CO preferential oxidation in a novel Au@ZrO$_2$ flow-through catalytic membrane reactor with high stability and efficiency

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ABSTRACT

CO preferential oxidation (CO-PROX) achieves much interest as a strategy to remove trace CO in reformed gases for hydrogen utilization. Herein, we reported a novel Au@ZrO$_2$ catalytic membrane reactor by embedding gold nano-particles in ZrO$_2$ hollow fiber membrane for CO-PROX. The flow-through catalytic membrane exhibited high catalytic activity and oxygen selectivity, which gave a turnover frequency of 4.73 s^{-1} at 60 °C, 2—3 times higher than conventional catalyst pellets. CO conversion of >95% was achieved over the catalytic membrane, which maintained great operational stability during 500-h operation even CO$_2$ and H$_2$O were added in the feed stream. The excellent catalytic performance of the flow-through catalytic membrane makes gold catalyst possible for practical application in the removal of CO from hydrogen.

Introduction

Hydrogen, as a green energy carrier derived from fossil fuels or biofuels, has been greatly attractive in last decades. Proton exchange membrane fuel cell (PEMFC) supplied with hydrogen is among the most advanced power generation devices for its high energy conversion efficiency, rapid start-up, and low operating temperature. It always requires an ultra-low CO content of <10 ppm to prevent Pt-based anode from poisoning. CO preferential oxidation (CO-PROX) in H$_2$-rich gas is a critical reaction for CO deep elimination due to its efficiency and simplicity [1—4]. Since Haruta et al. [5] discovered that small gold nano-particles finely dispersed on certain metal oxide supports exhibited high activity for CO oxidation below room temperature, extensive studies have addressed the structures and mechanisms associated with supported gold catalysts [6—10].

Reducible metal oxides, such as TiO$_2$, CeO$_2$, Fe$_2$O$_3$ and ZrO$_2$, are most commonly used as supports for gold catalysts in CO oxidation, which could not only create more contact between the metal and support but also activate oxygen through

oxygen-vacancy defects for the conversion of CO to CO_2 [11—16]. Schubert et al. [17] claimed that Au/TiO_2, Au/CeO_2 and Au/ZrO_2 exhibited a CO oxidation activity of up to one magnitude higher than the gold catalysts over inert supports like γ-Al_2O_3 and SiO_2. However, deactivation was a critical issue on supported gold catalysts as related to the accumulation of carbonate species. Denkwitz et al. [18] studied deactivation behaviour of Au/TiO_2, the initial activity suffered from a significant deactivation of 70—85% within 1000 min at 80 °C. Zhang et al. [19] reported a fast deactivation on Au/CeO_2 from 61% to 46% in 120 min in humid stream at room temperature with a CO concentration of 500 ppm. Widmann et al. [20] observed a gradual decrease in CO oxidation activity on Au/ZrO_2 and attributed it to the high coverage of carbon containing surface species on the catalyst. How to improve the catalytic efficiency and stability are still the challenges for gold catalysts in practical operation environments.

Flow-through catalytic membrane reactor (FTCMR) is constructed with a porous membrane loading with active catalyst, which is operated in a dead-end mode to force feed stream flowing over active sites [21]. The porous membrane structure could enhance the catalytic efficiency by increasing mass transfer of the reactant to the catalysts. Previously, FTCMR has been successfully demonstrated for catalytic reactions such as partial hydrogenation [22], VOC decomposition [23] and photocatalytic oxidation [24] with high catalytic efficiency. FTCMR was also developed for CO oxidation over Pt/NaY zeolite membrane at 200 °C [25,26], which achieved a reduction of CO concentration to below 10 ppm. The use of FTCMR for catalysis of gold nano-particles is of great interest because the membrane reactor could improve not only catalytic efficiency but also catalytic stability. We speculated that the flowing stream could sweep the generated product and control residence time to avoid accumulation of carbonate species.
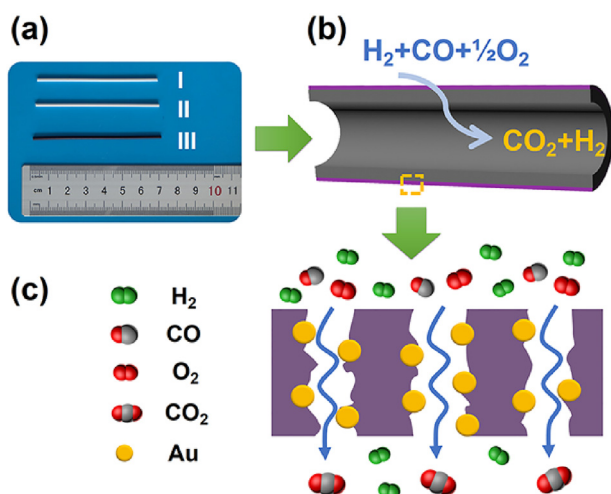

Fig. 1 — Schematic diagram of hollow fiber configured Au@ZrO$_2$ catalytic membrane for CO-PROX. (a) Photographs of the Al$_2$O$_3$ hollow fiber (I), ZrO$_2$ membrane supported by Al$_2$O$_3$ hollow fiber (II) and Au@ZrO$_2$ membrane (III). (b) CO-PROX reaction carried out on the catalytic membrane. (c) Reaction process in Au@ZrO$_2$ membrane.

In this study, we developed a novel hollow fiber configured $Au@ZrO_2$ catalytic membrane for CO-PROX (Fig. 1). We aimed to obtain superior activity and stability for CO oxidation at relatively low reaction temperature by the use of FTCMR loading with gold catalysts. Hollow fiber configured ZrO_2 membranes with small diameters were used to provide high membrane area/volume ratio (>1000 m^2 m^{-3}) in membrane modules, which is very important in reduction of fabrication cost and improvement of throughput for industrial scale. We will demonstrate that both catalytic efficiency and stability of $Au@ZrO_2$ catalytic membranes could be achieved for CO-PROX, which makes it a promising candidate for the removal of CO from hydrogen in practical application.

Experimental

Preparation of hollow fiber Au@ZrO$_2$ catalytic membranes

Fig. 2 shows the preparation procedure of $Au@ZrO_2$ catalytic membrane. Porous α-Al_2O_3 hollow fibers were fabricated by a dry-wet spinning technique [27,28]. They offered an outer diameter/inner diameter (O.D./I.D.) of 1.8 mm/0.9 mm, an average pore size ~0.65 μm and a porosity about 48%. α-Al_2O_3 powders (d_{50} = 0.8 μm, Hai-Gang-Hua-Tai functional ceramics Co., Ltd.), polyethersulfone (PESf, BD-5, Bei-Shi-De synthetic plastics company), n-methyl-2-pyrrolidone (NMP, $\geq$98%, Sinopharm Chemical Reagent Co., Ltd.) and poly-vinylpyrrolidone (PVP, $\geq$95%, Sinopharm Chemical Reagent Co., Ltd.) were respectively used. A detailed procedure for the fabrication of these hollow fibers was reported in our previous publication [29,30]. ZrO_2 membranes were prepared by hydrothermally secondary growth using ZrO_2 particles as seeds. 7 g zirconium (IV) nitrate pentahydrate ($Zr(NO_3)_4 \cdot 5H_2O$, $\geq$99.5%, AR, Sinopharm Chemical Reagent Co., Ltd.) was added into 100 mL deionized water and dissolved adequately. The pH of this aqueous solution was then adjusted to 9.0 by 0.5 M NH_4OH solution while the solution was being stirred. After aged for 12 h and freeze-dried for 24 h, the original ZrO_2 powders were collected. The ZrO_2 seeds with an average particle size around 1.5 μm were obtained by milling original ZrO_2 powders for 6 h using a planetary ball mill (Retsch. Ind. Ltd., PM-100) with zirconium oxide balls as grinding media. Al_2O_3 hollow fiber substrates were firstly ultrasonically cleaned in deionized water and then dried in an oven at 60 °C. Both ends of hollow fibers were wrapped by Teflon tapes. The substrates were dipped into an aqueous seed suspension with seeds content of 1 wt% for 10 s and dried at 60 °C. This process was repeated twice. Subsequently the seeded substrates were sintered at 450 °C for 4 h. A seed layer with uniform and good coverage was formed on outer surface of the hollow fibers. The synthesis gel for ZrO_2 membranes were prepared from the $Zr(NO_3)_4$ solution pre-adjusted to pH = 9. The seeded support was immersed into synthesis solution for hydrothermal crystallization at 180 °C for 60 h. The as-synthesized membranes were then calcined at 450 °C for 4 h. A close-packing ZrO_2 membrane with regular thickness of about 10 μm was grown on the outer surface of the hollow fiber. A $HAuCl_4$ stock solution was prepared by dissolving 1.0 g of Tetrachloroauric (III) acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$, Shanghai Reagent,