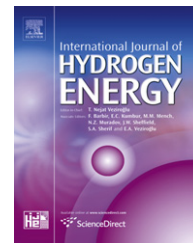


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# Kinetics of methane reforming over Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-catalyzed metallic foam at 650–900 °C for solar receiver-absorbers

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## ARTICLE INFO

### Article history:

Received 20 July 2010

Received in revised form

10 September 2010

Accepted 14 September 2010

Available online 18 November 2010

### Keywords:

Solar heat

Reforming

Thermochemical process

Kinetics

catalyst

Reticulated metallic foam

## ABSTRACT

The kinetics of methane reforming over Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-catalyzed high porosity Ni–Cr–Al foam were examined at temperatures of 650–900 °C in a quartz tubular reactor using an electric furnace. The kinetic data were analyzed by four different types of kinetic models based on the basic, Eley–Rideal, Langmuir–Hinshelwood, and stepwise mechanisms. Validation of the kinetic models was carried out by calculating the determination coefficient  $r^2$  between the predicted and the experimental results for each model. The absolute average deviation percentage (AAD%) between the predicted and the experimental results was also estimated for each model. The kinetic model based on the reversible stepwise mechanism provided the best prediction of the experimental reforming rates with an AAD value of 6% in the range 650–850 °C.

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## 1. Introduction

Currently, hydrogen is mainly produced from fossil fuels, in particular from natural gas consisting primarily of methane. Several hydrogen production processes, such as methane reforming, partial oxidation of heavy oils, catalytic methane decomposition, and coal gasification, have reached maturity for commercial exploitation, and non-commercial hydrogen sources, such as methane pyrolysis, electrochemical processes, thermochemical water-splitting cycles, biomass gasification, and photobiological processes are being developed [1]. The development of renewable energy sources for hydrogen production is a major challenge in providing more sustainable and environmentally acceptable energy supplies for a future low-carbon energy economy. One promising

option is solar thermochemical hydrogen production, which has high potential for solving the problems related to storing and transporting solar energy in chemical form.

In a solar thermochemical process, the endothermic reaction of catalytic steam or CO<sub>2</sub> methane reforming is carried out in a high-temperature reactor heated by concentrated solar radiation. The only energy input to the reforming reaction is supplied by the solar reactor, which is the key point of the whole process of achieving solar energy absorption and conversion into chemicals [2–4]. Solar-driven synthesis gas has calorific values 22–28% higher than that of a methane feedstock:

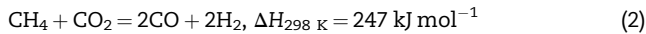


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doi:10.1016/j.ijhydene.2010.09.042



Several types of solar-specific reformer have been developed and demonstrated for solar-driven reforming in large-scale solar tests [5–13]. One of these solar reformers, which has a pressurized volumetric receiver and reformer vessel with a domed quartz window covering the receiver's aperture, was designed to supply process heat from concentrated solar radiation [4]. In the volumetric receiver–reactor, a porous receiver/absorber matrix was catalytically activated for the reforming reaction and directly heated by concentrated solar radiation, which passes through the transparent quartz window and is absorbed by the absorber mounted behind the window. Metal or ceramic foam was selected as the absorber material, depending on the process temperature needed to enable chemical reaction at temperatures of 500–900 °C or higher [14].

Reticulated porous ceramic foams are made of alumina or SiC because of the high mechanical strength of these materials at high temperatures [7,11,13]; the foams are further coated with  $\gamma\text{-Al}_2\text{O}_3$  as a catalyst support to increase the surface area and to ensure catalytic activation of the loaded catalyst. Highly active catalysts based on Rh metal are frequently used for solar  $\text{CO}_2$  reforming of methane [15,16]. In the CAESAR (Catalytically Enhanced Solar Absorption Receiver) project, volumetric solar receiver–reactors with  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ /alumina foam absorbers were constructed and tested for solar  $\text{CO}_2$  reforming of methane on a parabolic dish concentrator capable of using up to 150 kW of solar power [7–9]. In the SCR (Solar Chemical Receiver–reactor) project,  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed alumina and SiC foam absorbers were extensively tested for solar reforming of methane using solar-concentrating systems capable of using up to 100–300  $\text{kW}_{\text{th}}$  [7,11,13]. This technology was scaled up in the SOLASYS (Novel Solar Assisted Fuel Driven Power System) project to 250–400  $\text{kW}_{\text{th}}$ .  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed SiC foam absorbers were tested under solar power inputs of 100–220  $\text{kW}_{\text{th}}$  at reforming temperatures of 700–765 °C [17]. In the ongoing EU project SOLREF (Solar Steam Reforming of Methane Rich Gas for Synthesis Gas Production), the test setup used by the SOLASYS project was scaled up to 400  $\text{kW}_{\text{th}}$ , and aimed to achieve a higher temperature of above 900 °C [18,19].

Reticulated porous metallic foams, which are suitable for use at low flux levels of concentrated solar radiation, have better thermal conductivity and plasticity than those of ceramic foams such as alumina and SiC, resulting in a homogenized temperature distribution on the illuminated surface of the foam absorber and improved resistance to thermal shock caused by temperature variations under fluctuant insolation [13].  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed Ni–Cr–Al metallic foams have been tested for  $\text{CO}_2$  reforming on a laboratory-scale using direct solar-simulated Xe-light irradiation with a relatively low flux [20–23]. Cost-effective Ru catalysts have been extensively used as highly active alternatives to Rh catalysts for use in methane reforming [24–27].  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed Ni–Cr–Al metallic foam showed a greater chemically absorbed power density than  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed alumina foam for the same foam size and similar cell size and surface area under a relatively low average flux of 120–180  $\text{kW m}^{-2}$ . The kinetics of  $\text{CO}_2$  reforming of methane over  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ /metallic foams have been studied at a total pressure of 1 atm and at relatively low temperatures of 600–750 °C [23]. The kinetic model based

on the irreversible Langmuir–Hinshelwood mechanism provided the best prediction of the experimental reforming rates in the range of 600–700 °C.

In the present work,  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed Ni–Cr–Al foam was examined for studying the kinetics of  $\text{CO}_2$  reforming of methane at temperature in the range 650–900 °C. This paper focuses on the kinetics of methane reforming at temperatures above 700 °C. In addition, reverse reactions, which was not taken into consideration in the previous paper [23], was newly built into mechanistic kinetic models. The Arrhenius parameters, such as the activation energies and the adsorption energies, of  $\text{CH}_4$  and  $\text{CO}_2$  were estimated for an appropriate temperature range.

## 2. Kinetic models

Different kinetic models based on the basic (BA), Eley–Rideal (ER), Langmuir–Hinshelwood (LH), and stepwise (SW) mechanisms were tested for analyzing the kinetics of  $\text{CO}_2$  reforming over a  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ -catalyzed Ni–Cr–Al foam. In these kinetic models, reversible reactions, i.e., forward and back reactions, are taken into consideration because of the relatively high reaction temperature and the high methane conversion compared to those in previous kinetic studies [23].

The BA model consists of a simple equilibrium reaction assuming first-order behavior for the  $\text{CH}_4$  and  $\text{CO}_2$  reactant species [28]. The only parameter which needs to be optimized for the BA model is the rate constant.

The models based on the ER mechanism assume that only one of the two reactant species  $\text{CH}_4$  and  $\text{CO}_2$  is adsorbed onto the catalyst surface in adsorption equilibrium. Subsequently, the adsorbed species react with the other reactant from the gas phase, leading directly to production of  $\text{H}_2$  and  $\text{CO}$  [29–31]. As either  $\text{CH}_4$  or  $\text{CO}_2$  can theoretically be regarded as the adsorbed species, two resulting models are considered (ER I and ER II).

The LH model is based on the assumption that both reactant species  $\text{CH}_4$  and  $\text{CO}_2$  are adsorbed onto the catalyst active site in thermodynamic equilibrium, and that the adsorbed  $\text{CH}_4$  and  $\text{CO}_2$  associatively react on the catalyst active site to form  $\text{H}_2$  and  $\text{CO}$ . The adsorbed  $\text{H}_2$  and  $\text{CO}$  are released as  $\text{H}_2$  and  $\text{CO}$  [28,29].

The kinetic expression based on the SW mechanism assumes that  $\text{CH}_4$  is adsorbed onto the catalytic surface and is subsequently dissociated into active carbon and hydrogen, after which the active carbon reacts with the  $\text{CO}_2$  gas phase to form two equivalents of  $\text{CO}$  [28,32].

Validation of the kinetic models was carried out by calculating the determination coefficient  $r^2$  between the predicted and experimental results for each model. The absolute average deviation percentage (AAD%) between the predicted and experimental results was also estimated for each model.

## 3. Experimental procedure

### 3.1. Materials

Table 1 shows the foam absorbers used in the present study. A Ni–Cr–Al alloy foam disk (CELMET; Ni-based alloy containing

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