



Kinetic analysis of the Ru/SiO₂-catalyzed low temperature methane steam reforming

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ARTICLE INFO

Article history:

Received 10 June 2011

Received in revised form

25 November 2011

Accepted 26 November 2011

Available online 6 December 2011

Keywords:

Hydrogen production

Steam reforming

Kinetic mechanism

Model discrimination

ABSTRACT

The performance of a Ru/SiO₂ catalyst for methane steam reforming at 450–550 °C is studied in the present. These conditions are suitable for coupling the fixed-bed reactor with a hydrogen-selective membrane for hydrogen recovery, with the subsequent equilibrium shift. A reaction mechanism based on the dissociative adsorption of steam and methane has been proposed (from a total of six possible mechanisms compared), in terms of the statistical analysis of reaction data obtained at different temperatures and contact times in an integral, lab-scale reactor.

The proposed model shows that hydrogen inhibition plays an important role in the reaction. Finally, the Ru/SiO₂ catalyst prepared in this work is found to be one of the most active catalysts, among other Ru-based catalysts reported in the literature.

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1. Introduction

The manufacture of alternative fuels, such as hydrogen or synthetic gasoline, is currently a mayor challenge in chemical technology. Methane steam reforming reaction plays a key role in the production of these fuels from either natural gas or biogas [1,2]. Nickel catalysts are the most used at industrial scale, which operates at high temperature (600–900 °C), pressure and steam to methane ratio, to minimize coke formation. However, these conditions are not suitable for using novel technologies to separate the products, H₂ and CO₂, such as 'in situ' CO₂ capture [3] or membrane reactors [4,5]. Membrane reactors consist of a multi-tubular fixed-bed reactor equipped with a palladium-based membrane that is selective to hydrogen. Thus, this gas is separated with high purity from the reaction products, and at the same time the shift of the reforming reactor is favored. This reduces the size of the reactor and the required amount of catalyst.

In these situations, an active catalyst providing high reaction rates at low temperatures (<550 °C) is required. In addition, low steam to methane ratios are desirable in order to reduce reactor volume, requiring catalyst less prone to bear carbonaceous deposits. Noble metals (Ru, Rh, Pd, Ir and Pt) are very active for

steam reforming. Among them, Ru and Rh have been shown to be the most active and stable catalyst, but Ru is significantly cheaper [1,6–8].

Due to the economic importance of commercial steam reforming process, the kinetic of methane steam reforming over Ni-based catalysts has been extensively studied. Nevertheless, there is not an agreement in the reaction mechanism and the corresponding kinetic model for methane steam reforming. This is explained by the different nature of the catalyst and the support, the catalyst particle size and metal loading, the catalyst physical structure, the preparation method, or gas temperature, pressure and concentration ranges. Generally, the dissociative methane adsorption reaction is thought to be the rate determining step at most conditions, but at low temperature CO formation reaction may became dominant [3,9–11].

The kinetic models proposed to describe the kinetic behavior consist of Langmuir–Hinshelwood, power-laws equations, and expressions based on microkinetic analysis [12]. Temkin [13] studied the reforming kinetics on a nickel foil: at high temperature (900 °C) the reaction follows a first-order kinetic equation with respect to methane concentration, whereas at low temperature (470–530 °C) hydrogen affects the reaction with negative reaction order. Xu and Froment [14] developed one of the most popular methane steam reforming kinetic models for Ni/MgO–Al₂O₃ at 500–670 °C. The model is a Langmuir–Hinshelwood model accounting for the adsorption of CO, CO₂ and H₂ on the same

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