Applied Catalysis A: General 471 (2014) 118–125

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

A detailed kinetic model for biogas steam reforming on Ni and catalyst deactivation due to sulfur poisoning

Srinivas Appari[a], Vinod M. Janardhanan[a,*], Ranjit Bauri[b], Sreenivas Jayanti[c], Olaf Deutschmann[d]

[a] *Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Andhra Pradesh 502205, India*
[b] *Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India*
[c] *Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India*
[d] *Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstr. 20, 76131 Karlsruhe, Germany*

ARTICLE INFO

Article history:
Received 21 September 2013
Received in revised form
12 November 2013
Accepted 1 December 2013
Available online 8 December 2013

Keywords:
Biogas
Reforming
Catalyst poisoning
Kinetics
Deactivation
Modeling

ABSTRACT

This paper deals with the development and validation of a detailed kinetic model for steam reforming of biogas with and without H_2S. The model has 68 reactions among 8 gasphase species and 18 surface adsorbed species including the catalytic surface. The activation energies for various reactions are calculated based on unity bond index-quadratic exponential potential (UBI-QEP) method. The whole mechanism is made thermodynamically consistent by using a previously published algorithm. Sensitivity analysis is carried out to understand the influence of reaction parameters on surface coverage of sulfur. The parameters describing sticking and desorption reactions of H_2S are the most sensitive ones for the formation of adsorbed sulfur. The mechanism is validated in the temperature range of 873–1200 K for biogas free from H_2S and 973–1173 K for biogas containing 20–108 ppm H_2S. The model predicts that during the initial stages of poisoning sulfur coverages are high near the reactor inlet; however, as the reaction proceeds further sulfur coverages increase towards the reactor exit. In the absence of sulfur, CO and elemental hydrogen are the dominant surface adsorbed species. High temperature operation can significantly mitigate sulfur adsorption and hence the saturation sulfur coverages are lower compared to low temperature operation. Low temperature operation can lead to full deactivation of the catalyst. The model predicts saturation coverages that are comparable to experimental observation.

1. Introduction

Biogas is an important source of renewable energy produced by the anaerobic digestion of biomass. The composition of biogas depends on the biomass source and duration of digestion process. Generally it contains 50–75% CH_4, 50–25% CO_2, 0–10% N_2, and 0–3% H_2S. Biogas may be combusted to produce electricity or can be converted to synthesis gas by reforming over Rh or Ni catalyst [1–4]. However, the presence of H_2S or other sulfur containing compounds is a major problem for reforming of biogas due to its poisoning effect on most transition metals [5]. Although poisoning of Ni in the presence of H_2S is well known, the mechanistic details of poisoning and regeneration are lacking in the present literature, particularly in biogas environment. The blocking of active catalytic sites is the root cause for poisoning. In general poisoning effect varies exponentially with time on stream and the final activity of the catalyst depends on the uncovered active surface available. The saturation coverage of sulfur and other species depends on the operating temperature, metal loading, and the partial pressure of reacting gases. Catalysts with lower metal loading lose activity at a faster rate compared to catalysts with higher metal loading [6]. Essentially for low metal loading the sulfur adsorption capacity is lower due to the low surface area.

The chemisorption of sulfur on Ni is a reversible process [7]. Therefore, exposing it to appropriate operating conditions can regenerate the sulfur deactivated Ni catalyst. Removal of H_2S from the feed gas can recover the catalyst activity or in other words lower H_2S concentrations in the feed gas leads to lesser extend of poisoning. Since chemisorption is an exothermic process, adsorbed sulfur can be removed by increasing the temperature [8]. Therefore, for any given H_2S partial pressure, high temperature operation leads to low activity loss. Based on the available information in literature and our own experiments this work develops a detailed kinetic model for poisoning of Ni catalyst during biogas reforming. There are several review articles outlining various aspects of catalyst poisoning [9,10]; however, models that deal with catalyst poisoning are really scarce in literature. The general practice in modeling catalyst poisoning is to express the activity, i.e., the ratio of true rate

---

* Corresponding author. Tel.: +91 40 2301 6073; fax: +91 40 2301 6032.
E-mail address: vj@iith.ac.in (V.M. Janardhanan).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.12.002

to the initial rate, as a function of time and poison concentration [11–14]. This work appears to be the first attempt to model sulfur poisoning on Ni catalyst using a detailed kinetic model. The root of the kinetic model is a previously published mechanism for steam reforming of CH_4 on Ni [15]. Additional reactions are incorporated into this mechanism to account for sulfur adsorption, desorption, disproportionation, and recombination reactions. The activation energies for the elementary step reactions are calculated by UBI-QEP method [16]. The developed kinetic model is validated by comparing the model predictions with our own experiments and the experiments reported by other research groups [3,17,18]. These experiments were performed in isothermal fixed bed reactors. Therefore, a one-dimensional fixed bed reactor model is used to simulate the experiments.

2. Reactor model

A one-dimensional transient fixed bed reactor model is used for the simulations presented in this work. Assuming ideal gas behavior and constant pressure, the partial differential equation that describes the species transport in a fixed bed reactor with constant mass flow rate is:

$$\rho\frac{\partial Y_k}{\partial t} = -\dot{m}\frac{\partial Y_k}{\partial x} + \frac{\partial}{\partial x}\left(D^{\mathrm{e}}_{\mathrm{km}}\frac{\partial \rho Y_k}{\partial x}\right) + A_{\mathrm{v}}W_k\dot{s}_k, \quad k = 1,\ldots,N_{\mathrm{g}} \tag{1}$$

Here, ρ is the density, Y_k is the mass fraction of species k, t is the time, $\dot{m}$ is the mass flux, $\mathcal{D}^{\mathrm{e}}_{\mathrm{km}}$ is the effective diffusion coefficient of species k in the mixture, A_{v} is the active area available for chemical reactions per unit volume, $\dot{s}_k$ is the molar production rate of gasphase species k, W_k is the molecular weight of species k, N_{g} is the number of gasphase species, and x is the axial coordinate. The density ρ is calculated from the ideal gas equation:

$$p\overline{M} = \rho RT, \tag{2}$$

where $\overline{M}$ is the average molecular weight, R is the gas constant, and T is the temperature. The effective diffusion coefficient is defined as

$$\mathcal{D}^{\mathrm{e}}_{\mathrm{km}} = \frac{\epsilon}{\tau}\mathcal{D}_{\mathrm{km}}, \tag{3}$$

where ϵ is the porosity and τ is the tortuosity of porous pellets. The mixture diffusion coefficient of species k in the mixture $\mathcal{D}_{\mathrm{km}}$ is calculated according to

$$\mathcal{D}_{\mathrm{km}} = \frac{1 - Y_k}{\sum_{j \neq k}^{N_{\mathrm{g}}} X_j/\mathcal{D}_{\mathrm{jk}}}. \tag{4}$$

Here X_j is the mole fraction of species j, and the binary diffusion coefficient $\mathcal{D}_{\mathrm{jk}}$ is calculated according to Chapman–Enskog theory [19]. Since the catalyst poisoning is mainly due to loss in active surface area A_{v} is not a constant and changes with sulfur coverage. In the present calculations, we assume a linear dependence of A_{v} on the sulfur coverage [20], i.e.,

$$A_{\mathrm{v}} = A_{\mathrm{v0}}(1 - \theta_{\mathrm{s}}), \tag{5}$$

where A_{v0} is the active area available before poisoning and θ_{s} is the surface coverage of sulfur. When the surface is fully covered with sulfur, the active area becomes zero. Assuming surface diffusion to be negligible, the fractional surface coverage θ_k of various species is calculated from [21]

$$\frac{\mathrm{d}\theta_k}{\mathrm{d}t} = \frac{\sigma_k\dot{s}_k}{\Gamma}, \quad k = N_{\mathrm{g}} + 1,\ldots,N_{\mathrm{g}} + N_{\mathrm{s}}. \tag{6}$$

Here σ_k is the number of sites occupied by adsorbed species k, Γ is the total site density, $\dot{s}_k$ is the molar production rate of surface adsorbed species k, and N_{s} is the number of surface species. Calculation of $\dot{s}_k$ from an elementary like reaction mechanism is published in a number of previous articles [21–23]. Method of lines is applied to solve Eqs. (1) and (6) simultaneously by using the ODE solver CVODE [24]. The entire model is implemented in C++.

3. Kinetic model

The detailed kinetic model developed for reforming of biogas on Ni is given in Table 1. The mechanism contains 68 reactions among 8 gasphase species, 17 surface adsorbed species, and the catalytic surface. While solving Eq. (6), the catalytic surface is also considered as a surface species. i.e., N_{s} includes the surface adsorbed species and the free catalytic surface. The adsorption of gas phase species on the catalytic surface is expressed as sticking reactions. It is generally well accepted that, H_2S chemisorbs dissociatively on Ni surface. However, there is no consensus on the number of Ni sites required for dissociative adsorption or the number of active sites that a sulfur atom may occupy. It is likely that at low temperature, the dissociative adsorption involves two Ni sites and at high temperature it involves only one Ni site. Although Rostrup-Nielsen [25] postulates the following scheme:

$$H_2S(g) + Ni \rightleftharpoons Ni - S + H_2(g) \tag{7}$$

for the adsorption of H_2S on Ni at high temperature, he does not make a final claim on this. Nevertheless, his data fitting to Langmuir isotherm leads to the conclusion that sulfur occupies only one site at high temperature. Since the mechanism developed here is for use at high temperature, sulfur is assumed to occupy only one site. Formation of bulk sulfide is not considered in this study as they form only at significantly high H_2S partial pressures [25]. For the disproportionation and recombination reactions the activation energies are calculated by applying UBI-QEP method [16], which requires the chemisorption energies and bond dissociation energies of various surface adsorbed and gas-phase species. Table 2 lists the chemisorption energies and bond dissociation energies of all the species involved in the reaction mechanism.

The pre-exponential factors are adjusted to reproduce the experimental observations and the entire mechanism is made thermodynamically consistent. One of the major problem in developing a thermodynamically consistent surface reaction mechanism is the non-availability of thermochemistry data for the surface adsorbed species. The lack of thermochemistry data does not allow the calculation of equilibrium constant and hence the calculation of reverse reaction rate from equilibrium constant. Therefore, the forward and reverse reaction rates are defined with their own rate laws. However, the rate laws for every single reaction must follow the thermodynamic rules

$$\Delta H_{\mathrm{r}} = E_{\mathrm{f}} - E_{\mathrm{r}} \quad \textit{and} \quad \frac{\Delta S_{\mathrm{r}}}{R} = \ln\left(\frac{A_{\mathrm{f}}}{A_{\mathrm{r}}}\right). \tag{8}$$

Here ΔH_{r} and ΔS_{r} are respectively the enthalpy change and entropy change for the reaction, E_{f} and E_{r} are respectively the enthalpy of the forward and reverse reactions, and A_{f} and A_{r} are respectively the forward and reverse reaction pre-exponential factors. A given reaction may contain gasphase species and/or surface adsorbed species. If only gas-phase specie are involved then there is no difficulty in ensuring the thermodynamic consistency due to the availability of thermochemistry data. When the reaction involves surface species whose thermochemistry is unknown, the free energy change for the reaction can be expressed in terms of linear combination of known and unknown free energies as

$$\Delta_i G_0 = \sum_{k=1}^{N_{\mathrm{u}}}\nu_{\mathrm{ki}}\tilde{G}^0_k(T) + \sum_{k=N_{\mathrm{u}}+1}^{N}\nu_{\mathrm{ki}}G^0_k(T). \tag{9}$$