Kinetic analysis of the Ru/SiO$_2$-catalyzed low temperature methane steam reforming

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ABSTRACT

The performance of a Ru/SiO$_2$ 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/SiO$_2$ 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, H$_2$ and CO$_2$, such as 'in situ' CO$_2$ 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–Al$_2$O$_3$ at 500–670 °C. The model is a Langmuir–Hinshelwood model accounting for the adsorption of CO, CO$_2$ and H$_2$ on the same

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Table 1
Summary of methane reforming kinetic models for Ru-based catalysts from the literature.

Reference	Catalyst	Loading	Dispersion	Kinetic model	Conditions
Rostrup-Nielsen and Hansen [16]	Ru/MgO				550–650 °C 1 atm
Wei and Iglesia [7]	Ru/Al$_2$O$_3$	3.2%	44.2%	$r_f = kp_{CH_4}$ $k = 4.7 \times 10^4 \exp(-10945/T)\,\mathrm{s}^{-1}\,\mathrm{kPa}^{-1}$	550–700 °C 1–5 bar
Berman et al. [17]	Ru/(α-Al$_2$O$_3$ + 4.8% MnO$_x$)	2%		$r_f = \dfrac{kp_{CH_4}}{b_{CH_4}p_{CH_4} + b_{H_2O}p_{H_2O}^{0.5}}$ $b_{CH_4} = 4.42 \times 10^{-6} \exp(5694.2/T)\,\mathrm{atm}^{-1}$ $b_{H_2O} = 8.366 \times 10^{-6} \exp(4531.7/T)\,\mathrm{atm}^{-0.5}$ $k = 2.68\,\mathrm{mol/h\ kg_{cat}\ atm}$	500–900 °C
Carrara et al. [18]	Ru/La$_2$O$_3$	0.6%	5%	$r_f = \dfrac{K_1 k_2 K_3 K_4 p_{CH_4} p_{CO_2}}{K_1 K_3 k_4 p_{CH_4} p_{CO_2} + K_1 k_2 p_{CH_4} + K_3 k_4 p_{CO_2}}$ $K_1 = 1.46 \times 10^{-6} \exp(7242/T)\,\mathrm{kPa}^{-1}$ $k_2 = 2.94 \times 10^3 \exp(-12949/T)\,\mathrm{mol/g_{cat}\,s}$ $K_3 = 4.05 \times 10^8 \exp(15891/T)\,\mathrm{mol/g_{cat}\,s\,kPa}$ $K_4 = 2.04 \times 10^8 \exp(-26226/T)\,\mathrm{mol/(g_{cat}\,s)}$	510–590 °C
Jakobsen et al. [10]	Ru/ZrO$_2$	1%	20%	$r_f = \dfrac{kp_{CH_4}}{[1 + K_{CO}p_{CO} + K_{H_2}(p_{H_2})^{1/2}]^2}$ $k = 4.39 \times 10^7 \exp(-12990/T)\,\mathrm{mol/(g_{cat}\,h\,bar)}$ $K_{CO} = 2.19 \times 10^{-5} \exp(10454/T)\,\mathrm{bar}^{-1})$ $K_{H_2} = 7.31 \times 10^{-6} \exp(8540/T)\,\mathrm{bar}^{-0.5}$	425–575 °C 1.3 bar

adsorption sites occupied by CH$_4$ and H$_2$O; the reactions between adsorbed species are assumed to be the rate determining steps with reaction order <1 in CH$_4$ and <0 in H$_2$.

Kinetic studies for Ru-supported catalysts are scarcer [15]. Table 1 summarizes the most important works carried out to elucidate the kinetic model for methane reforming over Ru-based catalysts. Rostrup-Nielsen and Hansen [16] studied Ni and noble metal catalysts supported on MgO and found that Ru and Rh were the most active ones. Reaction order with respect to methane was found to be about 1 for Ru/MgO in the temperature range of 550–650 °C. Wei and Iglesia [7], who studied methane steam and CO$_2$ reforming in Ru supported on Al$_2$O$_3$, ZrO$_2$, and NaY zeolite, found that the rate limiting step is the dissociative adsorption of methane. No dependency on H$_2$O or CO$_2$ concentration was observed, neither the type of catalyst support has influence on catalyst dispersion. They proposed a first-order kinetic equation on methane concentration in the temperature range of 550–700 °C and total pressure range of 1–5 bar. In the same way, Berman et al. [17] worked with MnO$_x$ promoted Ru/α-Al$_2$O$_3$ catalysts, suggesting reaction orders with respect to methane lower than 1 at 450–500 °C and close to 1 at 700–900 °C (in good agreement with the findings of Wei and Iglesia [7]). Carrara et al. [18] focused their attention on Ru/La$_2$O$_3$ catalysts. After a detailed stability and characterization study, they performed a kinetic study and fitted a model with dependency on CH$_4$ and CO$_2$ concentrations.

Jakobsen et al. [10] studied the kinetics of steam and CO$_2$ methane reforming on Ru/ZrO$_2$ at 425–575 °C and 1.3 bar. The results were consistently modeled using a Langmuir–Hinshelwood expression, developed by considering that the rate limiting step is methane dissociative adsorption. Ru-based catalysts have also been proposed to carry out the reforming of organic feed stokes, such as ethanol [19–21].

As shown in Table 1, the kinetic models proposed for methane reforming on Ru-based catalysts are quite different to each other, mainly depending on the operating conditions and the catalyst preparation method. Moreover, the temperature range of interest for palladium-based membrane reactors (<550 °C) has been scarcely studied. The scope of the present work is to elucidate the behavior of the methane steam reforming reaction at low

temperature (450–550 °C) for a Ru/SiO$_2$ catalyst. For accomplishing this scope, reaction data have been fitted to different mechanistic models proposed in the literature, discriminating between these mechanisms using statistical criteria. The presence of mass transfer limitations has been also considered in this manuscript. Finally, the performance of the catalyst tested in this work has been compared to other Ru catalyst reported in the literature.

2. Experimental

2.1. Catalyst preparation and characterization

The supported Ru catalyst was prepared using a commercial support: SiO$_2$ (silica gel from Fluka). Prior to metal loading the support was calcined in air at 500 °C for 4 h after this treatment the specific surface area of the support was 400 m^2/g. Then the support was impregnated with Ru (4 wt%) by means of the wet impregnation method using an aqueous solution of RuCl$_3$·H$_2$O (Sigma–Aldrich) precursor. After Ru impregnation, the catalyst precursor was dried in air at 110 °C overnight [22].

The Ru/SiO$_2$ catalyst was characterized by BET, TPR-H$_2$, XPS and differential CO adsorption heat-flow microcalorimetry. Characterization results for this catalyst have been detailed in a previous work [6]. Metal dispersion measured by CO chemisorption was 16%. The mean size of Ru particle derived from metal dispersion was 8.4 nm. The shape of the CO adsorption microcalorimetric profile indicates a homogeneous distribution of the ruthenium surface centers for the chemisorption of CO, that is, they mostly have very similar geometry and energetic interaction with the CO. The XPS Ru/Si atomic ratio for Ru/SiO$_2$ sample is nearly the same before and after reaction, suggesting that Ru particles still remain well dispersed after test.

2.2. Experimental set-up

Steam reforming reaction was carried out at atmospheric pressure in a fixed-bed tubular reactor. The reactor with an inner diameter of 11.8 mm was heated in an electric furnace equipped with a programmable temperature controller. A fresh catalyst