and different heating rates, $\beta$. The plots of $\ln \beta$ versus $1/T$ at constant $\alpha$ will give straight line and from the slope activation energies are determined.

Friedman differential method [25] is based on the intercomparison of the rates of conversion, $d\alpha/dT$ for a given degree of conversion $\alpha$, at different heating rates. This method requires measurement of both temperatures and conversion rates, at different heating rates.

$$\ln \left( \beta \frac{d\alpha}{dT} \right) = \ln [A f(\alpha)] - \frac{E_a}{RT}$$

According to Budurgeac et al. [26], Friedman method is more suitable if activation energy depends on conversion. Moreover FWO method involves a systematic error, as it uses integral function which involves the history of the system.

**Determination of $f(\alpha)$**

In the present chapter the suitable kinetic model ($f(\alpha)$) was determined by Malek’s procedure [27]. The procedure involves estimation of two special functions $Y(\alpha)$ and $Z(\alpha)$. These functions are as follows

$$Y(\alpha) = (d\alpha / dt) \times \exp(x)$$

$$Z(\alpha) = \pi(x) \times (d\alpha / dt) \times T / \beta$$

where, $x = E_a / RT$
\( \pi(x) \) is the approximation of the temperature integral [28] which has the form

\[
\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}
\]

The \( Y(\alpha) \) function is proportional to \( f(\alpha) \) function and the shape of \( Y(\alpha) \) can be used as a diagnostic tool for kinetic model discrimination. The shapes of \( Y(\alpha) \) functions for different kinetic models are depicted in Figure 3.

![Figure 3. Shapes of \( Y(\alpha) \) functions corresponding to different models; JMA(1), (3) (Johnson Mehl Avrami), R2, R3 (Reaction order), D2, D3, D4 (Diffusion).](image)

The \( Z(\alpha) \) function has a maximum for all the kinetic models. The maximum of \( Z(\alpha) \) function termed as \( \alpha_p \) has characteristic values corresponding to each kinetic model and some of them are given in Table 2.
Table 2. Values of $\alpha_p$ corresponding to different models

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Typical value of $\alpha_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnson Mehl Avrami (n=1, 2, 3)</td>
<td>0.632</td>
</tr>
<tr>
<td>Reaction order model (2 dimensional)</td>
<td>0.750</td>
</tr>
<tr>
<td>Reaction order model (3 dimensional)</td>
<td>0.704</td>
</tr>
<tr>
<td>Diffusion (two dimensional)</td>
<td>0.834</td>
</tr>
<tr>
<td>Diffusion (three dimensional)</td>
<td>0.704</td>
</tr>
<tr>
<td>Diffusion (four dimensional)</td>
<td>0.776</td>
</tr>
</tbody>
</table>

The maximum $(\alpha)_m$ of the $Y(\alpha)$ function, maximum $(\alpha)_p$ of $Z(\alpha)$ function and the shape of $Y(\alpha)$ function can be used to select the best kinetic model of the process. Figure 4 shows a schematic diagram for the selection of suitable kinetic model from the values of $(\alpha)_m$ and $(\alpha)_p$.

![Figure 4. Kinetic model determination from values of $(\alpha)_m$ and $(\alpha)_p.$](image)

The objectives of this study are

i) to study the influence of crystallite size on NiO reduction kinetics
ii) to study the influence of structural parameters of NiO (from different precursors—chapter 2) on the reduction kinetics.

3.2 Experimental

3.2.1 Preparation of nickel oxides

Synthesis of nickel oxide nanocrystallites

To obtain homogeneous NiO nanoparticles, the reported procedure of Estelle et al. [29] was adopted. Ni(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O (Merck +99.5\%) was dissolved in 50 mL distilled water and was slowly evaporated to get the crystals. The crystals were separated from the mother liquor and dried in an air oven at 120 °C for five days. The basic nickel nitrate – Ni\textsubscript{3}(NO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{4} was formed which was confirmed by the single stage decomposition in theromgravimetry experiment (Figure 5) which is in accordance with the reported procedure. This basic nickel nitrate was then divided to three parts. One part was calcined at 400 °C, the second part at 600 °C and the third part was calcined at 800 °C in a static muffle furnace for two hours by heating at a rate of 5 °C min\textsuperscript{-1} from room temperature to the desired temperature and was named as NiO-400, NiO-600 and NiO-800 respectively.

![DTG graph of Ni\textsubscript{3}(NO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{4}](image_url)
Nickel oxide from different precursors

Nickel oxides were prepared by thermal decomposition of the complexes. Details of the preparation are given Chapter 2. The samples were NiO-A, NiO-B, NiO-C and NiO-D.

3.2.2 Characterization techniques

The XRD patterns were recorded on Bruker model D8 (CuKα source) diffractometer. The peaks were subjected to Lorentzian curve fit, and the fwhm (τ) were determined after deducting the instrumental broadening. The X-ray line broadening analysis (XLBA) was done with the well known Scherrer equation to determine the crystallite size.

\[
d_{\text{vol}} = \frac{0.9 \lambda}{\tau \cos \theta}.
\]

\(d_{\text{vol}}\) = Volume average crystallite size; \(\lambda\) = wavelength of X’Ray; \(\tau\) = fwhm (full width at half maximum)

SEM-EDX was recorded on Jeol JSM-6390 LA scanning electron microscope with EDX assembly. BET surface area was measured on a Micromeritics Tristar surface area analyzer.

3.2.3 Reduction reaction-experimental conditions

In a recent study on nickel oxide reduction kinetics, Erri \textit{et al.} [30] identified the importance of diffusion effects on the reduction kinetics and recommend low heating rates for nonisothermal experiments. Recently Criado \textit{et al.} have emphasized the use of low heating rates for processes involving overlapping reactions when using the isoconversional methods of kinetic analyses [31]. Utigard \textit{et al.} [32] got varying kinetic results when they changed the hydrogen concentration.
experiments were designed in such a way to eliminate the mass transfer limitations as far as possible.

The TG experiments were done on a Perkin Elmer TG-DTG Pyris Diamond instrument and the experimental conditions were, low sample mass (2.2±0.3 mg), low grain size (74μm-105μm (sieved through mesh size -100,+140)), high hydrogen concentration (99.95%), high hydrogen flow (500 mL min⁻¹), low heating rates (1,2,3 and 4 °Cmin⁻¹). Prior to each experiment the sample was dried in an air oven at 150 °C to avoid the presence of residual water. Necessary safety precautions were adopted as the studies involved hydrogen gas at high temperatures. The degree of conversion ‘α’ was calculated from the TG data as

\[
\alpha = \frac{w_T - w_f}{w_0 - w_f}
\]

Where \(w_T\) is the mass of the sample at temperature T, and \(w_0\) and \(w_f\) are mass of the sample at the beginning and at the end of the process respectively.

3.3 Results and Discussion

3.3.1 Kinetics of reduction of nickel oxide nanocrystallites

XRD & SEM

The XRD patterns in Figure 6 indicate decrease of fwhm (full width at half maximum) of the major peaks with increase of calcinations temperature. The crystallite sizes calculated by Scherrer equation were 13, 21 and 29 nm for samples NiO-400, NiO-600 and NiO-800 respectively.
The surface areas decreased as 20.2, 9.3 and 4.2 m$^2$ g$^{-1}$ with increasing calcination temperature. Particles were nearly in cubic shape as evidenced from SEM micrographs (Figure 7). The calcination temperature had less influence on particle shape; however the particles aggregated together as the temperature increased.
Figure 7. SEM of nickel oxide calcined at (a) 400 °C, (b) 600 °C and (c) 800 °C
Thermogravimetric results

The percentage mass losses during the temperature programmed reduction of the samples are shown in Figure 8 (a) to (c), and the corresponding $\alpha$ - $T$ curves are shown in Figure 9 (a) to (c). An average of $21.5\pm 0.2\%$ of mass loss was recorded in all the experiments. The dependence of $d\alpha/dt$ versus $T$ at different heating rates for the samples are shown in Figure 10 (a) to (c) and the results are summarized in Table 3. With increasing heating rate, the rate of reduction process of the samples increased. The $T_{\text{max}}$ (temperature of peak maxima) and $\alpha_{\text{max}}$ (degree of conversion at $T_{\text{max}}$) read from $\alpha$-$T$ curve (Figure 8 (a) to (c)) shifted to higher values as the crystallite size increased. The $\Delta T$ values (peak width) decreased as the crystallite size increased.

More number of defects and vacancies are expected on NiO-400 sample because of its low crystallite size. This should be the reason for the low reduction temperatures for this sample and this observation is in accordance with the previously reported literature [13, 14] in which a direct correlation between reduction temperature and vacancies has been pointed out.

Table 3. Values of $T_{\text{max}}$, $\Delta T$ and $\alpha_{\text{max}}$ for the samples at different heating rates.

<table>
<thead>
<tr>
<th>Heating rate $^\circ\text{C min}^{-1}$</th>
<th>NiO-400</th>
<th>NiO-600</th>
<th>NiO-800</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$ (K)</td>
<td>$\Delta T$</td>
<td>$\alpha_{\text{max}}$</td>
<td>$T_{\text{max}}$ (K)</td>
</tr>
<tr>
<td>1</td>
<td>500.3</td>
<td>58.7</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>512.2</td>
<td>61.9</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>520.2</td>
<td>63.6</td>
<td>0.31</td>
</tr>
<tr>
<td>4</td>
<td>523.9</td>
<td>70.0</td>
<td>0.29</td>
</tr>
</tbody>
</table>
**Activation energies**

The activation energies were determined by Flynn-Wall-Osawa method and Friedman method for the samples and the values are plotted against $\alpha$ in the Figures 11 (a) to (c).
Figure 11 (a) NiO-400, (b) NiO-600 and (c) NiO-800. Variation of the Activation energy with conversion, determined by Friedman and FWO method.

The activation energies were determined within the range 0.05 to 0.95 $\alpha$. For all samples the activation energies determined by Friedman method were lower than that of FWO method. Also it can be seen that the activation energy is a function of $\alpha$ with high values at both initial and final states. However, the variation with $\alpha$ were similar for both the methods. The activation energies for all samples were almost constant within the range 0.3 $\alpha$ to 0.7 $\alpha$. The NiO-400 sample had the lowest activation energy and the activation energy increased as the crystallite size increased. The variation of $E_a$ with $\alpha$ indicates the complex nature of the nickel oxide reduction. Vyazovkin [33] has assigned such an $E_a$ - $\alpha$ dependence to occurrence of a parallel independent reaction which has higher activation energy. Comparing the curves, it can be seen that this step of higher activation energy is more important as
the crystallite size increases. As per the reported mechanism [12] of NiO reduction, the reduction in interfacial area of reduced phase and unreduced phase cause higher activation energy towards the end. In case of NiO-800 the overlapping of nickel grains will be difficult and the process will have high activation energy because of its higher crystallite size. The activation energy was averaged from the Friedman curve (in the range 0.3α to 0.7α) and was 105.1 kJ mol$^{-1}$, 108.4 kJ mol$^{-1}$ and 111.6 kJ mol$^{-1}$ for NiO-400, NiO-600 and NiO-800 respectively.

**Note:** For the sample NiO-600 the rate curve at 4 °C min$^{-1}$ is distinctively different from others, indicating a change in mechanism. For activation energy determination data from heating rates 1 °C min$^{-1}$, 2 °C min$^{-1}$ and 3 °C min$^{-1}$ was used.

**Kinetic model by Malek’s procedure**

The $Y(\alpha)$ and $Z(\alpha)$ functions were calculated for NiO-400 sample. The normalized $Y(\alpha)$ and $Z(\alpha)$ were plotted against $\alpha$ in the Figure 12 (a) and (b).

![Figure 12](image-url) (a) $Y(\alpha)$ function and (b) $Z(\alpha)$ function of NiO-400

The values of $(\alpha)_m$ and $(\alpha)_p$ extracted from Figure 12 are given in Table 4.
Table 4. Values of \((\alpha)_m\) and \((\alpha)_p\) for NiO-400 different heating rates.

<table>
<thead>
<tr>
<th>Heating rate °C min(^{-1})</th>
<th>NiO-400</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\alpha)_m)</td>
<td>((\alpha)_p)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.188</td>
<td>0.264</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.223</td>
<td>0.291</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.222</td>
<td>0.322</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.205</td>
<td>0.285</td>
<td></td>
</tr>
</tbody>
</table>

Considering the shape of \(Y(\alpha)\) function and the fact that \((\alpha)_m\) values are lower than \((\alpha)_p\) values, the kinetic model can be either Johnson Mehl Avrami (JMA) or Sestak Berggren (SB). The fact that \((\alpha)_p\) value is lower than 0.632 indicates that Sestak Berggren model \(f(\alpha) = \alpha^m (1 - \alpha)^n\) is suitable for both samples. The ratio of kinetic exponents \(s = m / n\) can be determined from \((\alpha)_m\) values as \(s = (\alpha)_m / (1 - (\alpha)_m)\).

To determine \(n\), the following relation is used:

\[
\ln \left[ \left( \frac{d\alpha}{dt} \right) \exp \left( \frac{E_a}{RT} \right) \right] = \ln A + n \ln \left[ \alpha^m (1 - \alpha) \right]
\]

The pre exponential factor \(A\) and kinetic exponents \(n\) and \(m\) \((m = s \times n)\) were determined at each heating rates and the results are presented Table 5.

Table 5. The kinetic parameters \(n\), \(m\) and \(\ln A\) for NiO-400 at different heating rates and their average values.

<table>
<thead>
<tr>
<th>Heating rate °C min(^{-1})</th>
<th>NiO-400</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n)</td>
<td>(m)</td>
<td>(\ln A) (min(^{-1}))</td>
</tr>
<tr>
<td>1</td>
<td>1.86</td>
<td>0.491</td>
<td>19.37</td>
</tr>
<tr>
<td>2</td>
<td>1.92</td>
<td>0.507</td>
<td>19.55</td>
</tr>
<tr>
<td>3</td>
<td>1.67</td>
<td>0.441</td>
<td>19.34</td>
</tr>
<tr>
<td>4</td>
<td>1.87</td>
<td>0.494</td>
<td>19.40</td>
</tr>
<tr>
<td>Average</td>
<td>1.83</td>
<td>0.483</td>
<td>19.42</td>
</tr>
</tbody>
</table>
The kinetic triplet obtained for the NiO-400 sample is

\[ \text{NiO-400} \quad [E_a = 105.1 \text{ kJ mol}^{-1}, \ln A = 19.42 \text{ min}^{-1}, f(\alpha) = \alpha^{0.48} (1 - \alpha)^{1.83}] \]

Above procedure was repeated for NiO-600 and NiO-800 samples and the kinetic triplet obtained were

\[ \text{NiO-600} \quad [E_a = 108.4 \text{ kJ mol}^{-1}, \ln A = 20.34 \text{ min}^{-1}, f(\alpha) = \alpha^{0.69} (1 - \alpha)^{1.42}] \]

\[ \text{NiO-800} \quad [E_a = 111.6 \text{ kJ mol}^{-1}, \ln A = 20.56 \text{ min}^{-1}, f(\alpha) = \alpha^{0.60} (1 - \alpha)^{0.91}] \]

The validity of the obtained kinetic parameters can be checked by comparing the experimental curve with the calculated rate curve. The rate curve is calculated using the above kinetic triplet in the equation

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)
\]

Figure 13 shows the experimental and the calculated rate curves. It can be seen that the curves match very well within the range 0.01 \( \alpha \) to 0.9 \( \alpha \) (the \( \alpha \) was read from the corresponding \( \alpha - T \) curves; Figure 9 (a), (b) and (c))

The solid state reaction of nickel oxide with hydrogen consists of various chemical and physical processes such as adsorption-desorption, reaction of hydrogen gas with nickel oxide, and polymorphous transition when nickel nuclei grows in nickel oxide lattice. Therefore, the effective activation energy of the process is generally a composite value determined by the activation energies of various processes as well as by the relative contributions of these processes to the overall reaction rate.
Figure 13. Experimental vs. Calculated rate curves
**Discussion on kinetic parameters n, m and r**

The empirical two parameter kinetic model of Sestak and Berggren [34] when proposed was of the form

\[ f(\alpha) = \alpha^n (1 - \alpha)^m \ln(1 - \alpha) \]

where n, m and r are the kinetic exponents. Mathematical analysis of above equation [35] has shown that only two kinetic exponents are necessary, and the above equation was reduced to the form

\[ f(\alpha) = \alpha^m (1 - \alpha)^n \]

where m and n are the kinetic exponents. Sestak Berggren model is usually denoted as SB \((m, n)\). The kinetic exponent m and n should be linked with the mechanism of reduction process but due to the empirical nature of the Sestak Berggren model such links are hard to find in the literature. However some recent studies [36-38] has attempted to relate the SB \((m, n)\) exponents to the structure of the material. Comparing the kinetic exponents, it can be seen that the n value decreases from 1.83 to 0.91 as crystallite size increases. It has been proposed such a shift of n value indicates the shift of mechanism from Langmuir-Hinshelwood to Eley-Rideal [38]. The m values increases from 0.48 to 0.60 as crystallite size increases. An increase of m value indicates the role of reduced phase in the overall reduction process.

The macroscopic process of reduction (nucleation/crystal growth) strongly depends on the concentration and distribution of nuclei in the sample. The nuclei can be of two types, surface nuclei and bulk nuclei. The surface nuclei are already present on the sample, while the bulk nuclei, termed as secondary nuclei, form during the course of reduction. Because of the low crystallite size and higher surface area of NiO-400 sample, these surface nuclei initiate the reaction early. Thus the reaction is more Langmuir-Hinshelwood type, as hydrogen dissociates rapidly on the surface nuclei and the dissociated hydrogen reacts with nickel oxide. For this case the important process is the reaction of adsorbed hydrogen and the surface nuclei-
probably the oxygen vacancies. This is indicated by a high value of \( n \). For NiO-800 sample, the number of oxygen vacancies and correspondingly the surface nuclei are small. But as its reduction happens at a higher temperature a larger number of bulk nuclei are formed. These bulk nuclei which are present inside the NiO crystals, tend to grow faster. The higher value of \( m \) for NiO-800 sample indicates that the major reduction happens between the interphase of reduced and nonreduced phase.

The work of Sestak, Satava and Wendlandt [39] has shown that the SB \((m, n)\) equation is equivalent to the JMA \((r)\) equation to a first approximation. The empirical SB \((m, n)\) model thus includes JMA \((r)\) model as a special case [40] and the kinetic parameters are related as

\[
r = \frac{1}{1 + \ln(n) - \ln(n + m)}
\]

The average value of \( r \) and the \( m, n \) values for the samples are tabulated in Table 6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n )</th>
<th>( m )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO-400</td>
<td>1.83</td>
<td>0.48</td>
<td>1.31</td>
</tr>
<tr>
<td>NiO-600</td>
<td>1.42</td>
<td>0.69</td>
<td>1.66</td>
</tr>
<tr>
<td>NiO-800</td>
<td>0.91</td>
<td>0.60</td>
<td>2.04</td>
</tr>
</tbody>
</table>

The JMA model is derived from first principles and hence, its parameter \((r)\) has physical significance. The value of \( r \) depends on the shape of the nuclei and dimensionality of their growth, as well as on the rate of their formation [41]. The Avrami exponents of the samples show that the dimensionality of the reduction process increases as crystallite size increases. This indicates that under the
experimental conditions, the hydrogen reduction of nickel oxide takes place in a surface oriented fashion for NiO-400 sample. Thus the reduction mechanism of nickel oxide depends on the crystallite size of the sample under the studied experimental conditions.

**A special mention on NiO-600**

The $\alpha$-$T$ curve of NiO-600 shows that at low heating rates the reduction happens in two stages, but as the heating rate increases the two stages merges together to a single peak. This indicates a change in mechanism with heating rates and is attributed to the complex nature of the reduction process. The change in $\alpha_{\text{max}}$ values (Table 3) also indicates a change in reduction mechanism. The calculated rate curve deviates from the experimental one as shown in Figure 13. The shape of the experimental curve at 4 °C min$^{-1}$ is more similar to that of NiO-800. The rate curve was again calculated with the kinetic model \( f(\alpha) = \alpha^{0.60} (1 - \alpha)^{0.91} \) for NiO-800. Figure 14 shows that now the curve matched better with the experimental curve. This shows that the mechanism has changed at higher heating rate. Oxidation of tungsten carbide is shown to happen in two stages at low heating rates whereas as single stage on higher heating rates [42].

![Figure 14](image-url)

**Figure 14.** Experimental vs. Calculated rate curve of NiO-600 at 4 °C min$^{-1}$. When calculated with kinetic model of NiO-800; both $T_{\text{max}}$ and shape matches better.
The relative contribution of the two competitive reactions to the overall process depends on the heating rate, as the reaction with higher activation energy will become dominant at higher temperatures. Thus while selecting the heating rates, one should be sure that the rate of individual processes does not vary within the selected heating rates.

### 3.3.2 Kinetics of reduction of nickel oxide derived from different precursors

The nickel oxides prepared by thermal decomposition of metal complexes (Chapter 2) were subjected to kinetic study. The procedure for kinetic analyses was same as that in the previous section, and only the results will be discussed in this section. The $T_{\text{max}}$ values for the samples are given Table 7.

<table>
<thead>
<tr>
<th>Heating rate $^\circ\text{C}\text{ min}^{-1}$</th>
<th>$T_{\text{max}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO-A</td>
</tr>
<tr>
<td>1</td>
<td>509.9</td>
</tr>
<tr>
<td>2</td>
<td>523.6</td>
</tr>
<tr>
<td>3</td>
<td>528.4</td>
</tr>
<tr>
<td>4</td>
<td>534.1</td>
</tr>
</tbody>
</table>

**NiO-A (derived from $[\text{Ni(H}_2\text{O)}_6\text{]}(\text{NO}_3)_2$)**

The kinetic triplet obtained for the sample was

\[
\text{NiO-A} \quad [E_a = 114.3 \text{ kJ mol}^{-1}, \ln A = 20.65 \text{ min}^{-1}, f(\alpha) = \alpha^{0.38} (1 - \alpha)^{0.68} ]
\]

The Ea-$\alpha$ curve and the rate curves are shown in Figure 15 and Figure 16 respectively.
The experimental and calculated curves matched up to 0.87 \( \alpha \). After the conversion of 0.87 the calculated curves lie above the experimental ones. This may be due to higher activation energy involved in later stages of reduction. At higher conversions the remaining NiO is covered with Ni crystallites and it requires higher activation energy to reduce the deeply seated nickel oxide particles. This may be due to the difficulty for hydrogen to diffuse inside or the product water to diffuse outside [43, 16].

\textit{NiO-B (derived from [Ni(en)\(_2\)(H\(_2\)O)\(_2\])(NO_3)\(_2\)\)}

The Ea-\( \alpha \) dependence (Figure 17) is almost constant for NiO-B. The kinetic triplet obtained for the sample was

\[
\text{NiO-B} \quad [\text{Ea} = 88.5 \text{ kJ mol}\(^{-1}\), \ln A = 20.14 \text{ min}\(^{-1}\), \( f(\alpha) = \alpha^{0.81} (1 - \alpha)^{1.28} \)]
\]

The activation energy was considerably low for this sample. The \( T_{\text{max}} \) values were also low. The rate curves (Figure 18) matched at all conversion values.

\textbf{Figure 15.} Ea-\( \alpha \) curve of NiO-A \hspace{1cm} \textbf{Figure 16.} Rate curve of NiO-A
NiO-B was obtained by oxidation of nickel metal (Chapter 2). Some nickel crystallites remnant in the sample can act as nucleating sites. If the nucleating sites are present on the onset of reduction, the reduction can start early. The $T_{\text{max}}$ values indicate a low induction period for the sample. The SEM of the sample (Chapter 2) shows it has foam like structure. This special structure can enhance the hydrogen diffusion inside and water diffusion outside, during the reduction reaction. The high value of SB parameter ‘m’ (0.81) indicates the increased dependence on the crystallized (Ni crystallites) phase.

**NiO-C (derived from \([\text{Ni(en)}_2(\text{H}_2\text{O})_2](\text{CH}_3\text{COO})_2\)**

The kinetic triplet obtained for the sample was

\[
\text{NiO-C} \quad [E_a = 118.5 \text{ kJ mol}^{-1}, \ln A = 21.03 \text{ min}^{-1}, f(\alpha) = \alpha^{0.58}(1-\alpha)^{1.02}]
\]

Both $T_{\text{max}}$ and activation energy was highest for this sample.
The SEM picture (Chapter 2) indicates a compact shape for the amorphous structured sample. This tough structure may be retarding the diffusion of hydrogen or water vapour; thus increasing the activation energy.

**NiO-D (derived from [Ni(en)$_2$(H$_2$O)$_2$]Cl$_2$)**

The $T_{\text{max}}$ values are higher compared to NiO-A (which has almost same morphology as NiO-D; Chapter 2), but the activation energy is lower. The kinetic triplet obtained for the sample was

$$\text{NiO-D } [\text{Ea} = 110.8 \text{ kJ mol}^{-1}, \ln A = 19.04 \text{ min}^{-1}, f(\alpha) = \alpha^{0.65} (1 - \alpha)^{1.03}]$$
The EDX analysis of the NiO-D (Figure 23) sample before reduction indicates presence of chlorine in the sample (0.2 wt%). The reduced sample (Figure 24) does not contain any chlorine which indicates chlorine has escaped during the reduction.

![Figure 23. EDX results before reduction of NiO-D](image)

![Figure 24. EDX results after reduction of NiO-D](image)

The Ea-α values show decreasing dependence towards the end. Vyazovkin [44] has identified such decreasing dependence of activation energy due to diffusion limited process which involves conversion of solid → solid + gas. Generally a process becomes diffusion limited when the reaction rate is high. The low activation energy observed for the NiO-Cl sample should be because of the effect of chlorine, which acts as a catalyst for the reduction reaction. The following mechanism can be suggested. During the induction (nucleation) period the gas phase hydrogen dissociates on the NiO surface. The surface disorders like defects, kinks and vacancies activate this step on the NiO surface.

\[
H_2 (g) \rightarrow 2H_{(ads)}
\]

In the nucleation step the adsorbed hydrogen reacts with nickel oxide to form nickel metal which acts as nucleating sites for the further steps of nucleation growth.

\[
\text{NiO} + 2H_{(ads)} \rightarrow \text{Ni} \text{(metal)} + H_2O (g) \quad (2)
\]
Chlorine is present on the nickel oxide as nickel chloride. The chlorine atoms present on the NiO lattice reduces the reactivity of NiO surface by its electron withdrawing property and the reduction starts at higher temperature on this sample. Once sufficient number of nuclei is formed, Ni (metal) acts auto catalytically and the reaction becomes faster. On the NiO-D sample the following reaction also takes place

\[ \text{NiCl}_2 + 2\text{H}_{(ads)} \rightarrow \text{Ni (metal)} + 2\text{HCl}_{(g)} \quad (3) \]

The formed HCl can either be transported away through the gas phase or can be adsorbed on NiO surface and Ni surface or may get dissolved in evolving H₂O. If HCl gets adsorbed on NiO it forms nickel chloride by the reaction

\[ \text{NiO} + 2\text{HCl}_{(g)} \rightarrow \text{NiCl}_2 + \text{H}_2\text{O}_{(g)} \quad (4) \]

Activation energy for reduction of NiCl₂ is lower (54 kJ mol⁻¹) than that for NiO [45]. Thus during the process, a part of nickel oxide gets reacted as nickel chloride for which the activation energy is lower. This explains the lowering of activation energy as conversion increases. If the HCl gets dissolved in water it reduces the volatility of water vapour, consequently escape of water vapour from Ni surface becomes slow. During the process the HCl gets transported away through the gas phase. The final EDX analysis shows the absence of chlorine. As the particle size increases (by sintering) the diffusion of hydrogen to the reacting interphase (surface between nickel metal and nickel oxide) becomes the rate determining step in the latter stages. Because of the above reasons the reaction becomes more and more diffusion limited and the activation energy gets lower. The activation energy for diffusion is always lower than the activation energy for the reaction.

### 3.4 Conclusions

i) Crystallite size influences the NiO reduction mechanism.

ii) Reduction starts earlier for low crystallite sized sample probably due to higher number of surface nuclei.
iii) The SB \((m, n)\) exponents vary with the crystallite size. Comparison of the exponents indicated that, when the crystallite size is lower the reduction follows a surface oriented mechanism under the experimental conditions.

iv) The NiO-B sample, which probably has the presence of Ni crystallites, reduces at a low temperature with low activation energy.

v) Nucleation period is longer for reduction on chlorine containing sample (NiO-D) as Cl\(^-\) reduces the reactivity of NiO surface by its electron withdrawing effect.

vi) The rate of reaction is much lower at the end for the NiO-D sample; which may be due to (a) inhibition of reaction because of slow water desorption or (b) difficulty in diffusion of hydrogen through the sintered nickel metal surface to the reaction interphase.

vii) There is an indication that morphology of the sample influences the reduction kinetics.

References


Chapter 3


Kinetics of Temperature Programmed Reduction (TPR) of NiO.


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