



Synthesis and characterization of gallium-promoted copper–ceria catalyst and its application for methanol steam reforming in a packed bed reactor



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ABSTRACT

A co-precipitation method was used for the synthesis of a novel copper–ceria catalyst promoted with gallium. Structural characterization was performed by SEM, EDS, BET, XRD, and XPS techniques. Methanol steam reforming was conducted inside a miniaturized LTCC packed bed reactor in the temperature range of 300–400 °C, and hydrogen was successfully produced from a water and methanol mixture. The kinetics of the reforming process were evaluated and the operation of the miniaturized reactor was described with a 3D finite element model, which included all governing mechanisms: fluid dynamics, transport phenomena and reaction kinetics.

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1. Introduction

Proton exchange membrane fuel cells require hydrogen for their operation and methanol steam reforming is one of the most efficient processes utilized for hydrogen production. Due to the fact that hydrogen is in gaseous form at normal temperature and pressure conditions, it is more convenient to produce it on site from methanol. Unlike hydrogen, methanol can easily be stored and transported through the existing infrastructure, which is why it is considered as one of the most promising logistic fuels. Methanol is an efficient hydrogen carrier with a high energy density and hydrogen to carbon ratio. It does not contain carbon–carbon bonds, which considerably reduces the risk of coke formation during its reactions [1]. It can readily be obtained from renewable sources.

Copper oxide-based catalysts exhibit particularly high activity and high selectivity for the reforming of methanol [2]. They are considered more suitable than noble metal catalysts, since they are more active and selective than gold or platinum based catalysts at the operating temperature of PEM fuel cells, and also due to their lower cost [3,4]. Successful operation of the methanol steam reforming process requires an active and stable catalyst and

Cu/ZnO₂/Al₂O₃ catalysts have been extensively investigated in the past [5]. Various power-law and Langmuir–Hinshelwood reaction rate expressions have been put forward in literature and were summarized by Lee et al. [5]. The most acknowledged and extensively used kinetic expression was published by Peppley et al. [6].

Recently, a new class of copper, zinc, and gallium mixed oxides catalyst were discovered for methanol steam reforming, which were highly active at temperatures lower than 200 °C [7]. The superior activity of the catalysts was attributed to Ga incorporation into the Cu–Zn oxide, which leads to the formation of a nonstoichiometric cubic spinel phase containing interstitial Cu⁺ ions, which can produce *in situ* a high population of extremely small 5 Å copper clusters at high dispersion [8].

The application of CeO₂, as either a support material or a promoter, has been found to improve the efficiency of Cu-based catalysts [1]. It has been shown that it provides a high oxygen mobility and strong interaction with the supported metal [9]. Ceria is not only an inert carrier for supported species, but also affects the degree of dispersion, redox behavior and catalytic activity of supported catalysts [10]. It has been shown, that pure ceria is a poor catalyst for methanol steam reforming, but an important synergistic effect between copper and ceria exists [3]. Men et al. [3] found that pure ceria had the lowest catalyst activity, which emphasizes the important role of copper in the methanol steam reforming reaction.

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Baneshi et al. [11] studied the effect of ceria on methanol conversion. They found, that the addition of ceria produced smaller copper crystallites and that it enhanced surface homogeneity. In another work by Baneshi et al. [12], they found that ceria containing catalysts ($\text{CuO}/\text{CeO}_2/\text{Al}_2\text{O}_3$) were the best among different ceria and zirconia samples. Patel and Pant [13] discovered that the high catalytic activity and hydrogen selectivity shown by ceria promoted $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts are attributed to the improved specific surface area, dispersion and reducibility of copper. Zhang and Shi [14] studied hydrogen production by steam reforming of methanol on CeO_2 promoted $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts. They found that ceria promoted $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts exhibited higher activity and stability as compared to the unpromoted ones.

The reaction mechanism of methanol steam reforming, in the case of copper/ceria catalyst, presumes that the copper/ceria boundary is the active site for steam reforming of methanol, and that oxygen reverse spillover from ceria to copper is involved in the catalysis cycle [3]. In a microkinetic study, Frank et al. [15] proposed that the rate determining step is the dehydrogenation of the methoxy group, while all of the other elemental reactions are in thermodynamic equilibrium.

In this work, a gallium-promoted copper–ceria catalyst was synthesized, characterized, and applied for methanol steam reforming in miniaturized packed bed reactor. The small dimensions of the reformer allow for the development of a portable system. The operation of the miniaturized reactor was described with a mathematical model, which included all governing mechanisms: fluid dynamics, transport phenomena and reaction kinetics. Modeling is a useful tool to predict the process behavior upon the variation of operating conditions, to optimize the reactor geometry in terms of pressure drop and heat/mass transfer, and to provide an insight into the distribution of the reacting species.

2. Materials and methods

2.1. Catalyst preparation

A gallium-promoted copper–ceria catalyst for methanol steam reforming was synthesized with a pH-controlled co-precipitation method. 9.75 g of copper ceria precursor $\text{Cu}_{0.20}\text{Ce}_{0.80}\text{O}_{2-x}$ and 1.23 g of $\text{Ga}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ were dissolved in 100 mL of deionized water, and 100 mL solution of 3.50 g Na_2CO_3 (for the production of the precipitate) was also prepared. Each solution was placed into a 50 mL glass syringe. 100 mL of distilled water was heated to 80 °C on an electric heater, equipped with a magnetic stirrer. The prepared solutions were simultaneously fed into the flask, while the solution was stirred at 1200 rpm with a magnetic mixer. Co-precipitation was performed at the pH of 6.5, which was monitored with a pH electrode, and regulated by adjusting the flow rate of the Na_2CO_3 solution.

The precipitate was aged in the solution for 24 h, centrifuged, washed with distilled water to remove Na^+ ions, and dried overnight. Calcination was performed in static air with the temperature increasing at 3 °C min^{-1} from 20 °C to 380 °C.

Further preparation included pressing, grinding and sieving. Appropriate sieves were used to obtain a 250–500 μm size fraction. The catalyst was inserted into the reactor. Before experimentation, it was reduced *in situ* at 220 °C for 4 h with 5 vol% H_2 in Ar.

2.2. Catalyst characterization

2.2.1. SEM, EDS and XPS

The catalyst was structurally characterized after pre-treatment by field emission scanning electron microscopy (FEG-SEM) (SUPRA

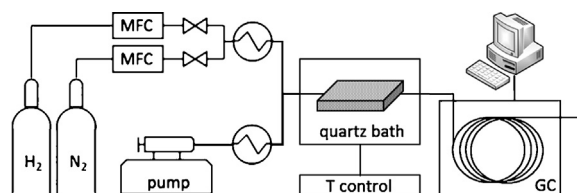


Fig. 1. The process flow diagram of the experimental set-up.

35 VP, Carl Zeiss, Jena, Germany) and energy dispersive X-ray spectroscopy (EDS) (Inca 400, Oxford Instruments, Tubney Woods, UK).

The spectra from X-ray photoelectron spectroscopy (XPS) of the catalyst sample were collected with a TFA XPS Physical Electronics spectrometer. Analysis of the surface composition in terms of atomic ratios was performed.

2.2.2. BET

The Brunauer–Emmett–Teller (BET) surface area and the pore structure of the synthesized catalyst were determined by measuring nitrogen physisorption at liquid nitrogen temperature with an ASAP2020 instrument (Micromeritics Apparatus).

2.2.3. XRD

X-ray diffraction (XRD) patterns of the catalyst powder sample were obtained with a PANalytical X'Pert PRO MPD apparatus. The diffraction patterns were recorded at room temperature with a $\text{CuK}\alpha$ radiation source at $\lambda = 0.15406$ nm from a generator operating at 45 kV and 40 mA in the 2θ range between 10° and 70°.

2.3. Methanol steam reforming

The miniaturized packed bed reactor used for performing the methanol steam reforming reactions was developed with LTCC (low temperature co-fired ceramic) technology, which is suitable for the production of complex 3D structures [16]. The reactor had an inner reaction chamber with the dimensions of 33.8 mm × 4 mm × 41.4 mm (width × depth × length). The reaction chamber was separated from the inlet and outlet ports with 76 ducts, each with the dimension of 1 mm × 0.15 mm, for the entrapment of the catalyst particles. 6.73 g of the produced catalyst particles were inserted into the inner reaction chamber through a service hole, which was sealed afterwards.

The reactor was positioned inside an electric heater in a quartz sand bath (Fig. 1). During experimentation, it was heated to the operational temperature. A laboratory syringe pump (TSE Systems, Chesterfield, USA) was used for the dosage of the liquid methanol/water mixture, which was evaporated in a coil evaporator prior to entering the reactor. The gaseous products were analyzed with a gas chromatograph. Calibration was performed with standard gas mixtures. 5% hydrogen in argon cylinder was connected through a mass flow controller to the reactor for catalyst activation, and a nitrogen cylinder was connected for reactor purging.

The catalytic behavior was monitored under varying operational parameters such as temperature (300–400 °C), flow rate (10–200 $\mu\text{L min}^{-1}$), and steam to methanol ratio (1, 1.5, and 2). Apart from the unreacted methanol and water, CO, CO₂, and H₂ were identified in the product stream. Minute amounts of methane could also be observed.

2.4. Analysis

An Agilent 7890A gas chromatograph (Agilent Technologies, Santa Clara, USA) with two capillary columns: HP-PLOT-Q (30 m × 0.53 mm × 40 mm) and HP-PLOT-5A

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