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Full Length Article

Steam gasification of a cellulosic biomass surrogate using a Ni/La_2O_3-γAl_2O_3 catalyst in a CREC fluidized riser simulator. Kinetics and model validation

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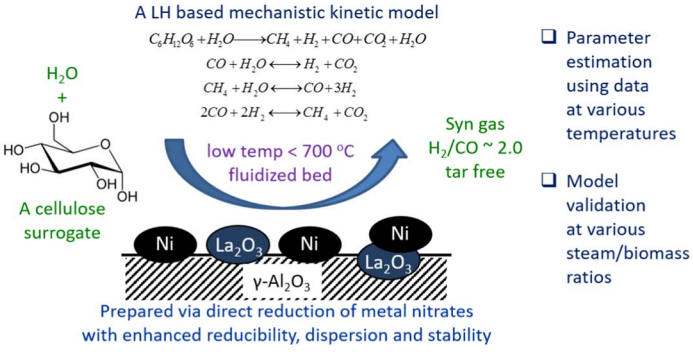
GRAPHICAL ABSTRACT



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ABSTRACT

This study describes a Langmuir-Hinshelwood based mechanistic kinetic model for the catalytic steam gasification of glucose, a biomass surrogate. This model accounts for the algebraic addition of dominant reactions: water gas-shift, the steam reforming of methane and the reverse dry reforming of methane. Reaction runs are developed in a mini-fluidized CREC Riser Simulator reactor using a highly performing Ni/La_2O_3-γ-Al_2O_3 catalyst. H_2, CO, CO_2, CH_4 and H_2O are the major product species observed with negligible coke and tar being formed. For adequate parameter estimation and model validation, two experimental data sets are considered. The first data set includes runs at different temperatures and reaction times. This data set is used to establish intrinsic kinetic parameters with narrow 95% confidence spans and low cross-correlation. The proposed model is validated using a second data set obtained by varying S/B ratio and reaction time. Thus, the proposed model includes phenomenologically based parameters that can successfully account for various observable chemical species in a wide range of operating conditions.

1. Introduction

Biomass is considered as a primary renewable resource to gradually replace depleting fossil fuels given its abundance, its CO_2 neutral emissions and its lower sulphur content. Catalytic steam gasification of biomass facilitates tar reforming into gaseous products inside the gasifier and eliminates the requirement of costly downstream processing for tar disposal [1–3]. While tar formation creates numerous problems in gasifier operation, the conversion of tar adds value to the syngas by increasing the yields of H_2 and/or CO [1,4,5]. Therefore, catalytic biomass steam gasification yields higher energy efficiency by producing a high quality and tar free synthesis gas. Ni-based catalysts

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offer great promise for biomass gasification due to their high reforming activity and affordability [6–12].

In our previous studies [13–15], a highly active and stable fluidizable Ni/La_2O_3-γ-Al_2O_3 catalyst was developed for steam gasification of biomass in a twin-circulating fluidized bed gasifier. This catalyst was prepared using an incipient wetness multi-step impregnation technique with subsequent reduction of metal precursors in a fluidized bed [15]. Catalyst preparation conditions and catalyst formulation were also optimized [13,14]. These studies reported that a controlled amount of La_2O_3 improves Ni dispersion as well as reduces acidity and enhances CO_2 adsorption capacity of γ-Al_2O_3 resulting in lower coke formation on the catalyst surface. Moreover, the catalyst precursor reduction step has to be carefully designed to prevent a possible temperature runaway due to exothermicity of the metal nitrate reduction process. Gas flow during reduction can control the rise of bed temperature and hence, plays a central role in defining the resulting catalyst properties. Surface structure, acid-base properties, metal dispersion and crystal size can be controlled by tuning this parameter. Performance of these catalysts for steam gasification of biomass surrogate species was reported and correlated with Ni dispersion and basicity/acidity ratio by Mazumder and de Lasa 2015 [14].

The use of glucose as a surrogate species for biomass gasification, has been acknowledged in the technical literature [16]. Cellulose is a main carbohydrate constituent of biomass. Typically, cellulose content in biomass ranges from 22.5 to 50.3 wt%. Cellulose is a polymer of glucose with repeating units of $C_6H_{10}O_5$ which are linked together via β-glycosidic linkages [16]. The selection of glucose as a model compound is based on the fact that glucose closely approaches the monomer of cellulose both in terms of oxygen, carbon, and hydrogen content as well as on various chemical functionalities [17].

Furthermore, the development of an efficient steam gasification process also requires insights into biomass gasification reaction mechanisms. Thermodynamic equilibrium models [18–26] provide valuable information to predict the maximum achievable yields of hydrogen and syngas. In this respect, previous studies by our research team [18] emphasize the value of stoichiometric and non-stoichiometric thermodynamic equilibrium models. Equilibrium model predictions were compared with experimental data. These predictions while showing adequate trends, displayed significant differences with respect to the experimental data at reaction times smaller than 20 s. Therefore, non-equilibrium kinetic models are also required to calculate various chemical species in a catalytic fluidized gasifier.

To address this issue, kinetic models of different degrees of complexity, for various biomass feeds, were proposed in the technical literature [27–32]. These reported models, lump together a complex network of heterogeneous reactions into one single kinetic rate equation. While this approach may circumvent overparameterization, the resulting rate equations provide an empirically fitted kinetics only. In a previous study, Salaices et al. [33] established that kinetic model for catalytic biomass steam gasification can be successfully established using reaction engineering principles. This was done using a linear combination of dominant reactions for glucose gasification using a 2.5%Ni/α-Al_2O_3 catalyst.

In the present study, a comparable mechanistic kinetic approach is considered for a significantly improved 20% Ni/5% La_2O_3-γ-Al_2O_3 biomass gasification catalyst. This improved catalyst was prepared by using a high reduction gas flow and by optimizing the catalyst formulation. This catalyst is highly active and stable for gasifying biomass surrogate species [14]. The proposed kinetic model includes water gas-shift, steam reforming of methane and reverse dry reforming of methane as the major reactions. The rates of each of these reactions are modeled using Langmuir-Hinshelwood type equations, which take into consideration both the adsorption of chemical species as well as the reaction on the catalyst surface. The net rate of either the formation or the disappearance of various chemical species is expressed as an algebraic addition of the major reactions. The kinetic parameters are estimated using a first set of experimental data (Set 1) which includes runs with different temperatures and reaction times at a set steam/biomass (S/B) ratio of 1. The proposed model and the estimated parameters are validated using a second and independent experimental data set (Set 2) obtained at 650 °C using different reaction times and S/B ratios.

2. Experimental methods

2.1. Catalyst preparation and characterization

γ-Al_2O_3 (Sasol Catalox® SSCa5/200) was used as a catalyst support. Using this support, 20 wt% Ni/5 wt% La_2O_3-γ-Al_2O_3 catalysts were prepared using a specially designed multi-step incipient wetness technique with direct reduction of metal precursors after each impregnation in a fluidized bed [14]. Three main steps were involved in the catalyst preparation: a) support impregnation, b) drying, and c) metal precursor reduction. After impregnation of the precursor solution, the resulting paste was dried slowly at 140 °C overnight. The dried powder was then reduced in a fluidized chamber at 700 °C (3 °C/min) for 8 h under the flow of 10% H_2-He.

It has been found in our earlier study [14] that a local bed temperature rise inside the catalyst bed can occur due to exothermicity of the metal nitrate reduction process. This increase in temperature can cause severe sintering via γ-Al_2O_3 dehydroxylation. Therefore, the catalyst precursor reduction step has to be carefully considered to prevent temperature runaway. Control of the rise of bed temperature plays a major role in the resulting catalyst properties such as surface structure, acidity-basicity, metal dispersion and crystal size. These were discussed in details in our previous work [14]. On this basis, a 20 wt% Ni/5 wt% La_2O_3-γ-Al_2O_3 catalyst prepared under bubbling fluidization, designated as *HF*, is considered in the present study. Properties of this catalyst are summarized in Table 1. Details of catalyst characterization techniques and results can be found in [14].

2.2. Gasification under twin circulating fluidized beds conditions

Steam gasification of glucose (a cellulose surrogate) was performed using a fluidized CREC Riser Simulator, operating under the expected conditions of an industrial twin bed circulating fluidized gasifier. The CREC Riser Simulator is a bench scale mini fluidized bed with a total volume of 50 cm^3. This bench scale reactor is designed for catalyst evaluation under close to industrial circulating fluidized bed reactors. A schematic diagram of the CREC Riser Simulator experimental setup is shown in Fig. 1. A detailed description of the CREC Riser Simulator can be found elsewhere in the literature [34].

The Ni catalysts which were thermally treated during the preparation process were loaded into the basket. The reactor system was sealed, leak tested and heated to the reaction temperature in an argon atmosphere. Then, the liquid feed was injected, and once the reaction time was reached, the reaction products were evacuated from the reactor unit to a vacuum box. Reactor and vacuum box pressure data against time were recorded by the Personal Daq Acquisition Card. Gasification products were sent to a GCMS system via heated transfer lines. The GCMS system is equipped with both a packed bed column (HaysSep® D)

Table 1
Characterization results of the HF catalyst.

S_{BET}	166 m^2/g
Pore Volume	0.32 cm^3/g
Avg. Pore Diameter	76 Å
Ni Reducibility	95%
Ni Dispersion	4.52%
Total Acidity	550 μmol NH_3/g γ-Al_2O_3
Total Basicity	188 μmol CO_2/g γ-Al_2O_3