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MICROKINETIC MODELING FOR WATER-GAS SHIFT REACTION OVER NICKEL-BASED CATALYST

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Abstract
This report presents the development and application of a microkinetic model of the water-gas shift (WGS) reaction on a nickel catalyst. Based on a published mechanism consisting of initially

19 elementary steps that were reduced using sensitivity and principal component analysis to only
12 elementary steps and corresponding rate constants (k-values) which we calculated using E (kJ/mol) and A (mol cm s) values. Using the 12 elementary steps and pseudo-steady-state hypothesis (PSSH) the rate expressions for the reaction were solved.
Our approach utilized reduced mechanism equations, where the rate of formation equaled the rate of consumption, ensuring steady-state conditions. These equations were solved alongside the site balance equation (summation of θ=1) to determine all surface coverages (θ values). Once the θ values were known, we computed the overall reaction rate for the formation of product.
Keywords: Water-Gas Shift, Nickel Catalyst, Adsorption/Desorption, Catalytic Activity, H_2 Formation

Introduction

The water-gas shift (WGS) reaction played a crucial role in chemical engineering processes, particularly those involving catalysis. This reaction converted carbon monoxide (CO) and water (H_2O) into carbon dioxide (CO_2) and hydrogen (H_2), serving as a fundamental process in hydrogen production and CO elimination technologies. The significance of WGS extended to multiple industrial applications, including steam reforming and fuel cell systems, making it an ideal candidate for detailed kinetic analysis. The industrial relevance of WGS lay in its dual functionality: hydrogen production for the growing hydrogen economy and carbon monoxide removal in sensitive processes like fuel cell operations. Previous research established that the rate-limiting step in the WGS reaction over Ni (111) surfaces involved the COH group formed when CO reacted with OH. This finding emerged from microkinetic modeling of a plug flow reactor using simulation techniques. Our project built upon this foundation by examining the WGS reaction kinetics over nickel catalysts, borrowing methodologies from several established works in the field. We developed a simplified kinetics model that investigated the effects of temperature variations and gas composition on reaction

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rates. One objective of this project extended beyond theoretical estimation of WGS reaction and encompassed the understanding of chemical engineering challenges, including microkinetic modeling and mechanism reduction techniques.

Methodology

A microkinetic model of elementary reactions for the Water-Gas Shift reaction was proposed in the works of Catapan et al.[3] The reactions were then reduced in the works of de Carvalho et al.[4] and are listed in Table 1 below.

	Reaction	A_j (mol cm s) Pre-Exponential Factor	Bj Temperature Exponent	$E_{a,j}$ (kJ/mol) Activation Energy
R1	$H_2O + * \leftrightarrow H_2O*$	0.5	0	0
R2	$CO + * \leftrightarrow CO*$	0.8	0	0
R3	$CO_2 + ** \leftrightarrow CO_2**$	0.5	0	0
R4	$H_2 + 2* \leftrightarrow H* + H*$	0.1	0	3.8
R5	$H_2O* + * \leftrightarrow OH* + H*$	2.2978×10^{21}	1	87.9
R8	$CO* + O* \leftrightarrow CO_2**$	5.2995×10^{23}	1	145.6
R9	$CO* + OH* \leftrightarrow COOH* + *$	3.4328×10^{22}	1	113.0
R10	$COOH* + ** \leftrightarrow CO_2** + H*$	4.4257×10^{31}	1	103.3
R11	$COOH* + O* \leftrightarrow CO_2** + OH*$	1.1071×10^{32}	1	45.2
R12	$COOH* + OH* \leftrightarrow CO_2** + H_2O*$	4.0643×10^{21}	1	4.2

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Table 1. Reduced Microkinetic Reaction Steps for Water-Gas Shift Reaction over Nickel[4]

Asterisk (*) denotes the number of surface sites occupied by surface species and the Nickel catalyst

The table listed the reduced 10 elementary reaction reversible steps, involving 4 overall species and 7 adsorbates. The steps involved the adsorption and desorption of the products and reactants (R1-R4), the chemistry of water (R5), oxidation of CO (R8), and carboxyl mechanisms (R9-R12). Coke formation was not included since the reactions were not favored over the nickel catalyst and the adsorption/desorption steps of intermediates were omitted since they were important at higher temperatures. Using a modified Arrhenius law the forward constants for *j*th reaction could be calculated at any temperature:

$$k_{f,j} = \frac{A_j}{\Gamma^{n-1}} \left(\frac{T}{T_0}\right)^{\beta_j} \exp\left(-\frac{E_{a,j}}{R_g T}\right) \quad \text{Eq. (1)}$$

where A_j, β_j, and $E_{a,j}$ could be found in Table 1 and n was the number of reactants that were surface species including the vacancies (n=1 or 2). Then to maintain thermodynamic consistency, the reverse rate was calculated using the ratio of the forward rate constant of *j*th to the equilibrium constant of *j*th reaction:

$$k_{r,j} = \frac{k_{f,j}}{K_{c,j}} \quad \text{Eq. (2)}$$

where $K_{c,j}$ was the equilibrium constant of the *j*th reaction in concentration units, however, the equilibrium constant was more easily calculated using the partial pressures which related to $K_{c,j}$ as:

$$K_{c,j} = K_{p,j} \left(\frac{p^0}{R_g T}\right)^{\sum_{k=1}^{N_g} v_{k,j}} \Gamma^{\sum_{k=1}^{N_g} v_{k,j}} \prod_{k=1}^{N_g} \sigma_k^{-v_{k,j}} \quad \text{Eq. (3)}$$

where p^0 was standard pressure (1 atm) and $v_{k,j}$ was the stoichiometric coefficient of species k.

Equilibrium constant was calculated as:

$$\Delta S_k^0 \quad \Delta H_k^0 \quad \text{Eq. (4)}$$

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$$K_{P,j} = exp\left(\quad - \right) Rg \quad RgT$$

Table 2. Surface Thermochemistry of WGS Adsorbates on Nickel Surface[a]

Species	$H_k^0\ [kJ/mol]$	$S_k^0\ [J/mol]$
H_2O	-293.8	41.8
OH	-262.3	37.6
O	-221.7	16.8
H	-53.9	5.6
CO	-240.5	44.9
COH	-203.1	70.5
COOH	-434.5	90.7
CHO	-185.0	69.8
HCOO	-458.8	93.7
CO_2	-370.6	153.6

[a]Surface enthalpies are valid at 298 K and are provided by de Carvalho et al.[4]

Then using PSSH assumption and the simplified adsorbate balances[4], the surface site balances per species could be written with the forward and reverse rates and represented as:

$$\frac{d\Theta H_2O}{dt} \quad 1\ H2O\ v - 1\ H2O \text{ Eq. (5)} = K\ P\ \Theta - K\ \Theta = 0$$

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$$\frac{d\Theta}{dt_{CO}} = K2PCO\Theta v - K{-}2\Theta CO = 0 \quad \text{Eq. (6)}$$

$$\frac{d\Theta CO_2}{dt} 3\ CO2\ v - 3\ CO2 \text{ Eq. (7)} = K\ P\ \Theta - K\ \Theta = 0$$

$$\frac{d\Theta_H}{dt} = 2 * (K_4 P_{H_2} \Theta_v{}^2 - K_{-4}\Theta_H) + (K_5 P_{H_2O}\Theta_v - K_{-5}\Theta_H\Theta_{OH}) = 0 \quad \text{Eq. (8)}$$

$$\frac{d\Theta_{OH}}{dt} = K5PH2O\Theta v - K{-}5\Theta H\Theta OH = 0 \quad \text{Eq. (9)}$$

$$\frac{d\Theta}{dt_O} = -(K8\Theta CO\Theta O - K{-}8\Theta CO2) = 0 \quad \text{Eq. (10)}$$

$$\frac{d\Theta}{dt} \quad 9\ CO\ OH \quad -9\ COOH\ v \quad 12\ COOH\ OH$$

where P_j is partial pressure and overall site balance can be written as:

$$\Theta CO + \Theta CO2 + \Theta COOH + \Theta H + \Theta H2O + \Theta OH + \Theta O + \Theta v = 1 \quad \text{Eq. (12)}$$

and an overall reaction rate as:

$$\frac{}{COOH} = (K\ \Theta\Theta \quad - K \quad \Theta \quad \Theta\ ) - K \quad \Theta \quad \Theta \quad = 0 \quad \text{Eq. (11)}$$

$$\text{Eq. (13) } rWGS = k9{,}f\Theta CO\Theta OH$$

Using a combination of these equations, this paper aimed to relate and plot graphs for rate of overall reaction while changing the partial pressures of reactants or the temperature as well as the plots for site coverage versus the temperature or partial pressures. Equations 1-13 were taken from de Carvalho et al.[4]

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