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Kinetic models discrimination for the high pressure WGS reaction over a commercial CoMo catalyst

A.R. de la Osa*, A. De Lucas, A. Romero, J.L. Valverde, P. Sánchez

Chemical Engineering Department, Faculty of Chemistry, University of Castilla La Mancha, Avda. Camilo José Cela 12, 13071 Ciudad Real, Spain

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ABSTRACT

A mechanistic kinetic model has been studied to describe the bench scale water-gas shift reaction over a commercial presulfided CoMo catalyst using an industrial coal-derived gas feed. A rigorous kinetic network has been considered on the basis of formate, associative and direct oxidation mechanisms. Kinetic models were derived by using LHHW formalism and steady-state approximation for reaction intermediates. Kinetic parameters were estimated by nonlinear regression of the experimental data using the Marquardt–Levenberg algorithm. The WGS kinetic data were measured by experiments over a wide range of reaction conditions and comparisons for various rate equations were also established. A preliminary discrimination resulted in the necessity of rewrite models as a unique parameter models. The model based on direct oxidation mechanism successfully predicted the CO₂ formation within the range of experimental conditions (high pressure and temperature). WGS rate expressions based on the regenerative process (oxidation-reduction) with the assumption that CO₂ desorption reaction can be regarded as the rate determining step were found to be the best.

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1. Introduction

The depletion of fossil oil reserves and the pollution (anthropogenic greenhouse gas emissions) caused by the growing demand for energy generation have been a major objective of automobile, refinery and catalyst industries for many years [1,2]. The use of coal can be efficiently applied in coal-fuelled integrated gasification combined cycle (IGCC) power plants as a transition feedstock for a hydrogen economy is likely to be accomplished via gasification, i.e. the conversion of solid coal into a gaseous mixture of CO, CO₂, H₂O, and H₂. The hydrogen yield of such gasifier effluent may be increased by CO reacting with additional amounts of water, using the so-called water-gas shift reaction (WGS). Also, this step can be

followed by carbon dioxide capture and storage (CCS) prior to combustion of the hydrogen in gas turbines or its utilisation in fuel cells [3,4]. Although the WGS reaction is customarily used in industry, the reaction has not been explored at the conditions (temperature, pressure) envisioned in the gasification process. However, high temperature and high pressure provide a unique scenario to increase the hydrogen yield. Water-gas shift (WGS) is then applied to increase and adjust the H₂/CO molar ratio in the synthesis gas and to remove CO from the gas effluents. ELCOGAS shows an example of the mentioned IGCC technology through the plant operating in Puertollano (Ciudad Real, Spain). In fact, this plant is now coupled to a pilot plant for H₂ production and CO₂ capture that operates since October 2010.

* Corresponding author.

E-mail addresses: AnaRaquel.Osa@uclm.es, anraquel@gmail.com (A.R. de la Osa).

Nomenclature	
A	pre-exponential factor
b	estimate of β
E_a	activation energy, kJ mol^{-1}
Exp	experimental
F	F-test parameter
F_c	function defined by eq. (23).
F_{Pi}	molar flow rate of each component i, mmol s^{-1}
$F_{\text{exp},Pi}$	experimental molar flow rate of each component i, mmol s^{-1}
$F_{\text{th},Pi}$	theoretical molar flow rate of each component i, mmol s^{-1}
$f(x, \beta)$	mathematical model
GHSV	gas hourly space velocity, h^{-1}
IGCC	integrated gasification combined cycle
i	the species considered
i_{th}	diagonal term of the covariance matrix
$k_{i, i=1-6}$	kinetic constant
K_p	WGS equilibrium constant
$K_{i, i=1-7}$	adsorption group constant
LHHW	Langmuir-Hinshelwood-Hougen-Watson predictive model
N	total number of experiments
p	number of parameters in a model
P_i	partial pressure of species i
P_{CO}	CO partial pressure, bar
P_{CO_2}	CO ₂ partial pressure, bar
P_{H_2}	H ₂ partial pressure, bar
$P_{\text{H}_2\text{O}}$	H ₂ O partial pressure, bar
R	universal gas constant, $\text{kJ mol}^{-1} \text{K}^{-1}$
R_{Pi}	axial flow profiles through the reactor defined by eq. (21).
RQ_{WGS}	RCO ₂ , WGS reaction rate, $\text{mmol g}_{\text{cat}}^{-1} \text{s}^{-1}$ defined by eq. (26).
SSQ	sum of squared differences defined by eq. (22).
T	temperature, K
t	t-test parameter
t_{ci}	function defined by eq. (24).
th	theoretical
$V(b)$	covariance matrix
W	weight of catalyst, g
x	set of independent variables in $f(x, \beta)$ model
y	experimental dependent variable
Greek symbols	
α	significance level
β_i	parameter in $f(x, \beta)$ model
η	approach to the WGS equilibrium defined by eq. (27).
χ^2	statistic parameter to measure goodness of the fitting
Others	
*	adsorption site

Although the WGS reaction could be catalyzed by many materials [5–8], industrially, it is carried out by using iron oxide-based ($\text{Fe}_3\text{O}_4\text{--Cr}_2\text{O}_3$) and copper oxide-based (Cu--ZnO) catalysts [9–12]. However, in the case of coal-derived syngases, sulfur-resistant CoMo based catalysts are required [12–16]. Sulfide catalysts, similar to those used for hydrodesulfuration, have received much attention for the shift activity in presence of higher amounts of sulfur in the feed.

WGS reaction over Co–Mo catalysts has been extensively studied at laboratory conditions; however there are few papers [17] where industrial feed and bench scale set-up are used. None of them related to kinetics. In this sense, in a previous work, the effect of both operating conditions and catalyst pretreatment on the high pressure WGS reaction was investigated. A bench scale set-up, using a sulfur-resistant commercial catalyst and an industrial coal-derived feeding (from IGCC-ELCOGAS plant, Puertollano, Spain), were considered [18]. The aim of this research was to find a predictive model derived from a Langmuir-Hinshelwood-Hougen-Watson (LHHW) one for the bench scale WGS reaction that fits with the experimental results obtained with a commercial sulfide CoMo catalyst.

2. Experimental

2.1. Bench scale set-up description

The facility which is fully automated and computerized consisted of three physically separated parts: (gas and liquid) feed

mixing and supply system, reaction system and product analysis system.

N₂, H₂, CO and CO₂ (high purity supplied by PRAXAIR), were fed to the plant as the main gases, whereas H₂S (PRAXAIR) was introduced into it as the sulfide agent for the catalyst pretreatment. Each of these gases could be fed through two separate lines that had the same elements but different flow rates.

The water supply system consisted of a liquid dosing pump (Damovo) and a vaporizer, which achieved complete vaporization of the liquid driven by the pump before entering the reactor. The bench scale set-up included an Inconel fixed bed reactor (17.7 mm ID and 1000 mm length) for WGS experiments.

The gaseous effluent was connected to the input of a gas chromatograph by means of a Peltier cell. The analysis system consisted of a gas microchromatograph (CP-4900 Micro-GC VARIAN) with two analysis columns (Molsieve 5A for H₂, N₂, CH₄ and CO and Pora Pack Q column for CO₂, ethane and propane) using Ar and He as carrier gases, respectively.

The liquid effluent, after crossing a level control valve, was placed in a polyethylene tank positioned on a balance of 6 kg capacity.

Fig. 1 shows a schematic diagram of the experimental bench scale plant for WGS reaction.

2.2. Catalyst

The catalyst studied in this work was a high temperature industrial WGS catalyst, which consisted of a mixture of

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