

Kinetic study of combined steam and CO₂ reforming of methane over Ni-Sr/MgO-ZrO₂ catalyst

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Abstract. Combined steam and CO₂ reforming of methane (CSCRM) has gained increasing attention as a potential solution to mitigate global warming and addressing the demand for alternative energy resources. In this study, the reaction kinetics of CSCRM over high-performance Ni-Sr/MgO-ZrO₂ bimetallic catalyst is investigated in a fixed bed reactor. The rate of reaction was analyzed at a temperatures ranging from 700-800°C and reactant partial pressures of CH₄, CO₂ and H₂O ranging from 5-50 kPa. The apparent activation energies for CH₄ and CO₂ consumption were found to be 20.94 kJ/mol and 27.53 kJ/mol respectively. The experimental results obtained were then fitted with a Power Law kinetic model and showed good agreement with R² values of 0.86-0.91.

Introduction

As economies thrive to grow with steady increase in global population, the demand for energy is conveniently anticipated to rise. According to recent findings, energy consumption at global scale is soaring at a rate of approximately 1-2% per year [1]. This ever increasing energy consumption globally is causing proliferation of greenhouse gas (GHSs) as these emissions lead to detrimental phenomenon of global warming. As a direct consequence, technological advancement in the H₂ production and synthesis gas (syngas) has gained momentum in recent years. Hydrogen is a fuel that is considered environmental friendly and suitable for use in fuel cells [2]. On the contrary, syngas is a combination of hydrogen and carbon monoxide that is used in a variety of petrochemical and metallurgical processes such as the production of methanol or oxo-chemicals. Syngas is used as a varied feedstock in the Fischer-Tropsch process, which is used to produce methanol and hydrocarbons [3]–[5].

Dry reforming of methane (DRM) is a method used for producing syngas that involves effective utilization of two greenhouse gases namely CH₄ and CO₂ [6], [7]. Steam methane reforming (SMR) technique, a two-step reforming method along with Autothermal reforming (ATR) technique are considered to be conventional reforming approaches widely utilized in industrial sector. Another different technique known as combined CO₂ and steam reforming (CSCRM) is a single-step reforming method. The enticing benefit of this method is that it reduces the amount of

catalyst coking and modifies the ratio of hydrogen to carbon monoxide in syngas for methanol and hydrocarbons to be produced. Another potential approach for methane reforming to generate syngas is by combining hydrogen and carbon monoxide that is used as a source gas. This process is called Thermal Partial Oxidation (POX) [8]. However, this process has some disadvantages such as soot production and poor hydrogen yield [9], [10]. Therefore, the CSCRM method is considered to be energy efficient that utilizes waste flue gases, thereby rendering a viable approach for high quality syngas production [11], [12].

CSCRM reforming employs noble metals as catalyts that are widely recognized for their exceptional C-H bond cleavage, excellent catalytic characteristics and exhibit good resistance against coking. However, due to their exorbitant costs and rare availability, these precious metals are only rarely utilized in major commercial applications [13], [14]. These limitations prompted the non-nobel Nickel (Ni) metal which is affordable and easily accessible in vast quantities that made it the most promising candidate for the role of active metal replacement. Ni has been chosen above other transition metals for CSCRM reformation because of its catalytic performance, which is akin to that of noble metal. Even though Ni is frequently utilized in the reforming process, coke deposition and metal sintering are the two main downsides that might cause the catalyst to become inactive [15], [16]. In order to eviscerate catalyst deactivation, promoters (as pre-treatment strategy) mixed with oxides as support, improved catalyst synthesis technique and bimetallic systems are employed.

The kinetics and mechanistic of methane reforming over noble and non-noble catalysts had been extensively studied in the last decade. Oemar et al. [17] investigated the mechanism and kinetic modeling of La-doped Ni/SBA-15. According to the authors, the rate-determining step (RDS) of the DRM reaction in the 1% La promoted Ni/SBA-15 catalyst is the CH₄ decomposition. This step has low activation energy of 40.8 kJ mol⁻¹ when compared to other supported Ni catalysts. During CH₄ decomposition, the widely dispersed Ni catalyst has elevated level of activity which results in high CH₄ conversion. According to Gallego et al. [18], the CH₄ adsorption and subsequent CH₄ breakdown were caused by the Ni active sites. In addition, Jun et al. [3] investigated the kinetics modelling of Ni-CeO₂/MgAl₂O₄ catalysts and reported that solely the H₂/CO ratio was impacted by CO₂ % under the Ni-based catalyst, despite the fact that both methane conversion and the H₂/CO ratio were considered to be affected by wall temperature.

In this work, the kinetics of the Ni-Sr/MgO-ZrO₂ bimetallic catalyst for CSCRM reactivity were investigated at temperatures ranging between 600 °C to 800 °C under typical atmospheric pressure. The effect of the reactant partial pressure was considered a vital aspect in comprehending CSCRM kinetics and reactor design. The obtained data was analyzed using the Power law kinetic model for reaction kinetics.

Methodology

The kinetic data of CSCRM reaction over the screened bimetallic catalyst was collected under differential conditions using a fixed bed reactor used for catalyst screening. 0.1g catalyst mass was taken. Before carrying out the kinetic experiments at each stage of the reaction temperature ranging from 700 to 800 °C, the screened bimetallic catalyst was decreased to include 50% hydrogen and nitrogen. The temperature of the reduction was brought up to 800 °C at a rate of 5 °C/min and then maintained at that level for two hours so that active metals could be generated in the catalyst. Then, a combined flow of CH₄, CO₂, H₂O, and N₂ with a total of 60 mL min⁻¹ was introduced into the reactor. The output gas mixtures were sent via TCD online gas chromatography (model: (Agilent 7820) for examination. After reactant stabilization in a reactant stream for an hour, the first set of kinetic data was acquired. The change in the partial pressures of the reactants (CH₄, CO₂ and H₂O) alters the total pressure of the system. In order to maintain and keep the total pressure constant, nitrogen gas was introduced in the feed stream that acted as a balancing inert gas.

Based on the preliminary studies, the kinetic investigations were examined without transport limitations. The power law model (1) is fitted to the experimental kinetic data to determine the kinetic parameters. The effect of temperature on the kinetic constant is accounted by including the Arrhenius Equation (2) in the model.

$$r = k(P_{CH_4})^\alpha (P_{CO_2})^\beta (P_{H_2O})^\gamma \quad (1)$$

where r_i represents the reaction rates for the consumption of CH_4 and CO_2 , as well as the formation rates of H_2 and CO . The partial pressure of CH_4 , CO_2 and H_2O are denoted as P_{CH_4} , P_{CO_2} and P_{H_2O} respectively while α , β and γ are the corresponding reaction orders for CO_2 , CH_4 , and H_2O reactants respectively.

$$k = Ae^{\frac{-Ea}{RT}} \quad \text{or} \quad \ln k = \ln A - \frac{-Ea}{RT} \quad (2)$$

where A , R , T and Ea represent pre-exponential factor (frequency factor), universal gas constant, reaction temperature and activation energy respectively were used to explain the rate constant of the reaction.

In order to determine the kinetic parameters, including the order of reactions (α , β and γ) and the reaction rate constants (k_i), the rate of reactions for consumption as well as formation have been investigated and compared over a range of temperatures. The parameters were optimized using the Levenberg-Marquardt algorithm. For this purpose, a script was written in MATLAB (MathWorks, Inc.) using the FSOLVE function, where the objective function was the mean of absolute difference between the predicted and actual experimental data values (3). The summary of these kinetic parameters is shown in Table 1.

$$\sum_i^n \frac{|r_{pt} - r_{expt}|}{n} \quad (3)$$

Results and Discussion

This section presents the results and a discussion of the kinetic study of CSCRM reaction over the Ni-6Sr/MgO-ZrO₂ (6Sr) catalyst. The kinetic behaviors of the CSCRM over the optimum 6Sr catalyst were studied, where the effect of temperature (700-800 °C) and partial pressures of the reactants (CH_4 , CO_2 and H_2O) were investigated. The experimental kinetic data of the CSCRM was fitted to Power-law kinetic model.

Effect of CH_4 Partial Pressure

The impact of CH_4 partial pressure at various temperatures was investigated by keeping the partial pressures of CO_2 and H_2O constant at 15 and 30 kPa respectively and altering the CH_4 partial pressure between 35 and 50 kPa as shown in Figure 1. At all temperatures, the consumption rates of CH_4 and CO_2 increased to the point at which the CH_4 partial pressure was 45 kPa. Beyond this point, the increase retarded down significantly at 50 kPa CH_4 partial pressure. Analyzing the effect of the rate of formation of H_2 and CO on CH_4 partial pressure, a similar behavior pattern was also observed (see Fig 1 c and d). The decrease in catalytic efficiency in an environment with a high concentration of CH_4 may be attributed to an increase in the rate at which CH_4 is fissured into carbonaceous species, that encapsulates the active Ni metallic sites. [19]. Therefore, the amount of extra methane in the feed did not have an impact on the reactant conversion and yield product.

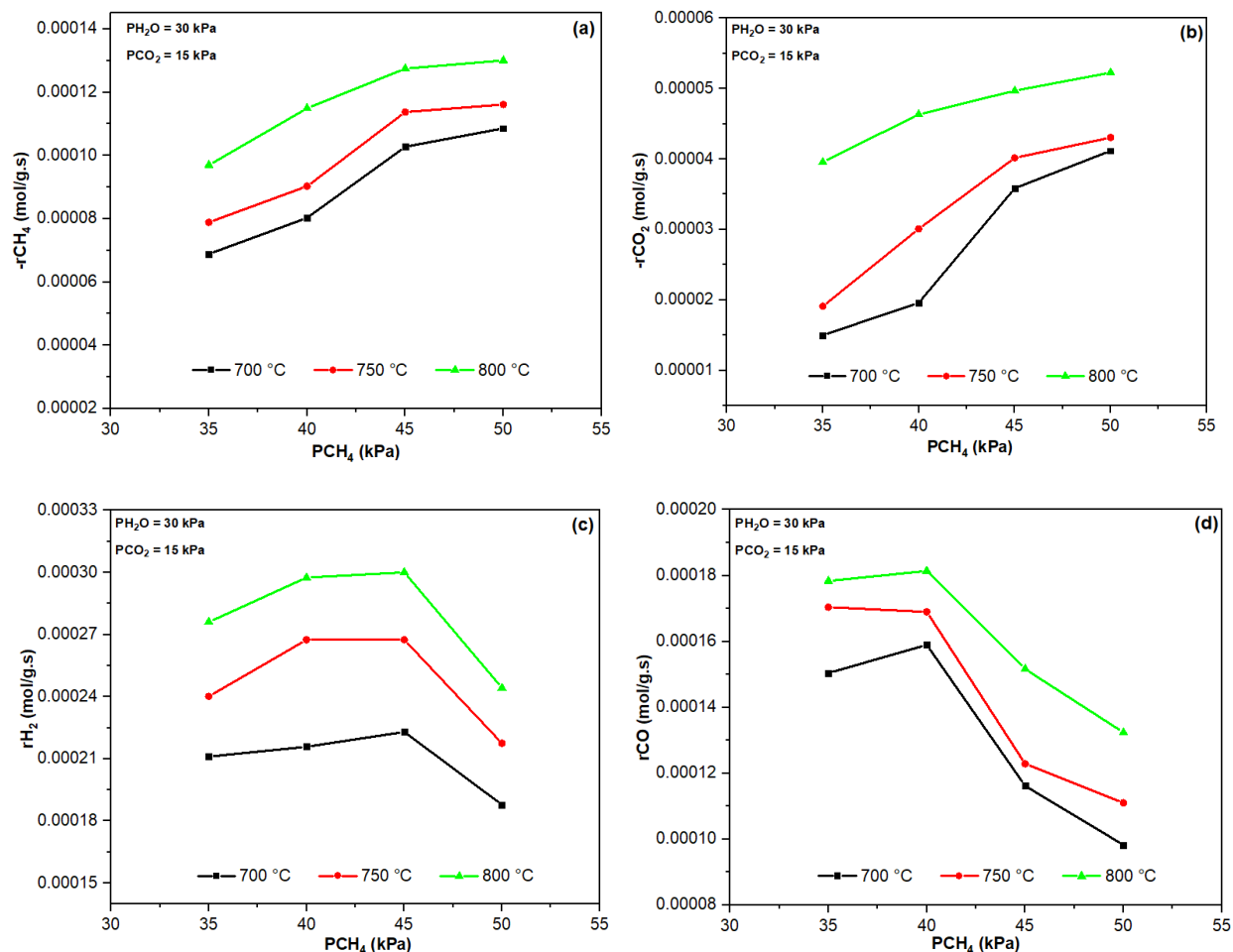


Figure 1: Effects of CH_4 partial pressure on the consumption rates of (a) CH_4 (b) CO_2 and formation rates of (c) H_2 (d) CO

Effect of CO_2 Partial Pressure

To investigate the effect of partial pressure of CO_2 on the rate of consumption and generation of products, the partial pressures of PCO_2 was varied from 5 to 20 kPa while the partial pressures of PCH_4 and PH_2O were held constant at 45 and 30 kPa respectively. Figure 2 (a-b) illustrates that there was a considerable rise in the consumption rates of both CH_4 and CO_2 as the pressure of PCO_2 raised from 5 to 20 kPa. It is assumed that the increase in consumption rates might be due to the amplification of the simultaneous DRM and WGS response over SRM. This finding was in line with studies that were done in the past [20], [21]. In addition, the effect of the partial pressure of CO_2 on the formation of H_2 and CO was also investigated. In the range of 5 to 20 kPa, a rise in the partial pressure of CO_2 caused a reduction in the rate at which H_2 was produced, while there was an increase in the rate for CO formation. The results are shown in Figure 2 (c-d) for temperatures of 700, 750, and 800 °C. The results shown here depict that hydrogen gas was used up at the RWGS reaction, whereas all the DRM, SRM, and RWGS processes result in the formation of extra carbon monoxide.

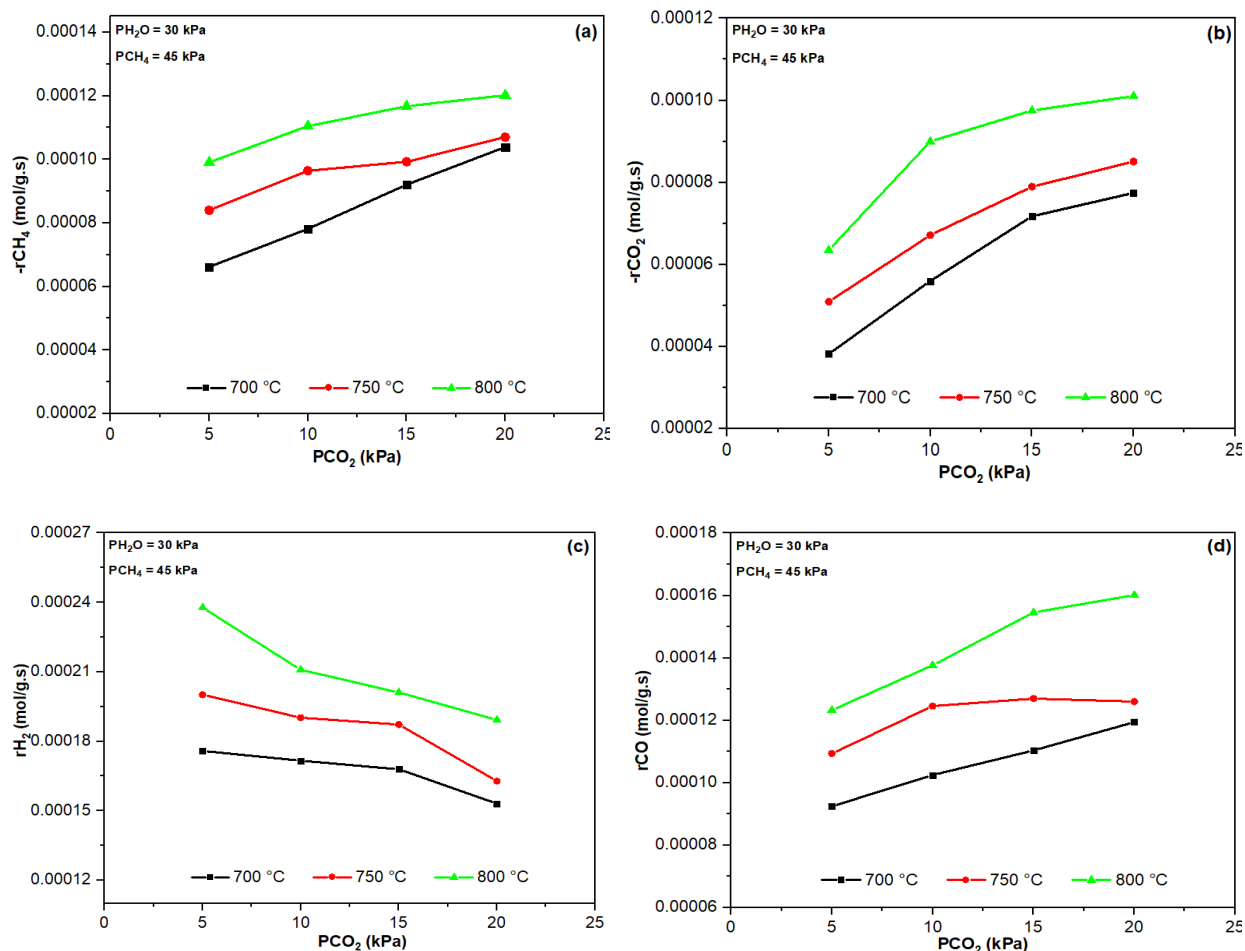


Figure2: Effects of CO₂ partial pressure on the consumption rates of (a) CH₄ (b) CO₂ and formation rates of (c) H₂, (d) CO

Effect of H₂O Partial Pressure

Apart from CO₂ reactant, H₂O is another oxidizing agent playing an important role in CSCRM reaction. The role of H₂O partial pressure in CSCRM reaction was investigated at fixed PCH₄ = 45 kPa and PCO₂ = 15 kPa while PH₂O was varied from 15 to 30 kPa as shown in Figure 3. The CH₄ consumption rate increased substantially with rising PH₂O from 10 to 30 kPa whilst a decrease in CO₂ consumption rate was observed at 700, 750 and 800 °C respectively as shown in Figure 3 (a-b). CH₄ consumption was directly proportional to PH₂O formation presumably due to the improvement of steam gasification of deposited carbon produced from CH₄ decomposition. In the thermodynamic study of CSCRM using Gibbs free energy minimization approach, Ozkara-Aydnolu [22] found that regardless of reaction temperature, the conversion of CH₄ increased noticeably with growth in H₂O:CH₄ ratio from 0:1 to 3:1. The decline in CO₂ consumption rate and increase in CH₄ consumption rate could suggest that SRM was more preferable than DRM reaction. Although both CO₂ and H₂O possess oxidizing properties, CH₄ would likely react with H₂O instead of CO₂ owing to the greater stable nature of CO₂ molecules as to H₂O species. The rate of the generation of H₂ increased as the partial pressure of H₂O in the atmosphere rose (see Fig. 3 c). In addition, the introduction of steam led to an increase in the rate of H₂ production through SRM and WGS reactions, which in turn caused the rate of CO formation to first accelerate before eventually slowing down (see Fig. 3 d).

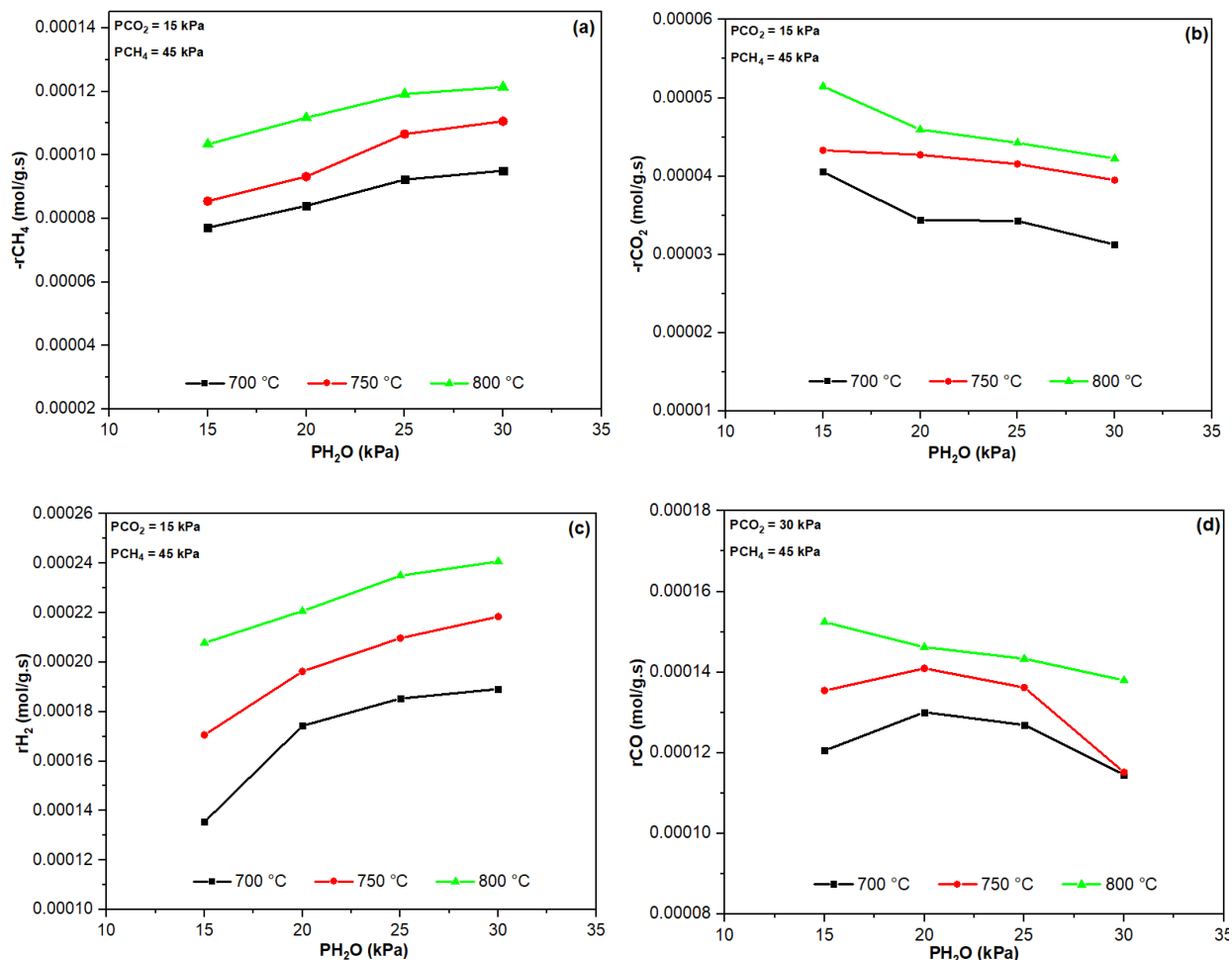


Figure 3: Effects of H_2O partial pressure on the consumption rates of (a) CH_4 (b) CO_2 and formation rates of (c) H_2 , (d) CO

Power Law Kinetic Modelling

During the kinetic evaluation of a $Ni/CeO_2-Al_2O_3$ catalyst at a reaction temperature between 700 and 800 °C, the values of apparent activation energy (E_a) for the rate of consumption of CH_4 and CO_2 were estimated to be 20.94 kJ/mol and 27.53 kJ/mol respectively. These values were in agreement with those reported by Karemore et al. [6]. The authors indicated that this tendency may be ascribed to the greater sensitivity of CO_2 to temperature fluctuations than CH_4 . As CH_4 also interacted with steam during the CSCRM reaction, its consumption rate was found to be greater than that of CO_2 . E_a values for the production of H_2 and CO were 19.70 kJ/mol and 23.05 kJ/mol respectively. This explains the reason for higher H_2 production than the yield of CO . This tendency can also be explained based on the impact of the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) on the rate of CO formation [23]. According to the findings of Kathiraser et al. [24], the activation energy required for the methane reforming process over various Ni-based catalysts can range from 26 kJ/mol to 243 kJ/mol.

Table 1: Estimated kinetic parameters for the power-law model

Reaction species	α	β	γ	A (mol/g.s.kPa ^($\alpha+\beta+\gamma$))	Ea (kJ/mol)	R ²
CH ₄	1.247	0.234	0.286	0.000021	20.94	0.910
CO ₂	1.815	0.111	0.508	0.000017	27.53	0.864
H ₂	-0.638	0.016	0.262	0.014	19.70	0.905
CO	1.137	0.167	-0.079	0.078	23.05	0.893

Figure 4 illustrates the adequacy of the power law model by showing the parity plots of the observed rates and the projected rates of the kinetic model. In each instance, the rates that were determined via experimentation had an R² value that is more than 0.85. The experimentally obtained rates were close to the rates that were anticipated using the Power Law kinetic model. It was observed that the predicted rates data fit the Power Law model and were close to the experimental rates, indicating that the kinetic data obtained from the power-law model was adequate to represent the kinetic performance of the Ni-Sr/MgO-ZrO₂ catalyst in CSCRM reforming, although this model could not explain the reaction mechanism.

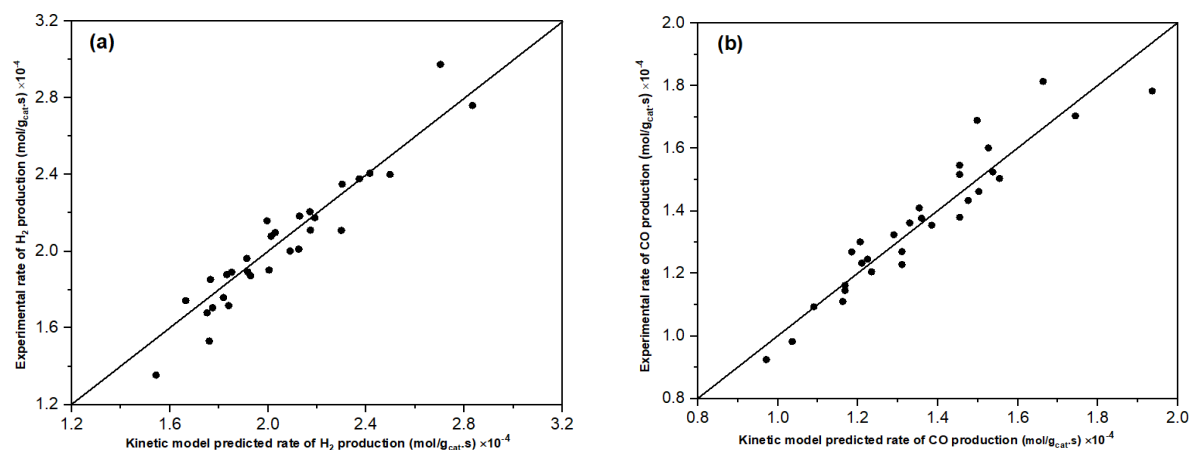


Figure 4: Comparison of the experimental rate with kinetic model predicted rate based on power law model (a) H₂ production (b) CO production

Conclusion

This work investigated the kinetics of the bimetallic catalyst Ni-Sr/MgO-ZrO₂ during the CSCRM reforming under reactant partial pressures ranging from 10 to 50 kPa. The study focused on the reactant impact of the partial pressures (CH₄, CO₂, and H₂O) on the CSCRM process at atmospheric pressure in the temperature range of 700-800°C. The Power Law model was utilized to predict the kinetic modelling of the CSCRM reaction over the ideal Ni-Sr bimetallic catalyst. The apparent activation energy for CH₄ consumption was determined to be 20.94 kJ/mol, while the activation energy for CO₂ consumption was found to be 27.53 kJ/mol. The results showed good agreement between the experimental rates and predicted rates with an R² value above 0.86.

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