



Apparent kinetics of the catalyzed water–gas shift reaction in synthetic wood gas



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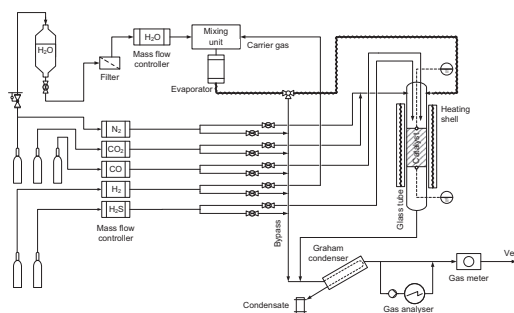
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HIGHLIGHTS

- Empirical power law rate models of two commercial WGS catalysts are established.
- The feed simulates the wood gas derived from the DFB steam gasification of biomass.
- Apparent reaction orders are estimated in the presence of hydrogen sulfide.
- Sulfur doubles the activity of catalyst 1 and reduces by 50% the activity of cat.2.
- From a certain temperature the activity of catalyst 1 is not influenced by sulfur.

GRAPHICAL ABSTRACT



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ABSTRACT

The catalysis of the water–gas shift reaction employing two commercially available catalysts was investigated. The applied feed was a synthetic gas mixture simulating the wood gas derived from the dual fluidized bed steam gasification of biomass. A Co/Mo- and an Fe/Cr-based catalyst were compared in a differentially operated plug flow reactor. The influence of the partial pressures of all reaction partners as well as the effect of temperature were studied, allowing the formation of two power law rate models.

$$r_{(\text{Co/Mo})} = 0.044 \exp\left(\frac{-66}{RT}\right) p_{\text{CO}}^{1.28} p_{\text{H}_2\text{O}}^{0.03} p_{\text{CO}_2}^{-0.11} p_{\text{H}_2}^{-0.35} \left(1 - \frac{1}{K} \frac{p_{\text{CO}_2} p_{\text{H}_2}}{p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \quad (1)$$

$$r_{(\text{Fe/Cr})} = 300 \exp\left(\frac{-102}{RT}\right) p_{\text{CO}}^{1.37} p_{\text{H}_2\text{O}}^{0.23} p_{\text{CO}_2}^{-0.16} p_{\text{H}_2}^{-0.11} \left(1 - \frac{1}{K} \frac{p_{\text{CO}_2} p_{\text{H}_2}}{p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \quad (2)$$

The CO conversion rates over both catalysts were strongly dependent on the sulfur load in the feed. The presented models were established at a constant H₂S concentration of 100 vol.ppm_{db}. At this sulfur load the Fe/Cr-based catalyst should be preferred to the Co/Mo-based catalyst. The partial pressure of H₂S could not be included in the power law models because of its influence on the other coefficients of the model.

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Nomenclature

Abbreviations & Acronyms

CEM	controlled evaporator mixer
DFB	dual fluidized bed
GHSV	gas hourly space velocity
MFC	mass flow controller
WGSR	water–gas shift reaction
WGS	water–gas shift

Indices

cat	catalyst
db	dry basis
in	inlet
n	at standard conditions (0 °C and 101.325 kPa)
out	outlet
wb	wet basis

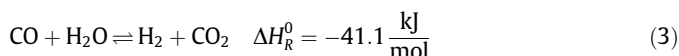
Symbols

A	pre-exponential factor in $\frac{\text{mol}}{\text{g}_{\text{cat}} \cdot \text{s}}$ $\text{kPa}^{-(a+b+c+d)}$
a, b, c, d, s	apparent reaction order with respect to component CO, H ₂ O, CO ₂ , H ₂ , H ₂ S; dimensionless

B	factor for sulfur modeling in $\frac{\text{mol}}{\text{g}_{\text{cat}} \cdot \text{s}}$ kPa^{-s}
β	approach to equilibrium, dimensionless
ΔH_R^0	enthalpy of reaction at standard conditions (0 °C and 101.325 kPa) in $\frac{\text{kJ}}{\text{mol}}$
d_p	particle diameter in μm
E	apparent activation energy in $\frac{\text{kJ}}{\text{mol}}$
K	equilibrium constant of the WGSR, dimensionless
R	universal gas constant, $8.314 \cdot 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$
k	reaction rate constant in $\frac{\text{mol}}{\text{g}_{\text{cat}} \cdot \text{s}}$ $\text{kPa}^{-(a+b+c+d)}$
\dot{n}	molar flow rate in $\frac{\text{mol}}{\text{h}}$
p_i	partial pressure of component i in kPa
r	reaction rate on a weight base in $\frac{\text{mol}}{\text{g}_{\text{cat}} \cdot \text{s}}$
T	temperature in Kelvin
\dot{V}	volumetric flow rate in $\frac{\text{L}}{\text{h}}$
X_{CO}	CO conversion rate, dimensionless

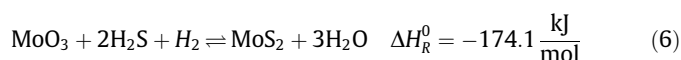
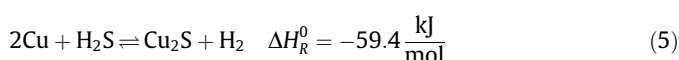
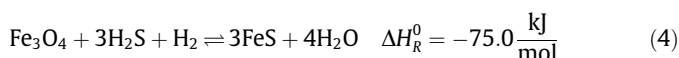
1. Introduction

Industrial hydrogen production is mainly based on the reforming or gasification of a fossil feedstock containing carbon. Downstream processing usually involves the catalysis of the water–gas shift reaction (WGSR, Eq. (3)) in order to produce additional hydrogen from the conversion of carbon monoxide [1,2].



Industrially, the catalysis is usually carried out in fixed bed reactors with a desulphurized feed (sweet shift). A two stage process is operated, employing a Fe/Cr-based catalyst at a high temperature level and a Cu/Zn-based catalyst at lower temperatures. The high temperature stage is usually operated at an inlet temperature of around 350 °C and GHSV (Eq. (10)) between 400 and 1200 h⁻¹. Inter-bed cooling is used to reduce the inlet temperature of the more active but temperature sensitive Cu/Zn-based catalysts (low temperature stage) down to 150–200 °C. Alternatively, Co/Mo-based catalysts are used for applications with H₂S in the feed (sour shift). The activity of sour shift catalysts depends strongly on the sulfur concentration in the feed. As a consequence, a wide range of operation temperature and GHSV is reported in literature [1,2].

According to Eqs. (4)–(6), sulfur exposition of the mentioned catalysts leads to the formation of the corresponding metal sulfides. Hydrogen sulfide is a strong poison for Cu/Zn-based catalysts. The activity of FeS is reported to be reduced by 50% compared to magnetite, which is the active species of Fe/Cr-based catalysts. Co/Mo-based catalysts with MoS₂ as the active species require sulfur to be present in the feed [1,3]. Sulfidation of Fe/Cr- and Co/Mo-based catalysts is generally reversible by lower sulfur partial pressures in the feed [4,5]



Renewable hydrogen production can be achieved based on thermal conversion of biomass. In this context, dual fluidized bed (DFB) steam gasification is an interesting technology, providing a gas mixture rich in hydrogen and poor in nitrogen. DFB gasification of wood chips is applied industrially in Güssing and Oberwart, Austria and in Ulm, Germany. On-site produced wood gas contains hydrogen (35–45 vol.%_{db}), carbon monoxide (20–30 vol.%_{db}), carbon dioxide (15–25 vol.%_{db}), methane (8–12 vol.%_{db}) and small amounts of nitrogen (1–5 vol.%_{db}) [6]. Minor quantities of hydrocarbons (C_xH_y), ammonia and sulfur components are present. Depending on the feedstock, 20–150 vol.ppm_{db} of hydrogen sulfide are contained [6–8].

Ongoing research projects in Güssing and Oberwart are dealing with hydrogen production by means of wood gas processing [7,9,10]. The established pilot plants also involve catalysis of the WGSR. An upscale of this catalysis requires an elaborate reactor design which relies on the prediction of the reaction rate [11]. In this context, macroscopic power law models (see Eq. (7)) are frequently employed. Such simple empirical expressions are considered useful tools for reactor design [12].

$$r = k p_{\text{CO}}^a p_{\text{H}_2\text{O}}^b p_{\text{CO}_2}^c p_{\text{H}_2}^d (1 - \beta) \quad (7)$$

$$\beta = \frac{1}{K} \frac{p_{\text{CO}_2} p_{\text{H}_2}}{p_{\text{CO}} p_{\text{H}_2\text{O}}} \quad (8)$$

The reaction rate r with respect to carbon monoxide is given in $\frac{\text{mol}}{\text{g}_{\text{cat}} \cdot \text{s}}$; a, b, c and d are the apparent reaction orders of each component; K is the equilibrium constant of the WGSR; p are the partial pressures in kPa of the relevant gas components; the reaction rate constant k is derived from the Arrhenius equation $k = A \cdot e^{-\frac{E}{RT}}$ (A is the pre-exponential factor, E is the apparent activation energy, and R is the universal gas constant). β values (defined in Eq. (8)) approaching zero indicate that the reaction occurs far from equilibrium.

The aim of this study was to establish empirical power law rate models of two commercially available WGS catalysts based on Co/Mo and Fe/Cr. Both catalysts were tested under comparable condi-

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