

REDUCTION KINETICS OF LANTHANUM MODIFIED Ni/ γ -Al₂O₃ OXYGEN CARRIER FOR CLC

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Summary

The reduction kinetics of Ni on La modified γ -Al₂O₃ oxygen carrier is investigated using temperature programmed reduction as well as the CREC fluidized Riser Simulator data. The power law, the shrinking-core and the nucleation-nuclei growth models are considered to describe the experimental reduction. Results show that the nucleation-nuclei growth model appropriately describes the experimental data with adequate statistical fitting indicators of the model parameters. The activation energy of the reduction for La modified Ni/La- γ -Al₂O₃ is found to be significantly lower than that of the Ni/ γ -Al₂O₃ sample, with this observation confirming the positive influence of the modification of γ -Al₂O₃ support by the addition of La.

Keywords

CO₂ capture, utilization and sequestration

Introduction

Mitigation of greenhouse CO₂ gas emissions is one of the major challenges of the 21st century. In this respect, chemical looping combustion (CLC) is considered as one of the promising approaches for CO₂ capture from fossil fuel based power generation¹.

CLC provides a novel process for fuel combustion with inherent CO₂ separation. It involves contacting of a solid fluidizable oxygen carrier with a fuel in a combustor reactor, where the oxygen carrier transfers the oxygen promoting the burning of the fuel with formation of CO₂ and water. The reduced solid is then returned to an oxidizer to form a metal oxide upon reacting with air. Thus, air never contacts the fuel to be burned directly. Furthermore, the CO₂ in the combustion gases is not diluted by N₂, as usually happens in conventional combustion processes. In this manner, CO₂ can be recovered at a low cost. In addition, CLC also minimizes NO_x formation since the fuel burns in the combustor where air is absent and with no flame. The captured CO₂ from CLC can be used in enhanced oil recovery from pressure depleted petroleum reservoirs⁽¹⁻³⁾.

This communication presents the solid-state kinetics of the reduction of a lanthanum modified Ni/La- γ -Al₂O₃ oxygen carrier involved in a fluidized bed CLC process.

Kinetic Modeling

Three models are considered in the present study: (1) power law, (2) shrinking-core and (3) nucleation and nuclei growth models. The power-law relation can be expressed in terms nickel oxide conversion having Arrhenius type of temperature dependant function. Therefore, the power law relation can be represented as⁴:

$$\frac{dX_p}{dt} = k_0 \exp\left[\frac{-E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right](1 - X_p)^\alpha (1 - aX_p)^\beta \quad (1)$$

The shrinking core model considers that the metal-metal oxide interface moves towards the center of the solid oxygen carrier particle, leaving behind a porous metallic/metal oxide product layer through which the gaseous reactant and product diffuses. Given, the size of the particles (maximum 110 μ m) used for this investigation has already found to be free from mass transfer limitations⁵, a chemical reaction controlled regime for the unreacted shrinking core model can be formulated as:

$$\frac{dX_p}{dt} = k_0 \exp\left[\frac{-E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right](1 - X_p)^{2/3}(1 - aX_p) \quad (2)$$

According to the nucleation and nuclei growth model, the gas-solid reaction proceeds as: (i) activation of sites, (ii) formation of nuclei, (iii) growth and further formation of nuclei, (iv) overlap of nuclei, (v) ingestion of a

nucleation site and (vi) continued crystal growth⁶. Based on the above steps, both the reduction and oxidation of the supported metal oxide can be described as^{3,6}.

$$\frac{dX_p}{dt} = nk_0 \exp\left[\frac{-E_{app}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] (1 - X_p) [-\ln(1 - X_p)]^{\frac{(n-1)}{n}} (1 - aX_p) \quad (3)$$

Model Discrimination and Parameters Estimation

The models presented in the previous section have been evaluated using the temperature-programmed reduction (TPR) data obtained at conditions where temperature is changed from ambient to 950 °C. The applicability of the established heterogeneous model is further validated by developing experiments in a CREC Riser Simulator⁷ at isothermal fluidized bed conditions and using methane as a fuel.

Model discrimination is based on correlation coefficients (R^2), lowest SSQ (sum of square) residuals and smallest individual parameter confidence intervals. Given the R^2 values and parameters spans ($\pm 5\%$) obtained, it is concluded that the nucleation and nuclei growth model best fits the experimental data, using a “n” value of one. The random nucleation model ($n = 1$) is also consistent with the stable crystallite size and metal dispersion observed during the repeated redox cycles². When comparing the power law, nucleation and shrinking core model, the nucleation model shows a more favorable R^2 values and a lower SSQ values. Fig. 1 displays the comparison between the experimental and nucleation model predicted conversions during reduction (in TPR) cycles of the oxygen carrier samples.

The estimated value of the activation energy for the La modified Ni/La- γ Al₂O₃ sample, is found to be 73 \pm 2 kJ/mole, which is significantly lower than the activation energy for the unmodified Ni/La- γ Al₂O₃ sample (104.5 \pm 3 kJ/mole). This indicates the unmodified sample requires higher activation energy, with this reflecting the increased difficulty of reducing the nickel phase of the oxygen carrier due to the intense interaction between nickel and alumina.

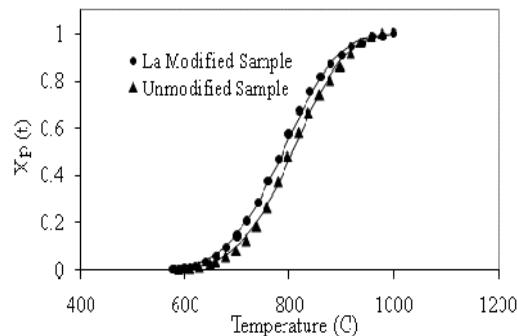


Fig. 1: $X_p(t)$ plots for programmed temperature reduction: (●) Ni/La- γ Al₂O₃ and (▲) Ni/ γ Al₂O₃ samples. Solid lines are the model predicted values. Note: More than 10 extra data points in between reported data. Extra data not shown to avoid graph overcrowding

Fig. 2 displays a parity plot for the experimental versus model predicted values of Ni/La- γ Al₂O₃ oxygen carrier conversion with nucleation and nuclei growth model during the reduction cycles in the CREC Riser Simulator using methane as reducing gas (fuel) at 600°C and 680 °C temperature levels. One can notice from this figure that the nucleation and nuclei growth model fits the CREC Riser Simulator experimental data adequately providing a good correlation between the experimental and the predicted conversions.

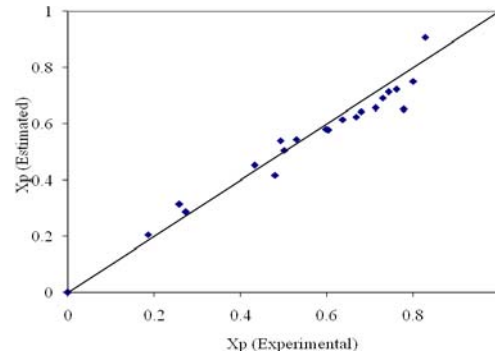


Fig.2. Experimental versus nucleation-nuclei growth model predicted values for Ni/La- γ Al₂O₃ in the CREC Riser Simulator using CH₄ as fuel (at 600-680 °C, 1 atm) Note: Reported data points are the average of at least 3 repeats.

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