Applied Catalysis B: Environmental 174 (2015) 67–76

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

CuO/ZnO catalysts for methanol steam reforming: The role of the support polarity ratio and surface area

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form 20 February 2015
Accepted 27 February 2015
Available online 28 February 2015

Keywords:
CuO/ZnO catalysts
Polarity ratio
Methanol steam reforming
CO selectivity
Pd-membrane

ABSTRACT

The effect of surface area and polarity ratio of ZnO support on the catalytic properties of CuO/ZnO catalyst for methanol steam reforming (MSR) are studied. The surface area of ZnO was varied changing the calcination temperature, and its polarity ratio was modified using different Zn precursors, zinc acetate and zinc nitrate. It was found that the copper dispersion and copper surface area increase with the surface area of the ZnO support, and the polarity ratio of ZnO strongly influences the reducibility of copper species. A higher polarity ratio promotes the reducibility, which is attributed to a strong interaction between copper and the *more polar* ZnO support. Interestingly, it was observed that the selectivity of CuO/ZnO catalysts (lower CO yield) increases with the polarity ratio of ZnO carriers. As another key result, CuO/ZnO$_{Ac375}$ catalyst has proven to be more selective (up to 90%) than a reference CuO/ZnO/Al_2O_3 sample (G66-MR, Süd Chemie).

The activity of the best performing catalyst, CuO/ZnO$_{Ac\text{-}375}$, was assessed in a Pd-composite membrane reactor and in a conventional packed-bed reactor. A hydrogen recovery of *ca.* 75% and a hydrogen permeate purity of more than 90% was obtained. The Pd-based membrane reactor allowed to improve the methanol conversion, by partially suppressing the methanol steam reforming backward reaction, besides upgrading the reformate hydrogen purity for use in HT-PEMFC.

1. Introduction

The methanol steam reforming (MSR) reaction has received much attention in the past few decades as an attractive route of producing hydrogen for small-scale polymer electrolyte membrane fuel cells (PEMFC):

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \Delta H^\circ = 49.7\,\text{kJ mol}^{-1} \quad (1)$$

MSR catalysts are usually divided in two main groups: Cu-based and the more recent Pd-based ones [1]. Regardless, the catalyst type ZnO support has a ubiquitous presence. Although CuO/Zn-based catalysts are used in industry since the 1960s, the role of ZnO in these catalysts systems remains unclear despite the efforts made to elucidate its role [2–6]. For instance, Karim et al. investigated the effect of ZnO morphology on the reactivity of PdZnO catalysts for MSR [7], and concluded that the activity was higher for faceted ZnO materials [7]. In line with the former work, the theoretical studies by Smith et al. demonstrated that the polar crystalline surfaces of ZnO has null energetic barrier for both methanol and water dissociation [8]. On this basis, one could assume that ZnO with higher ratio of polar surfaces, namely higher polarity ratio, would lead to MSR catalysts with enhanced activity. This concept has in fact gained more attention as evident from the studies by Boucher et al. [9,10], who investigated the influence of the properties of various carriers (mainly shapes and defects) on the reactivity of Au-based catalysts for WGS and MSR reactions. These authors concluded that for different ZnO nanoshapes the activity increased when the binary catalysts were prepared with *more polar* supports (higher polarity ratio). Nevertheless, to our knowledge there is no study over CuO/ZnO catalysts that establishes a relation between the support polarity ratio and the selectivity toward MSR. However, this aspect is of crucial importance for fuel cell applications where the

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Abbreviations: MR, membrane reactor; CR, conventional reactor; MSR, methanol steam reforming; WHSV, weight hourly space velocity; PEMFC, proton exchange membrane fuel cell.

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http://dx.doi.org/10.1016/j.apcatb.2015.02.039

presence of CO should be minimized as much as possible since even ppm levels of CO irreversibly poison Pt electrodes.

Recently, a simple urea-assisted hydrothermal method for tailoring the physicochemical properties of ZnO materials was reported by the research team [11]. It was found that the specific surface area, morphology and polarity ratio of the resulting ZnO solids were strongly affected by the synthesis conditions employed [11], in particular, the presence and concentration of surfactant (Pluronic P123) and type of metal salt precursor (Zn-acetate *vs* Zn-nitrate). The main conclusions of this study were: (i) the addition of Pluronic P123 results in better dispersion of ZnO particles (hierarchical ZnO microflowers are formed), higher polarity ratio (higher ratio of (0 0 2) polar planes), and ZnO materials with enhanced surface area; (ii) the morphology, polarity ratio and reactivity are also affected by the Zn salt used as precursor. The use of Zn-nitrate led to urchin-like ZnO structures (ZnO microflowers were formed when using Zn-acetate) with lower polarity ratio (higher proportion of (1 0 0) non-polar planes) than their acetate derived counterparts. The ZnO sample with the highest polarity ratio (the acetate derived ZnO) also exhibited the highest photoactivity, which is *ca.* 2 times higher than that of the "*less polar*" (lower polarity ratio) nitrate derived ZnO. These results suggest that both samples have different reactivity, being higher for the ZnO with higher polarity ratio [11].

MSR reaction should be carried out at low temperature to exploit the favorable thermodynamics to yield low CO, but it is equilibrium limited and then, for high conversions, the back reaction penalizes the overall reaction rate. The use of a Pd-based membrane reactor allows hydrogen product to be continuously removed from the reaction medium and then enhances the overall reaction kinetics resulting in enhanced conversions and in the production of a high purity hydrogen stream. Low temperature PEMFCs require hydrogen with very low concentrations of CO; the automotive standard imposes a maximum CO concentration of 0.2 ppm (ISO 14687-2). This high purity hydrogen can be obtained using a Pd-based purification process or, with advantages, using a Pd-based membrane reactor. However, Pd-membranes are poisoned by CO, which adsorbs on the membrane surfaces inhibiting the hydrogen permeation [12]. Pd-based composite membranes are characterized by a thin Pd layer deposited onto porous substrates and show high permeability and selectivity to hydrogen [13–16]. A growing attention is then been devoted to Pd-composite membranes that have – among others – the advantage of lower cost and higher permeability because of the reduced palladium content utilized in these membranes [13–18]. Numerous studies deal with MSR reaction carried out in both dense and composite Pd-based MRs [17–25]. In most of them, it has been demonstrated that these MRs made possible higher performances than conventional packed bed reactors (CR) in terms of methanol conversion and hydrogen yield with the further benefit of producing high-grade hydrogen. Dense self-supported Pd–Ag membranes with a thickness of 50 μm and composite Pd-based membranes with Pd-layers thicker than 10 μm were used in previous studies of steam reforming of methanol [18,21–23]. This work uses a thin composite membrane of *ca.* 8 μm deposited onto a ceramic support and the direct contact of the catalyst with the composite membrane is assessed in terms of methanol conversion, hydrogen recovery and hydrogen permeate purity as well as permeation characteristics stability.

In this context, the first part of this work investigates the role of ZnO surface area and polarity ratio on the activity–selectivity of CuO/ZnO catalysts at low temperature. Two types of ZnO samples were prepared as detailed in [11] and used as supports of CuO/ZnO catalysts: a series of ZnO samples with different specific surface area and similar polarity ratio and a group of ZnO samples with similar specific surface area but different polarity ratio. It should be noted, however, that in the present work the term "polarity ratio" is used to refer the relative intensities of the polar and the nonpolar planes of ZnO, ($I_{(0\,0\,2)}/I_{(1\,0\,0)}$). A commercial isotropic würtzite ZnO from Sigma–Aldrich was taken as a reference and studied by XRD. The reference ZnO sample gave a value of 0.73 for the (0 0 2)/(1 0 0) intensity ratio, thus, intensity ratio values higher than the würtzite reference ($I_{(0\,0\,2)}/I_{(1\,0\,0)} = 0.73$) denote a higher polarity ratio, and consequently, a higher ratio of exposed polar facets, and *vice versa*.

The second part of this work evaluates the performances of the best CuO/$ZnO_{Ac\text{-}375}$ catalyst, among the ones reported in this work, in a Pd-membrane reactor.

2. Experimental

2.1. Preparation of ZnO supports

ZnO samples were prepared by a modified hydrothermal method as detailed elsewhere [11]. In a typical preparation, 1.1 g of zinc salt precursor (zinc acetate or zinc nitrate), 6 g of urea and 3 g of P123 Pluronic block copolymer were mixed in 100 mL of water. The pH was adjusted to 5 and the solution was stirred for 2 h under ambient conditions. Then, the mixture was poured into a teflon lined autoclave and kept at 90 °C for 24 h. The precipitate was thoroughly washed with distilled water and dried at 110 °C overnight. The resulting solid was calcined in a muffle furnace at given temperature for 30 min.

Table 1 shows the ZnO samples prepared. The following nomenclature for ZnO samples was used (Table 1) $ZnO_{x\text{-}CT}$, where: *x* denotes the zinc precursor, zinc-acetate (Ac) or zinc-nitrate (N) and CT represents the calcination temperature in °C (Table 1). Accordingly, the $ZnO_{Ac\text{-}375}$ sample was prepared from zinc-acetate as precursor and calcined at 375 °C for 30 min. SEM images of the series of ZnO materials ($ZnO_{Ac\text{-}CT}$) obtained at different calcination temperatures are shown in Fig. 1.

2.2. Preparation of CuO/ZnO catalysts

CuO/ZnO catalysts were prepared by impregnation of the ZnO supports with an aqueous solution of copper nitrate (the amount of copper calculated to achieve a nominal metal loading of 15 wt.%). The pH was adjusted to 6 by dropwise addition of ammonium

Table 1
Experimental parameters studied for the preparation of ZnO samples, calcination temperature series ($ZnO_{Ac\text{-}CT}$: Ac Zn-acetate as precursor; CT: calcination temperature); Zn-precursor series (ZnO_x-375: *x* stands for Zn-acetate (Ac) or Zn-nitrate (N); both samples were calcined at 375 °C).

Parameter studied	Range	Sample name	S_{BET} ($m^2\,g^{-1}$)	Polarity ratio* $I_{(0\,0\,2)}/I_{(1\,0\,0)}$
Calcination temperature (CT) (°C)	300	$ZnO_{Ac\text{-}300}$	64	0.76
	350	$ZnO_{Ac\text{-}350}$	71	0.78
	375	$ZnO_{Ac\text{-}375}$	80	1.10
	400	$ZnO_{Ac\text{-}400}$	54	0.80
Zn-precursor	Zn-acetate	$ZnO_{Ac\text{-}375}$	80	1.10
	Zn-nitrate	$ZnO_{N\text{-}375}$	77	0.60

*Ratio between XRD plane (0 0 2) and plane (1 0 0) – indicates the polarity degree of the ZnO carriers. The polarity ratio of an isotropic würtzite ZnO from Sigma–Aldrich was 0.73.