A COMPARATIVE KINETIC STUDY ON THE REDUCTION OF UNSUPPORTED NANO NiO PARTICLES AND SILICA-SUPPORTED NiO

Syed Shatir Asghrar Syed-Hassan, Chun-Zhu Li[*]

Curtin Centre for Advanced Energy Science and Engineering,
Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia
[*]Email: chun-zhu.li@curtin.edu.au

ABSTRACT

This paper presents the results of our work conducted on studying the differences in the reduction of unsupported nano NiO particles and silica-supported NiO. The purpose of the study was to understand the effects of physical characteristics of NiO particles and their support on the reduction process. In this study, the kinetics of NiO reduction was investigated using an isothermal thermogravimetric method in the temperature range of 500 – 600 °C. From the study, we found that the silica support did not hold a significant effect on the NiO reduction. Instead, the change in the reduction behaviour was related to the size of NiO crystallites.

INTRODUCTION

The gaseous reduction of nickel oxide is a class of heterogeneous reaction that is very important to many different branches of modern science and engineering including catalysis (Delmon 1999), metallurgy (Hidayat et al., 2009) and, recently, the chemical-looping combustion (Sedor et al., 2008). The researches on this subject are extensive. However, many details of the reaction including its intrinsic kinetics and mechanisms are still obscure.

In this study, we have carried out a simple, yet systematic investigation on the reduction of NiO using a thermogravimetric technique in order to understand the importance of physical characteristics of NiO particles and their support in the reduction process. We observed that the behavioural change in the kinetics of NiO reduction is crystallite-size dependent. Above a certain critical crystallite size, the reduction of NiO showed the appearances of two kinetic compensation effects between the activation energies and the pre-exponential factors; one at lower levels of NiO conversion (5 – 30%) and the other at higher levels of conversion (50 – 30%). We believe that two different mechanisms were operative at different levels of conversion during the NiO reduction.

EXPERIMENTAL

Two types of nickel oxide were used in this study. The first one was the unsupported nano NiO particles and the second one was the silica-supported NiO (60 wt% NiO). The particle sizes of unsupported NiO were in the range of 5 – 10 nm, whilst the calculation using Debye-Sherrer equation based on the XRD peaks showed that the NiO crystallite size was 3.3 nm. For the supported NiO, the particle sizes of the silica support were in the range of 150 – 250 μm and the average crystallite size of NiO was 54.7 nm.

The reduction of NiO samples was carried out inside a thermogravimetric analysis unit (TA SDT-Q600). The sample was firstly heated at a heating rate of 10 °C/min inside the TGA under argon (99.999% purity) only flow of 100 ml/min from ambient temperature to the required isothermal temperature. Once the set temperature was reached, the H_2-Ar gas mixture (60% H_2) with a flow rate of 20 ml/min was introduced into the TGA through a separate gas inlet. The gas mixture mixed up with the argon purge gas to provide 120 ml/min total flow rate and 10% hydrogen concentration as the reducing gas. For each type of NiO, the isothermal reduction was studied separately at six different temperatures within the range of 500 to 600 °C.

RESULTS AND DISCUSSION

Fig. 1 shows the examples of isothermal thermogravimetric curves for the reduction of unsupported nano-sized NiO and silica-supported NiO with 10% hydrogen (in argon). As can be seen, the reduction of silica-supported NiO, even though it had a shorter induction period, was slower than the unsupported NiO.
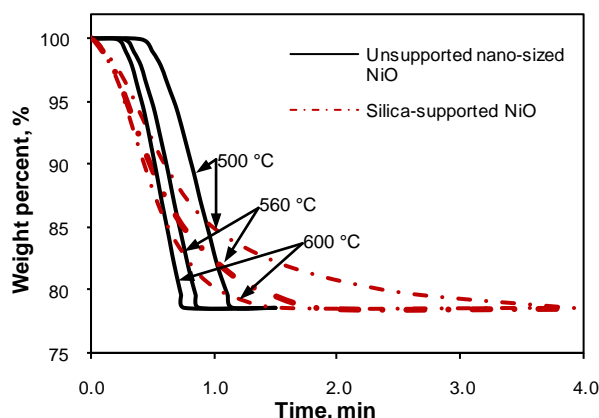

Fig. 1: The reduction of unsupported nano-sized NiO (a) and silica-supported NiO with hydrogen at 500 °C, 560 °C and 600 °C.

While the reduction curves for the unsupported NiO do not show a significant decrease in the reaction rate after the induction period up to the end of reduction, the shape of NiO/SiO_2 reduction curves, in contrast, clearly indicate that the reduction rate decreased significantly after a certain level of NiO reduction.

In order to examine the diffusional effects in the reduction of supported NiO, we ground the catalyst particles from its original sizes of around 150 – 250 µm to the new sizes of less than 25µm. The new (<25µm) NiO/SiO_2 particles were then reduced inside the TGA in the same manners as the original particles. It was found that the NiO reduction rate did not improve even after the size of NiO/SiO_2 has significantly been reduced. This implies that the consideration of molecular diffusion of H_2/H_2O into/from and inside the pore structures of silica cannot be used to account for the observed decrease in the reduction rate with time for the silica-supported NiO. This examination also indirectly ruled out the possible retardation effect of H_2O in the reduction of NiO

(Coenen 1979). This is because the retarding effect of water is largely associated with the difficulty in the removal of water vapour due to the diffusional resistance.

The next factor to be considered is the interaction of nickel oxide with its support material. Past studies (Coenen 1979, Zielinski 1995) have reported the formation of silicate compound in the silica-supported NiO. Researchers believed that one of the reasons for the difficult reducibility of silica-supported NiO is due to the presence of silicate compound. We, however, do not believe that the formation of silicate has caused the slowdown in the reduction rate observed for the supported NiO in our study. Our reasons are explained below.

Firstly, we found that the actual total weight loss in each experiment varied not more than 2% from the theoretical (stoichiometric) total weight loss estimation. If the nickel-silicate compound was present, it should be hard to achieve the same degree of reduction because the reduction of nickel-silicate is much more difficult than the reduction of nickel oxide. Usually, the reduction is far from complete. Secondly, in order to examine the possible effect of silicate formation, we have re-oxidised the nickel particles with air after its full reduction. We observed that the particles regained its weight to within ±2% of its original weight. After the re-oxidation, we analysed the particles using an XRD technique. No other phase except for NiO was detected from the XRD. The only difference observed was the crystallite size. We found that the crystallite size of NiO for the silica-supported NiO after the first reduction with hydrogen at 500 °C and its subsequent re-oxidation with air increased from 54.7 nm to 63.7 nm.

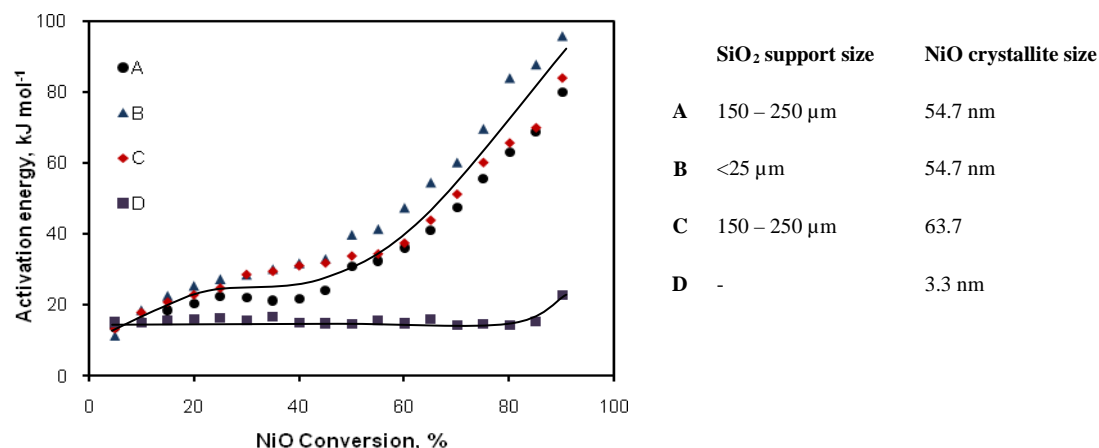|	SiO$_2$ support size	NiO crystallite size
A	150 – 250 µm	54.7 nm
B	<25 µm	54.7 nm
C	150 – 250 µm	63.7
D	-	3.3 nm

Fig. 2: Plots of activation energy versus percentage of NiO reduction for the reduction of supported (A, B, C) and unsupported (D) NiO with hydrogen.

We have also carried out the reduction of NiO/SiO$_2$ for the second time after its first complete reduction and re-oxidation. In this set of experiments, the first reduction was always carried out at 500 °C. In the second reduction of NiO/SiO$_2$ with hydrogen, we observed that the reduction rate decreased slightly but the value of the reduction activation energy at various conversion levels did not vary too much from the first reduction (Fig. 2).

The plot of activation energy (E$_a$) versus percentage of NiO reduction (Fig. 2) for the second reduction of NiO/SiO$_2$ shows a similar pattern to the first reduction (i.e.

continuous increase of E_a with the degree of conversion). If the formation of NiO-support compound is to be considered, firstly, the change of E_a with conversion should not be continuous. Secondly, the new value of E_a must be permanent and the trend of E_a increments should not be reproducible in the second reduction. Since the trend is reproducible, it shows that the change in E_a with the extent of reduction was not due to the formation of another compound.

Interestingly, the similar increase of E_a with NiO conversion, however, was not observed in the reduction of unsupported nano-sized NiO (3.3 nm). If the difference between the two types of NiO used in our study cannot be attributed to the presence and absence of silica support, other factors, therefore, have to be considered. The only clear distinction between the two types of NiO used was the size of NiO crystallites.

In order to examine the potential effect of crystallite size, we decided to carry out multiple reduction/re-oxidation cycle on the unsupported NiO. After the first reduction and re-oxidation at 500 °C, the average size of NiO crystal increased to 20.3 nm, and after the second reduction and re-oxidation at the same temperature, the average crystal size grew to 23.9 nm. As can be seen in Fig. 3, the trend showed in the plots of E_a versus NiO conversion for the second and third reduction of unsupported NiO differ significantly from the first reduction. Instead, they display a similar pattern to the supported NiO (Fig. 2).
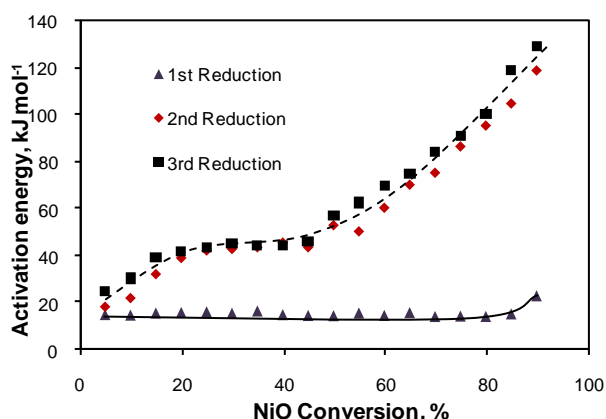

Fig. 3: Plot of E_a vs percentage of NiO reduction for the second and third reduction of unsupported NiO

We strongly believe that the main reason for the change in the reduction behaviour of unsupported NiO was due to the change in the crystallite size. At 3.3 nm, about 60 – 70% volume of the crystal is located on the surface, while above 20 nm, the surface represents less than 10% of the total volume of the crystal (Palumbo et al., 1990). Taking this into account, it is not surprising that there was a shift in the reduction behaviour from the very small to a bigger size of crystallite.

As mentioned earlier in this paper, except for the first time reduction of unsupported nano-sized NiO (3.3 nm crystallite size), the reduction of NiO with bigger crystallite

size (>20 nm) regardless of whether they are supported or not, showed an increase in the activation energy (E_a) with the extent of NiO reduction. A similar increase has also been observed in a number of studies in the past (Wang et al., 2006, Sannomiya et al., 1984, Coenen 1979) but so far, no plausible explanation is available to describe this phenomenon.

What is interesting from the results of our study is that, firstly, we found that the increase in activation energy (E_a) is always accompanied by the increase in the value of pre-exponential factor (A). Secondly, the Arrhenius plots for the reduction of bigger crystallite NiO (>20 nm) show the intersections of interpolated Arrhenius lines at two different points (the example is shown in Fig.4). One intersection for the conversion levels between 5 to 30% and the other intersection for the conversion levels of 50 to 90%.

Apparently, there exist the kinetic compensation effects in the reduction of bigger crystallite NiO. The appearances of two different kinetic compensation effects in this study give us indication that there are at least two different mechanisms involved in the reduction of nickel oxide with crystallite size bigger than 20 nm.
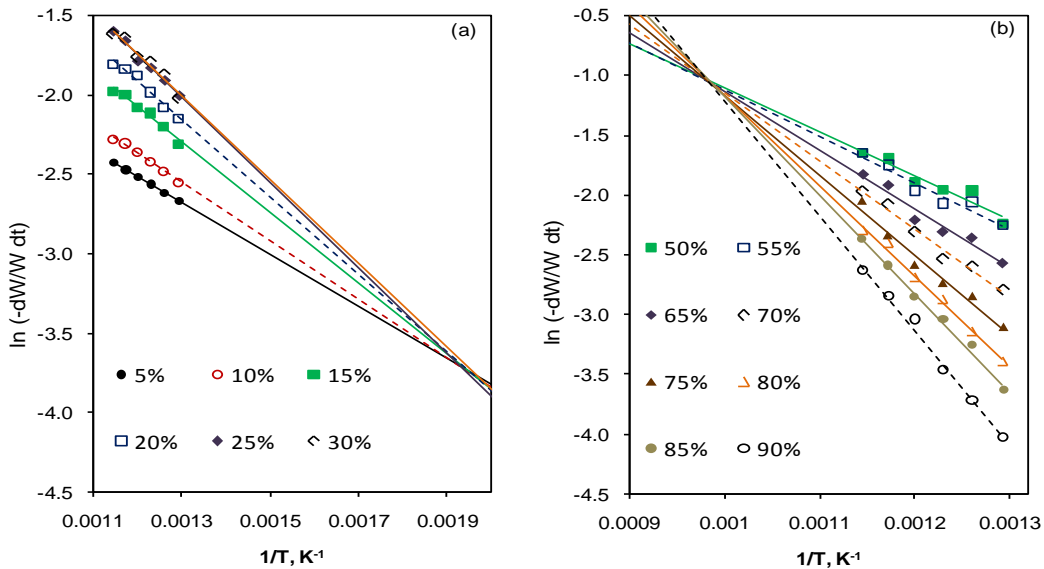

Fig. 4: Arrhenius plots for the first reduction of NiO/SiO$_2$ with hydrogen

CONCLUSIONS

A study was carried out to understand the fundamental differences between the reduction of unsupported nano NiO particles and silica-supported NiO. Our results have indicated that the change in the kinetic behaviour is largely attributed to the size of NiO crystallite. The reduction of very small NiO crystallite was found to be very simple. However, for a bigger crystallite, its reduction was found to be quite complicated. The appearances of kinetic compensation effects have given us indications that there are different mechanisms taking place in the reduction of nickel oxide. Further studies are, therefore, required to understand these mechanisms.

ACKNOWLEDGMENTS

REFERENCES

Coenen, JWE 1979, 'Reduction of silica-supported nickel catalysts', *Studies in Surface Science and Catalysis,* vol. 3**,** no. 1, pp. 89-111.

Delmon, B 1999, 'From the precursor to the final catalyst'. in Ertl, G, Knozinger, H & Weitkamp, J (eds.), *Preparation of Solid Catalysts.* Weinheim, Wiley-VCH.

Hidayat, T, Rhamdhani, MA, Jak, E & Hayes, PC 2009, 'On the Relationships between the Kinetics and Mechanisms of Gaseous Hydrogen Reduction of Solid Nickel Oxide', *Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science,* vol. 40**,** no. 4, pp. 474-489.

Palumbo, G, Thorpe, SJ & Aust, KT 1990, 'On the contribution of triple junctions to the structure and properties of nanocrystalline materials ', *Scripta Metallurgica Et Materialia,* vol. 24**,** no. 7, pp. 1347-1350.

Sannomiya, A, Ichimura, K, Yano, M & Harano, Y 1984, 'Reduction of supported nickel oxides and their interactions with supports', *Kagaku Kogaku Ronbunshu,* vol. 10**,** no. 2, pp. 158-165.

Sedor, KE, Hossain, MM & de Lasa, HI 2008, 'Reduction kinetics of a fluidizable nickel-alumina oxygen carrier for chemical-looping combustion', *Canadian Journal of Chemical Engineering,* vol. 86**,** no. 3, pp. 323-334.

Wang, XG, Wei, YD, Zhang, J, Xu, HY & Li, WZ 2006, 'On the reduction kinetics of coprecipitated $NiO-Al_2O_3$ and $NiO-La_2O_3-Al_2O_3$ catalysts', *Reaction Kinetics and Catalysis Letters,* vol. 89**,** no. 1, pp. 97-104.

Zielinski, J 1995, 'Reducibility of silica-supported nickle oxide', *Catalysis Letters,* vol. 31**,** no. 1, pp. 47-56.

BRIEF BIOGRAPHY OF PRESENTER

Professor Chun-Zhu Li obtained his PhD in Chemical Engineering in 1993 from Imperial College, London. He is currently the Director of Curtin Centre for Advanced Energy Science and Engineering, Curtin University of Technology in Western Australia.