CuO/ZnO/Ga$_2$O$_3$ catalyst for low temperature MSR reaction: Synthesis, characterization and kinetic model

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ABSTRACT

Highly active catalysts for the methanol steam reforming (MSR) capable of operating efficiently at the same temperature of high temperature polymer electrolyte membrane fuel cells (HTPMFCs) devices are strongly desired. A novel CuO/ZnO/Ga$_2$O$_3$ catalyst was synthesized by co-precipitation method and characterized by ICP-AES, N$_2$-physisorption, SEM-EDX and XRD. This catalyst showed a catalytic activity 2.2 times higher than commercial CuO/ZnO/Al$_2$O$_3$ catalysts at 453 K Two kinetic models one empirical and one mechanistic were applied to describe the methanol steam reforming reaction over one of the most promising catalyst family.

1. Introduction

Methanol can be produced from renewable sources, is easy to store and has higher volume energy density than compressed or chemically bonded hydrogen storage technologies [1,2]. Methanol, due to the absence of C−C bonds, has a low reforming temperature (513 K–533 K) [2] making it suitable for fuel cell applications as a hydrogen source. Moreover, the hydrogen-rich gas stream produced by methanol steam reforming (MSR) can be fed directly to high temperature polymer electrolyte membrane fuel cells (HT-PEMFC), due to the high CO tolerance (up to 3 % [3]). However, the low catalytic activity of commercial reforming catalysts at the operating temperatures of HT-PEMFCs (393 K–453 K) [4,5] increases the complexity and reduces the efficiency of power supplies based on HT-PEMFCs integrated with reformers. Thermodynamically, the methanol conversion by MSR reaction is almost complete at 453 K [6], therefore catalysts with high activity at *ca.* 453 K, are conceivable and strongly desired.

Copper-based catalysts, such as Cu/ZnO/Al$_2$O$_3$, are the most commonly used catalysts for MSR due to their low cost and considerably high activity at temperatures of *ca.* 523 K, despite the pyrophoric nature and low stability [7,8]. The change in oxidation state, reduction of the active area by sintering, coke deposition, catalyst poisoning (*e.g.* chloride and sulphur) are the main reasons for the catalyst deactivation [9,10]. To improve the copper-based catalyst several approaches are reported in literature, from the employment of different preparation methods [11,12] to the addition of promoters [13–16]. The Al$_2$O$_3$ is typically used as support and improves the surface area [8]; adding ZrO to Cu-based Al$_2$O$_3$ supported, improves the reducibility and copper

dispersion [14], while adding CeO has shown to increase the thermal stability and increases the CO conversion through WGS reaction [15,16]. Recently, a gallium-promoted copper-based catalyst prepared by co-precipitation method demonstrated to be highly active, stable and selective at temperatures lower than 473 K [15,17–19]. The incorporation of Ga into the Cu–Zn oxide showed to improve the catalytic activity, by originating a nonstoichiometric cubic spinel phase containing interstitial Cu^{1+} ions, resulting in extremely small (< 5 Å) and highly dispersed copper clusters [17,18].

The search for a more suitable catalyst for MSR has led to consider metals from groups VIII–X due to their high activity, stability and low CO production [20–25]. Pd-based catalysts, for instance display an unusual behaviour since it forms Pd-alloys (*e.g.* Zn and Ga) after proper reductive pre-treatment, modifying the catalytic function of Pd [20–22]. Pt-based catalysts on the other hand demonstrated very high activity; *e.g.* Pt/In$_2$O$_3$/Al$_2$O$_3$ showed an activity 10 times higher than commercial Cu-based catalyst [22–25]. This high activity of Pt/In$_2$O$_3$/Al$_2$O$_3$ has been assigned to the contact regions between the metallic Pt with partially reduced In$_2$O$_3$ [25]. The major challenges of using commercially noble metals for MSR is the prohibitive high noble metal loading (typical ranging from 5.0 to 15.0 wt.%), which limits their economic viability.

Kinetic modelling of the methanol steam reforming process is a very important tool for scaling, design and optimize reformers. Several power-law and Langmuir–Hinshelwood reaction rate expressions for MSR over CuO/ZnO/Al$_2$O$_3$ have been reported in literature, typically for operating temperatures above 473 K [26–31]. In this work two kinetic models, one empirical and one mechanistic are proposed for
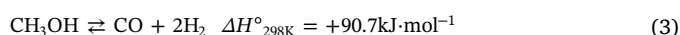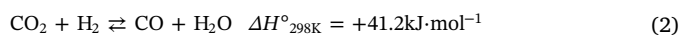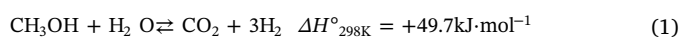
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characterizing one of the most promising catalyst for MSR, a novel highly active gallium-promoted copper-based catalyst supported on ZnO operating at temperatures between 453 K and 493 K. The CuO/ZnO/Ga$_2$O$_3$ catalyst was synthesized *by the co-precipitation method* and characterized concerning the morphology, structure and composition *by ICP-AES, N$_2$-physisorption, SEM-EDX and XRD.* Additionally, the catalytic activity of the *in*-house catalyst was compared with the one of two commercial catalysts, CuO/ZnO/Al$_2$O$_3$ from BASF RP60 (hereafter mentioned as RP60) and from Süd-Chemie G66MR (hereafter mentioned as G66MR). The proposed kinetic models were fitted to the experimental results using a 1D isothermal packed bed reactor simulator.

2. Kinetic models

The kinetic models proposed in this study only consider the MSR reaction (Eq. (1)); water gas shift (WGS, Eq. (2)) and methanol decomposition (MD, Eq. (3)) reactions were not considered due to their very low rates at temperatures below 493 K [32].

$$CH_3OH + H_2O \rightleftarrows CO_2 + 3H_2 \quad \Delta H°_{298K} = +49.7 kJ \cdot mol^{-1} \quad (1)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H°_{298K} = +41.2 kJ \cdot mol^{-1} \quad (2)$$

$$CH_3OH \rightleftarrows CO + 2H_2 \quad \Delta H°_{298K} = +90.7 kJ \cdot mol^{-1} \quad (3)$$

Two types of kinetic models were developed, one empirical (power-law model) and one based on mechanistic assumptions. Empirical models, despite their simplicity, can fit very accurately the experimental results and are easy to implement [30,31]. The mechanistic models, on the other hand, are based on physical assumptions and can express accurately the sequence of the reaction steps for the H$_2$ formation [26].

2.1. Empirical model

The power-law model expressed by Eq. (4) was adopted in this work to describe the MSR reaction on *in*-house catalyst (CuO/ZnO/Ga$_2$O$_3$). The temperature dependence of the reaction rate was assumed to follow an Arrhenius-type behavior (Eq. (5)).
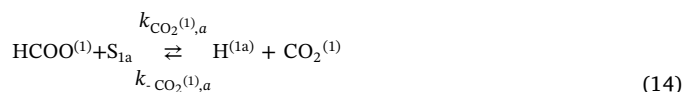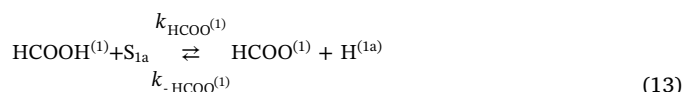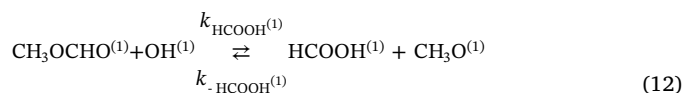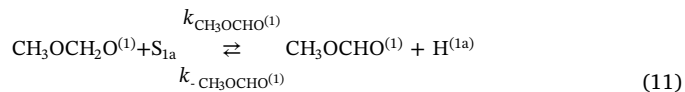
$$r_{MSR} = k_{MSR}(T) p_{CH_3OH}^a p_{H_2O}^b p_{H_2}^c p_{CO_2}^d \quad (4)$$

$$k_{MSR}(T) = k_0 e^{-\frac{Ea}{RT}} \quad (5)$$

where, r is the reaction rate of the methanol steam reforming reaction, k is the kinetic constant of the MSR reaction, p are the partial pressures of each component and a, b, c and d are the apparent reaction orders of methanol, water, hydrogen and carbon dioxide, respectively. k_0, is the Arrhenius pre-exponential factor and E_a is the activation energy. The model has a total of 6 parameters, including the activation energy and pre-exponential factor.

2.2. Mechanistic model

The mechanistic model suggested by Peppley et al. [26] to describe the physical processes that occurs in the MSR over the CuO/ZnO/Al$_2$O$_3$ catalyst was also considered in this work. The model comprises a set of Langmuir–Hinshelwood rate expressions, similar to those proposed by Jiang et al. [33], which can be describe as follows by Eqs. (6)–(14):

$$S_1 + S_{1a} + CH_3OH\,(g) \underset{k_{-CH_3O^{(1)}}}{\overset{k_{CH_3O^{(1)}}}{\rightleftarrows}} CH_3O^{(1)} + H^{(1a)} \quad (6)$$

$$S_1 + S_{1a} + H_2O\,(g) \underset{k_{-OH^{(1)}}}{\overset{k_{OH^{(1)}}}{\rightleftarrows}} OH^{(1)} + H^{(1a)} \quad (7)$$

$$2S_{1a} + H_2(g) \underset{k_{-H^{(1a)}}}{\overset{k_{H^{(1a)}}}{\rightleftarrows}} 2H^{(1a)} \quad (8)$$

$$CH_3O^{(1)} + S_{1a} \underset{k_{-CH_2O^{(1)}}}{\overset{k_{CH_2O^{(1)}}}{\rightleftarrows}} CH_2O^{(1)} + H^{(1a)} \quad (9)$$

$$CH_3O^{(1)} + CH_2O^{(1)} \underset{k_{-C_2H_5O_2^{(1)}}}{\overset{k_{C_2H_5O_2^{(1)}}}{\rightleftarrows}} CH_3OCH_2O^{(1)} + S_1 \quad (10)$$

$$CH_3OCH_2O^{(1)} + S_{1a} \underset{k_{-CH_3OCHO^{(1)}}}{\overset{k_{CH_3OCHO^{(1)}}}{\rightleftarrows}} CH_3OCHO^{(1)} + H^{(1a)} \quad (11)$$

$$CH_3OCHO^{(1)} + OH^{(1)} \underset{k_{-HCOOH^{(1)}}}{\overset{k_{HCOOH^{(1)}}}{\rightleftarrows}} HCOOH^{(1)} + CH_3O^{(1)} \quad (12)$$

$$HCOOH^{(1)} + S_{1a} \underset{k_{-HCOO^{(1)}}}{\overset{k_{HCOO^{(1)}}}{\rightleftarrows}} HCOO^{(1)} + H^{(1a)} \quad (13)$$

$$HCOO^{(1)} + S_{1a} \underset{k_{-CO_2^{(1),a}}}{\overset{k_{CO_2^{(1),a}}}{\rightleftarrows}} H^{(1a)} + CO_2^{(1)} \quad (14)$$
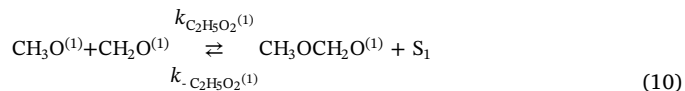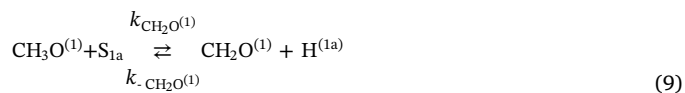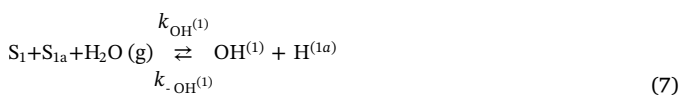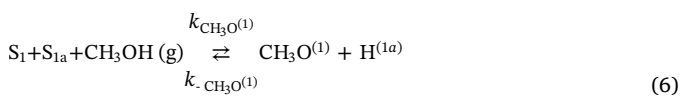
The final rate expression for the MSR reaction is expressed by Eq. (15). Details of the derivation are reported elsewhere [26].

$$r_{MSR} = \frac{\frac{k_{MSR} K^*_{CH_3O^{(1)}} p_{CH_3OH}}{p_{H_2}^{1/2}}\left(1 - \frac{p_{H_2}^3 p_{CO_2}}{k_{MSR} p_{H_2O} p_{CH_3OH}}\right) C_{S1}^T C_{S1a}^T S_a}{\left(1 + \frac{K^*_{CH_3O^{(1)}} p_{CH_3OH}}{p_{H_2}^{1/2}} + \frac{K^*_{OH^{(1)}} p_{H_2O}}{p_{H_2}^{1/2}} + K^*_{HCOO^{(1)}} p_{H_2}^{1/2} p_{CO_2}\right)\left(1 + \sqrt{K^*_{H^{(1a)}} p_{H_2}}\right)} \quad (15)$$

Eq. (15) considers the adsorption equilibrium constants (K^*_i) for the intermediate species (Eqs. (6)–(14)), the MSR equilibrium constant (K_{MSR}) and the total catalyst surface concentrations of sites 1 (C_{S1}^T) and 2 (C_{S2}^T). The temperature dependence of the kinetic constant was calculated according to the Arrhenius equation (Eq. (5)) and the temperature dependence of the adsorption equilibrium constants was calculated according to van't Hoff equation (Eq. (16)):

$$\ln K_i = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (16)$$

where ΔH and ΔS are the enthalpy and entropy of adsorption respectively. The model has a total of 10 parameters, including the activation energy and pre-exponential factor.

2.3. Parameter estimation

The parameters of the kinetic models (Eqs. (4), (15)) were obtained by non-linear regression method [34,35]. The experimental reaction rates were determined based on the first derivative of the polynomial equation used to fit the experimental methanol conversion as a function of space-time ratio (m_{cat}/F_{MeOH}); the parameters were then obtained minimizing the mean residual sum of the squares (MSRR) of the experimental and model reaction rates. The power-law model has 6 parameters, including the activation energy and pre-exponential factor. According to the values reported in the literature [28–31], the apparent reactions rates were allowed to be any real number between -2 and 2 and the activation energy between 60 and 100 kJ mol^{-1}. The mechanistic model has a total of 10 parameters or 20 when included the temperature dependence, by Arrhenius and by van't Hoff equations.