Article

Influence of Cerium on the Reduction Behaviour of Iron Oxide by Using Carbon Monoxide: TPR and Kinetic Studies

Tengku Shafazila Tengku Saharuddin[1,a], Nurul Syahira Ezzaty Nor Azman[1], Fairous Salleh[2], Alinda Samsuri[3], Rizafizah Othaman[2], Mohammad Kassim[2], Mohamed Wahab Mohamed Hisham[2], Mohd Ambar Yarmo[2,a]

[1]Faculty of Science and Technology, Universiti Sains Islam Malaysia (USIM), Bandar Baru Nilai, 71800 Nilai, Negeri Sembilan, Malaysia
E-mail: [a]shafazila@usim.edu.my

[2]Country Low Carbon Economy Research Group, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
E-mail: [a]ambar@ukm.edu.my

[3]Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia (UPNM), Kem Sungai Besi, 57000 Kuala Lumpur, Wilayah Persekutuan, Malaysia.
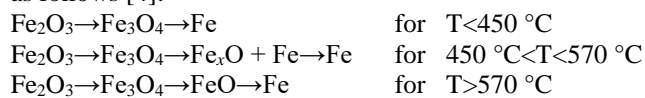
Abstract— **Reduction of iron oxide is one of the most studied topics owing to the importance of iron/steel industry and also has been used as a precursor and active component in a number of important chemical processes. The interaction between iron oxide and other metal additive have gained interest in the past two decades due to the ability on enhancing the reduction performance of the iron oxide. Therefore, this study was undertaken to investigate the influence of cerium on the reduction behaviours of iron oxide by (10%, v/v) carbon monoxide in nitrogen. The cerium doped (Ce-Fe$_2$O$_3$) and non-doped iron oxide reduction behaviour and the kinetic studies have been studied by temperature programmed reduction (TPR) and the phases formed of partially and completely reduced samples were characterized by X-ray diffraction spectroscopy (XRD) while the activation energy values were calculated from Arrhenius equation using Wimmer's method. TPR results indicate that the reduction of doped and undoped iron oxide proceeds in three steps reduction (Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO → Fe), while doped iron oxide showed a large shifted towards lower temperature especially in the transition steps of FeO → Fe. Furthermore, TPR results also suggested that by adding Ce metal into iron oxide the reduction of metal iron completed at lower temperature (700 ⁰C) compared to non-doped iron oxide (900 ⁰C). Meanwhile, XRD analysis indicated that doped iron oxide composed of Fe$_2$O$_3$ and a small amount of FeCe$_2$O$_4$. The increase in the rates of iron oxide reduction may relate to the presence of cerium species in the formed of FeCe$_2$O$_4$ and was confirmed by the decrease in the activation energy regarding to all transition phases (Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO → Fe) during the reduction process.**

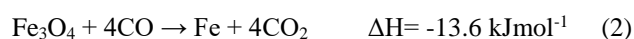*Keywords*— **Reduction; Iron oxide; Cerium; TPR; Kinetic.**

I. INTRODUCTION

Iron oxide was chosen as a potential material in the catalysis field as a regard to their easy handling, low cost, non-toxic, endure physical stress and thermal cycling and environmentally benign [1][2]. Some of the major applications of iron metal as an active component for many catalytic reactions, including hydrogen storage by a redox process, removal of hydrogen sulphide from reducing gas mixtures, ammonia synthesis and Fischere Tropsch synthesis [3]. As a result, reduction properties and the degree of iron oxide reduction were greatly important in the field of catalysis. The reduction process of Fe$_2$O$_3$ is somehow a complicated process and include different mechanisms that rely on several factors such as concentration of reducing gas, the temperature used and additives to the Fe$_2$O$_3$. The reduction process of the Fe$_2$O$_3$ could adopt a two-step mechanism (Fe$_2$O$_3$→Fe$_3$O$_4$→Fe), a three-step mechanism (Fe$_2$O$_3$→Fe$_3$O$_4$→FeO→Fe) and also direct formation to Fe
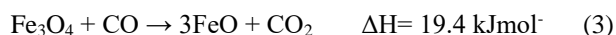
(Fe$_2$O$_3$→Fe) [2][4][5]. The mechanism of the reaction for reduction of iron oxide depends on reduction temperature is as follows [4]:

Fe$_2$O$_3$→Fe$_3$O$_4$→Fe	for T<450 °C
Fe$_2$O$_3$→Fe$_3$O$_4$→Fe$_x$O + Fe→Fe	for 450 °C<T<570 °C
Fe$_2$O$_3$→Fe$_3$O$_4$→FeO→Fe	for T>570 °C

In this work, the non-isothermal temperature programmed reduction was used to observe the reduction performance and intrinsic kinetics of doped and undoped iron oxide reduction by carbon monoxide. Reduction by carbon monoxide generally involves a two-step reduction, which can be described as follows:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2, \quad \Delta H = -47.2 \text{ kJmol}^{-1} \quad (1)$$

$$Fe_3O_4 + 4CO \rightarrow Fe + 4CO_2 \quad \Delta H = -13.6 \text{ kJmol}^{-1} \quad (2)$$

Besides, a three-step reduction is additional of another two subsequent steps of the final process of Fe_3O_4 directly reduced to metallic iron (equation 2) as described below:

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \qquad \Delta H = 19.4 \text{ kJmol}^- \qquad (3)$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad \Delta H = -11.5 \text{ kJmol}^{-1} \qquad (4)$$

Briefly, equations (1) and (2) are responsible for the two-step reduction and whereas a sequence of equations (1), (3) and (4) represents the three-step reduction. Furthermore, the thermodynamic calculations based on the Gibbs free energy change due to reaction and the equilibrium composition of the oxides for the equations above indicate that equations (1), (3) and (4) are spontaneous with ΔG between -102.3 to +9.61 kJmol^{-1} at temperature 300 °C to 900 °C. While, the reduction process for equation (2) is thermodynamically more favourable at rather lower temperatures (below 500 °C, $\Delta G < +20$).

Currently, cerium oxide and CeO_2-based materials are described to have the capability to enhance the redox properties of the transitional metals by improving the noble metal dispersion, improve the activity of CO oxidation and water–gas shift reaction, and possess the oxygen storage and releasing properties [6][7]. Hence, the used of cerium oxide has been studied widely as structural and electronic promoters for catalyst and sorbents used for catalysts or sorbents. The used of ceria (CeO_2) as a promoter and an oxidation catalyst is related to its unique redox properties with high oxygen storage capacity and good at stabilizing metal dispersion [8].

To enhance the reduction performance of iron oxide the addition of other metal additives was considered. In this study, we report the preferable effects of the addition of cerium species into iron oxide catalysts. The temperature programmed reduction (TPR) was performed to explore the isothermal reduction behaviour of Ce doped iron oxide by comparing it to none doped species. Moreover, the kinetics were also carried out using different heating rate.

II. EXPERIMENTAL

A. Materials

Iron (III) oxide with 99% purity was purchased from Sigma Aldrich and ammonium cerium (IV) nitrate (99%) was obtained from Merck. Gas mixture CO/N_2 (10% CO) was obtained from MOX.

B. Catalyst Preparation

Ce as an additive to iron oxide was prepared by impregnating Fe_2O_3 with cerium cation (3 mol %) in aqueous solution. Fe_2O_3 in 50 mL of distilled water with corresponding metal cation was added and stirred vigorously at room temperature for about 2 hours. The impregnated sample was then dried at 120 ºC overnight and calcined for 3 hours at temperature 600 ºC. The Fe_2O_3 sample with cerium and without are denoted as Ce-Fe_2O_3 and Fe_2O_3, respectively.

C. Characterization

Micromeritic Autochem 2920 Chemisorption Analyzer apparatus was used to measure the temperature programmed reduction (TPR). The reducing gas (10% CO) in N_2 was fed at a flow rate of 20 mL min^{-1} (STP). The 50 mg of samples were then heated up to 900 °C, at a rate of 10 °C min^{-1}. For the kinetic study, various heating rates (10, 13, 15 °C min^{-1}) were applied to the samples. The carbon monoxide consumption was monitored using a thermal conductivity detector (TCD). For the characterization of the reduced iron oxide, X-ray diffraction (XRD) Bruker AXS D8 Advance type with an X-ray radiation source of Cu Kα (40 kV, 40 mA) was used to record the 2θ diffraction angle from 10-80 degree at wavelength (λ = 0.154 nm) to detect the lattice of the structures. The crystalline phase of the samples obtained were matched with standard diffraction (JCPDS) files.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization by TPR

Fig. 1 shows the TPR profiles of prepared Ce-Fe_2O_3 and non-doped Fe_2O_3 in isothermal reduction under 10% CO in nitrogen. The TPR profile of Fe_2O_3 and Ce-Fe_2O_3 signified 3 reduction events (represented I, II and III). Event I is owing to peak displayed at lower temperature showing the reduction of $Fe_2O_3 \rightarrow Fe_3O_4$, while event II and event III are subsequent to reduction steps of $Fe_3O_4 \rightarrow FeO$ and $FeO \rightarrow$ metallic Fe, respectively.

Fig. 1 TPR profile of Fe_2O_3 and Ce-Fe_2O_3
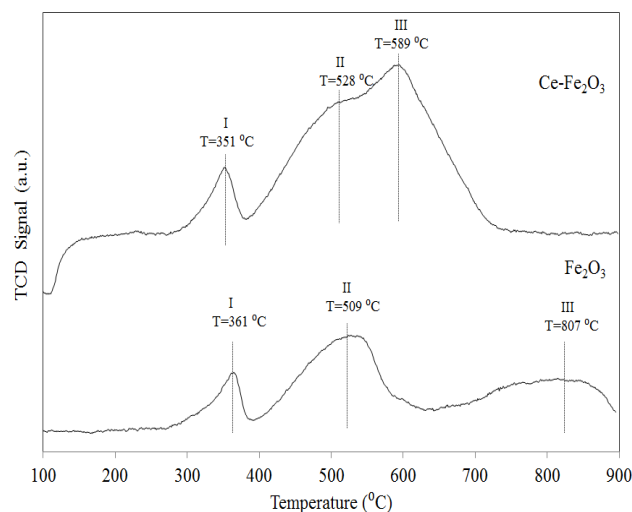
From the results, three reduction events of Fe_2O_3 were represented by three peaks around 361 °C (I), 509 °C (II) and 807 °C (III), showing a stepwise of Fe_2O_3 to Fe through Fe_3O_4 and FeO as an intermediate. While referring to the TPR pattern of Ce-Fe_2O_3, it should be noted that there were shifted for all events toward the low temperature region as compared to Fe_2O_3. The temperature for the peak obtained for event I was 351 °C and for further higher temperature, peaks for event II and II were found to be overlapping with one another with event II was observed as a shoulder at temperature 528 °C and event III give peak at 589 °C. This also in agreement with studies by Khan & Smirniotis [9] as promoting iron oxide with ceria (CeO_2) reduction in hydrogen atmosphere give the reduction peaks of event II and III shifted to lower temperature.

Moreover, the reduction process of Ce-Fe_2O_3 shows that the event III which the formation of Fe has accomplished at

700 °C which display a temperature lower than non-doped Fe_2O_3 (900 °C) as it has been confirmed by XRD analysis. Better reducibility of Fe_2O_3 after introduction of Ce was also in agreement with Zhu *et al.* (2013) as Ce doping heightened the reducibility of lattice oxygen of Fe species [10]. The residual obtained after each of the selected reduction temperature will confirm the phase formation by recording the XRD patterns.

B. Catalyst Characterization by XRD

Fig.2 depicts the XRD diffractogram of prepared Ce-Fe_2O_3 and fresh Fe_2O_3 before and after reduction with carbon monoxide. For single oxide, the pure iron oxide correlates with Fe_2O_3 phase (hematite, JCPDS 74-6271). From XRD pattern shown in Fig. 2, the 2θ Fe_2O_3 main peaks reveal the presence of contribution at about 24.2, 33.2, 35.7, 40.9, 49.5, 53.5, 57.2, 62.4, 64.2, 72.4 and 75.7. With the addition of Ce the peaks described above have slightly shifted toward the higher angles. This phenomenon is mainly because the lattice constant has changed with the interference of Ce element present. This can be attributed to the small atom radius of Fe (0.126 nm) compared to the atomic radius of Ce (0.181 nm) giving the lattice parameters and lattice spacing changed. The crystallinity of Ce loaded Fe_2O_3 was improved as shown by the diffraction peaks of fresh prepared Ce-Fe_2O_3. Furthermore, a mix phase corresponding $FeCe_2O_4$ was also observed.
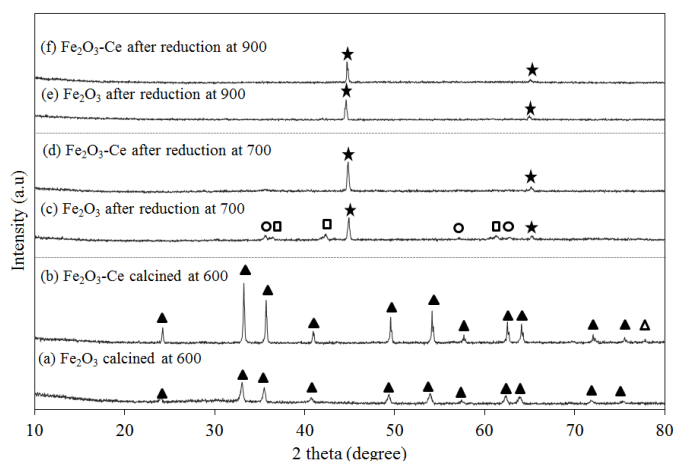

Fig. 2 XRD pattern of (a) fresh Fe_2O_3 calcined at 600 °C, (b) Ce-Fe_2O_3 calcined at 600 °C, (c) Fe_2O_3 after reduction by CO at 700 °C and (b) Ce-Fe_2O_3 after reduction by CO at 700 °C. ( ) Fe_2O_3, ( ) Fe_3O_4, ( ) FeO, ( ) metallic Fe and ( ) $FeCe_2O_4$

To further explore the role of Ce towards the reduction behaviour of Fe_2O_3, the samples were collected and XRD patterns were measured. The collected samples were chosen in accordance to the TPR pattern of Ce-Fe_2O_3 is expected to be completely reduced to metallic Fe at a temperature of 700 °C. For the comparison, Fe_2O_3 was also collected at 700 °C and XRD patterns were also measured. Ce as a doped to Fe_2O_3 could enhance the low-temperature reducibility of Fe_2O_3 as confirmed by the XRD patterns, which Ce-Fe_2O_3 gives only metallic Fe diffraction peak, while Fe_2O_3 still consist of the remaining unreduced $Fe3O_4$ and FeO at temperature of 700 °C.

C. Activation energy (Ea)

According to Wimmers's method [11], the activation energy can be calculated from TPR data by using equation (5) below:

$$\ln (\Psi/T_{max}) = -Ea/RT_{max} + \ln (AR/Ea) + C \qquad (5)$$

The activation energy is achieved from the shift of rate maximum temperature (T_{max}) against the heating rate (Ψ). If a straight line graph is obtained from the plot of $\ln (\Psi/T_{max})$ versus $1/ (T_{max})$, the slop is Ea/R which R is the gas constant. TPR measurements with heating rate of 10 °C/min, 13 °C/min and 15 °C/min were carried out to evaluate the activation energy. The results showed that by increasing the heating rate, the maximal temperature shifted to a higher temperature as shown in Fig. 3.
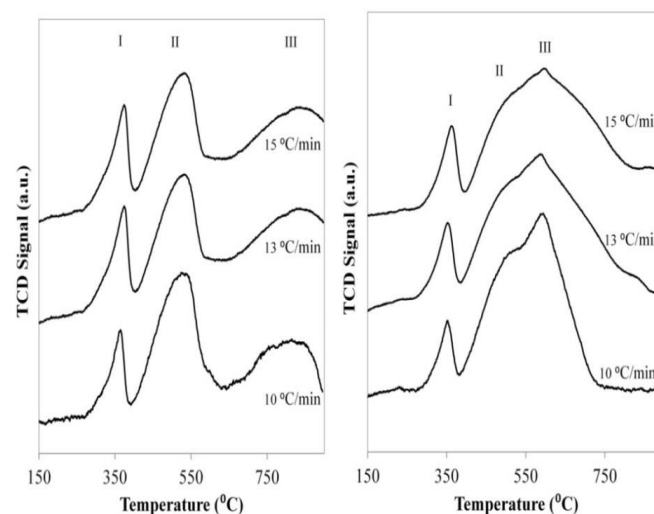

Fig. 3 TPR profiles of (a) Fe_2O_3 reduction by carbon monoxide with heating ramp of 10 °C/min, 13 °C/min and 15 °C/min and (b) Ce-Fe_2O_3 reduction by carbon monoxide with heating ramp of 10 °C/min, 13 °C/min and 15 °C/min

To briefly describe the process, we considered that during the TPR analysis, three steps involve when the doped and undoped iron oxides were reduced by carbon monoxide. The process was described in equation (6) below with the rate constant of k1, k2 and k3,

$$Fe_2O_3 \xrightarrow{k1} Fe_3O_4 \xrightarrow{k2} FeO \xrightarrow{k3} Fe \qquad (6)$$
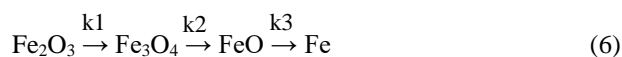
The E_a of Fe_2O_3 and Ce-Fe_2O_3 by referring to their transition phase was shown in Table I. The results suggest that by adding Ce metal into iron oxide will lower the reduction temperature owing to the decrease of the E_a value by 3.32% to 10.96%. This also in agreement with previous work by Ryu et al. [12] and Shafazila et al. [13], they use Ru as a metal additive to lower the reduction temperature of iron oxide in H_2 and CO atmosphere, respectively.

Furthermore, in Table 1, it has been seen that the activation energy for reduction steps of $Fe_2O_3 \rightarrow Fe_3O_4$ is higher compared to the two subsequent reduction steps $Fe_3O_4 \rightarrow FeO \rightarrow Fe$. The values were unpredicted but somehow the pattern is almost similar to the activation energy obtained by Munteanu et al. [14] for reduction of

fresh α-Fe$_2$O$_3$ by 10% hydrogen in argon with the reduction steps of Fe$_2$O$_3$ → Fe$_3$O$_4$ give 139.2 kJ mol^{-1} and Fe$_3$O$_4$ → FeO and FeO → Fe were 77.3 and 85.7 kJ mol^{-1}, respectively [14].

TABLE I
THE E$_A$ OF FE$_2$O$_3$ AND CE-FE$_2$O$_3$ ACCORDING TO THE TRANSITION PHASE

Sample	Fe$_2$O$_3$ → Fe$_3$O$_4$	Fe$_3$O$_4$ → FeO	FeO → Fe
	E$_a$^{I} (kJ mol^{-1})	E$_a$^{II} (kJ mol^{-1})	E$_a$^{III} (kJ mol^{-1})
Ce-Fe$_2$O$_3$	136.5	81.4	89.3
Fe$_2$O$_3$	141.2	82.5	100.3

IV. CONCLUSIONS

The kinetics and reduction behaviour of Cerium doped iron oxides and undoped iron oxide were investigated and compared using temperature programmed reduction (TPR) technique and characterized by X-ray diffraction spectroscopy (XRD) leads to the following conclusions:

- Cerium doped iron oxides have shown the enhancement on the reduction activity as confirmed by the XRD patterns which only metallic Fe peak was observed at the reduction temperature of 700 °C.
- Well dispersed of the Ce, present of a trace amount of FeCe$_2$O$_4$ and the decrease of the activation energy concerning to all transition phases (Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO → Fe) were the factors contributing to low reduction temperature of Ce-Fe$_2$O$_3$ compared to undoped one.

ACKNOWLEDGEMENT

REFERENCES

[1] K. Li, M. Haneda, Z. Gu, H. Wang, and M. Ozawa, "Modification of CeO$_2$ on the redox property of Fe$_2$O$_3$," *Materials Letters,* vol. 93, pp. 129-132, 2013.

[2] E. R. Monazam, R. W. Breault, and R. Siriwardane, "Reduction of hematite (Fe$_2$O$_3$) to wüstite (FeO) by carbon monoxide (CO) for chemical looping combustion," *Chemical Engineering Science,* vol. 242, pp. 04–210, 2014.

[3] E. Lorente, J. Herguido, and J. A. Peña, "Steam-iron process: Influence of steam on the kinetics of iron oxide reduction," *International Journal of Hydrogen Energy*, vol. 36 (21), pp. 13425–13434, 2011.

[4] Z. Chen, J. Dang, X. Hu, and H. Yan, "Reduction kinetics of hematite powder in Hydrogen," *Metals*, vol. 8(751), pp. 1–10, 2018.

[5] Z. Chen, C. Zeilstra, J. Stel, V. Der, J. Sietsma, and Z. Chen, "Review and data evaluation for high-temperature reduction of iron oxide particles in suspension in suspension," Ironmak & Steelmak, pp. 1–7, 2019.

[6] H. Zhao, D. Zhang, F. Wang, T. Wu, and J. Gao, "Modification of ferrite–manganese oxide sorbent by doping with cerium oxide," *Process Safety and Environment Protection,* vol. 86 (6), pp. 448–454, 2008.

[7] K. M. Dunnick, R. Pillai, K. L. Pisane, A. B. Stefaniak, E. M. Sabolsky, and S. S. Leonard, "The effect of Cerium Oxide nanoparticle valence state on reactive oxygen species and toxicity," *Biological Trace Element Research*, vol. 166, pp. 96–107, 2015.

[8] W. Dow, Y. Wang, and T. Huang, "TPR and XRD studies of yttria-doped ceria/alumina-supported copper oxide catalyst," *Applied Catalysis A: General,* vol. 190, pp. 25–34, 2000.

[9] A. Khan, and P. G. Smirniotis, "Relationship between temperature-programmed reduction profile and activity of modified ferrite-based catalysts for WGS reaction," *Journal Molecular Catalysis B: Enzymatic*, vol. 280, pp. 43–51, 2008.

[10] X. Zhu, Y. Wei, H. Wang, and K. Li, "Ce-Fe oxygen carriers for chemical-looping steam methane reforming," *International Journal of Hydrogen Energy*, vol. 8, pp. 253, 2013.

[11] O. J. Wimmers, "Analytical expressions for temperature programmed reduction patterns using solid-state kinetics," *Thermochimica Acta*, vol. 95, pp. 67–72, 1985.

[12] J.-C. Ryu, D.-H. Lee, K.-S. Kang, C.-S. Park, J.-W. Kim, and Y.-H. Kim, "Effect of additives on redox behavior of iron oxide for chemical hydrogen storage," *Journal of Industrial Engineering Chemistry,* vol. 14 (2), pp. 252–260, 2008.

[13] T. Shafazila, T. Saharuddin, F. Salleh, A. Samsuri, and R. Othaman, "Influence of noble metal (Ru , Os and Ag) on the reduction behaviour of Iron Oxide using Carbon Monoxide : TPR and kinetic studies," International Journal of Chemical Engineering and Applications, vol. 6(6), pp. 405–409, 2015.

[14] G. Munteanu, L. Ilieva, and D. Andreeva, "Kinetic parameters obtained from TPR data for α-Fe$_2$O$_3$ and Au/α-Fe$_2$O$_3$ systems," *Therrnochimica Acta,* vol. 291, pp. 171–177, 1997.