Research article

Synthesis, characterization and activity of CuZnGaOx catalysts for the water–gas shift (WGS) reaction for H_2 production and CO removal after reforming

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ABSTRACT

CuZnGaOx catalysts were prepared by co-precipitation synthesis method and their turnover performance was evaluated for the water–gas shift (WGS) reaction. The effects of pH on composition, structure and morphology were investigated. Materials were characterised using powder XRD, physisorption, chemisorption and electron microscopic techniques. Basic preparation conditions produced smaller, uniform and homogenously distributed particles, while a high interface concentration of bulk copper phase was observed at acidic pH. X-ray diffraction peak, corresponding to CuO(111), was broader at neutral/alkaline pH, which indicated small synthesized crystallites, disordered oxide arrangement and polymorphism. The analyses after H_2-TPR revealed that all Cu was in the metallic oxidation state after reduction. H_2-TPR profiles demonstrated that a stronger comparative interaction between Cu–ZnO_x and Cu–GaO_x existed for a higher applied syntheses pH. Continuous temperature-programmed surface reaction (TPSR) measurements showed that these also granted the thermodynamic equilibrium CO conversion at 240 °C. Time-on-stream catalytic activities were examined in a fixed bed reactor. An increase in the vaporised steam content in reactant feedstock mixture caused a rise in CO consumption and effluent hydrogen productivity. WGS process was thus structure-sensitive to the supported active metal in CuZnGa-based composite nano-catalysts. Intrinsic kinetic reactivity was proportional to Cu area, dispersion and sites, which could be altered by precipitation composite fabrication pH. The methane, methanol or ethanol reforming design with low-temperature WGS is particularly vital in high-temperature proton-exchange membrane fuel cells (PEMFC), in which thermal unit integration may be used to supply heat from the stack to WGS operation, and in the case of CH_3OH, even reformer.

1. Introduction

The water–gas shift reaction (WGS) plays a key role in the production of hydrogen, ammonia, methanol, and other chemicals [1]. It is an industrially relevant reaction, which takes place in large scale industrial processes [2]. It has recently received renewed interest because of its importance in hydrogen fuel processing for fuel cell applications, where the carbon monoxide produced by the steam reforming reactions must be removed or converted because of its poisonous nature for the electrodes in the fuel cells. The hydrogen, which is produced, can be used directly as fuel or for the powering of fuel cells. The reaction also takes place in parallel to steam reforming of hydrocarbons (e.g. methane, methanol, etc.), where it converts carbon monoxide to CO_2 [3]. It is also crucial as an intermediate clean-up step for hydrogen enrichment and CO reduction in the synthesis of the gas [4,5].

The WGS reaction is an exothermic reaction which is thermodynamically favourable at lower temperatures, while higher reaction rates are favourable at higher temperatures, which is why it is carried out in two distinct stages [6]. Two different types of catalysts are used: for the high-temperature shift reaction (HTS, 350–450 °C) a Fe-based catalyst, and for the low-temperature shift reaction (LTS, 180–250 °C) a Cu-based catalyst. For HTS, the reaction is regulated by the thermodynamic equilibrium, because the WGS reaction is exothermic. For LTS, the required amount of the catalyst is extensive for achieving a low CO concentration [7], because the reaction order for CO is close to 1. It is necessary to develop a WGS process that proceeds in a one-step reaction and to develop a catalyst that is stable at rather low temperatures, with a high tolerance for oxidative conditions in steam or air [8].

It has been established that gold catalysts on well-crystallized supports, Au/Fe_2O_3 and Au/ZrO_2, display higher catalytic activity in the WGS reaction in comparison with the samples on amorphous and not

well-crystallized supports: Au/ZnO, Au/ZrO$_2$, Au/Fe$_2$O$_3$–ZnO and Au/Fe$_2$O$_3$–ZrO$_2$. From these studies, it could be concluded that the catalytic activity of the metal oxide catalysts depends strongly not only on the dispersion of the metal particles but also on the state and the structure of the supports [9]. In literature, it is widely reported that the Pt/CeO$_2$ sol–gel and Au/CeO$_2$ co-precipitation catalysts exhibited high activity and selectivity for the WGS reaction [10]. Many studies for WGS catalysts have been reported in the past three decades. Noble metals reportedly enhance the activity of metal-based catalysts [11,12], but their scarcity raises their price, creating concerns when applying the catalysts in an industrial setting. Furthermore, several combinations of metals have been reported as candidates for use as LTS catalysts [3,9,13]. For the LTS reaction, Cu-based catalysts, for instance, Cu/ZnO/Al$_2$O$_3$, Cu/ZnO, Cu–Mn and Cu–CeO$_2$, show a high activity [14]. The catalytic performance of supported Cu catalysts depends strongly on the degree of reduction of the catalyst and partly on the dispersion of Cu [13]. Cu-based catalysts are especially interesting due to their low prices and good catalytic activity, selectivity and stability [15]. It has been reported that their catalytic performance is highly dependent in terms of their preparation methods. To date, copper-based catalysts have been prepared by various wet and dry chemical methods [16–19]. The structure of the catalyst determines the surface area, the active sites and the interactions between the active metal and support [20]. The spinel structure is ordinarily a cubic close-packed lattice of mixed metal oxides comprising copper. It showed remarkable effectiveness for methanol steam reforming, the WGS reaction, dimethyl ether reforming and carbon monoxide oxidation [15].

The enhancement of WGS activity over Cu catalyst is observed when it is combined with Ni metal. The formation of methane as the undesired side product is one of the major issues in the WGS reaction, particularly for nickel-based catalysts. The Ni–Cu alloy phase is found to be the active site for WGS reaction with methane suppression as Ni–Cu alloy can enhance CO adsorption which prevents CO dissociation during high-temperature WGS reaction [21]. LaNiO$_3$ perovskite has been successfully used as a catalyst precursor for high temperature water–gas shift reaction of reformate gas to produce additional hydrogen from the hydrocarbon reforming which can effectively suppress CO methanation during HT-WGS reaction using pure CO/H$_2$O gas [22,23]. The surface hydroxyl species generated by partially reduced Ni-containing phyllosilicate structures enhanced catalytic performances and methane suppression compared to the conventional Ni/SiO$_2$ catalyst [24]. Additionally, K was found to enhance reduction of CeO$_2$ and promote water dissociation on reduced CeO$_2$ to form hydroxyl (OH) groups, which dissociate further into adsorbed oxygen that reacts with adsorbed CO on Ni to form adsorbed CO$_2$ [25]. Ang et al. [26] showed that the bimetallic Ni–Cu alloy is vital in increasing the reactivity of CO and OH through a highly dispersed and homogeneous Ni–Cu alloy supported on SiO$_2$. They found that the interaction of Na and Ni leads to the absence of low coordinated Ni species, thereby preventing the formation of subcarbonyl nickel species which are the precursors for the CO methanation reaction [27]. 10 wt% bimetallic Ni-Cu catalyst encapsulated by CeO$_2$ exhibited high catalytic activity and stability at 500 °C in the high-temperature water–gas shift reaction [28]. With the well dispersed Ni–Cu alloys, this activates the surface lattice oxygen which takes part in catalyzing water–gas shift reaction at high temperatures. The water–gas shift reaction mechanism strongly depends on the Ni–Cu surface composition rather than the size of Ni–Cu alloys [29]. In addition to Ni-Cu catalyst, Ni-Mg nanotubular catalyst also shows excellent stability and activity for ultrahigh temperature WGS, which can be attributed to its unique nanotubular structure that confers good thermal stability and the introduction of weak basicity by Mg to promote H$_2$O dissociation and CO activation in WGS activity, respectively [30].

Recent studies for the production of hydrogen by the direct steam reforming of methanol over CuZnGaOx catalyst showed a high catalytic activity [20,31–33]. This can be attributed to the spinel structure of the CuZnGaOx catalyst, where Cu^{2+} in an O$_h$ site manifests the prolongation and weakening of the Cu–O bonds along the axial plain (Jahn–Teller effect), which leads to the removal of axial oxygen. It is assumed that substituting Cu^{2+} for Zn^{2+} (d10) removes or decreases the instability of the spinel structure, caused by the Jahn–Teller effect, and that there is a higher possibility for Ga^{3+} to enfold Zn^{2+} rather than Cu^{2+}, which leads to a large excess of free Cu^{2+} in the vicinity of the spinel structure [20]. Thus, from the practical point of view, the above-mentioned complex preparation methods will not be proposed. The traditional precipitation method is the most suitable for developing effective WGS catalysts. In fact, the precipitation method may contain some different precipitation processes, which may have an effect on the catalytic activities.

Various conditions maintained in the preparation such as pH, temperature, stirring, precursors, recovery and thermal treatments are significant key features which present themselves in the final material morphology, structure, and performance. Among these, pH is a key factor which influences the structure, metal dispersion and surface area of the catalysts. In the case of Cu/Zn/Al catalysts, titration experiments have shown that precipitation is preferably performed at constant pH. When the pH is slowly increased, a sequential precipitation results, whereby Cu is first precipitated followed by Zn [34]. The precipitation of Cu–Zn was studied by Baltes et al. [35] at different pH values (4.5–10) and temperatures (30–70 °C). The precipitation conditions had little effect on the Cu/Zn/Al ratio, which was similar in all precipitated samples and close to that of the initial solution (60:30:10). Conversely, large differences were observed in the Cu^0 surface areas after reduction at 300 °C in H$_2$. The lowest Cu^0 surface areas were found at a very low pH, where powder XRD revealed large CuO crystallites. High Cu^0 surface areas were generally found at a pH of 6–7 which is in agreement with the results of previous studies [34–36]. Under these conditions, small CuO particles and some residual zincian malachite, (Cu, Zn)$_2$ (CO$_3$) (OH)$_2$, were reported after calcination [4,34,37].

Since the catalyst structure determines the catalyst activity, selectivity, and stability, the co-precipitation parameters have a critical influence on the catalysts' structure. In this study, we prepared Cu-based catalysts by co-precipitation at different constant pH values, and their performance was tested for the LTS reaction. To evaluate the physical properties of CuZnGaOx, the catalysts were characterised by various techniques such as Brunauer–Emmett–Teller (BET) surface analysis, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), powder X-ray diffraction (XRD), temperature programmed reduction with hydrogen (H$_2$–TPR), CO$_2$ and H$_2$ temperature programmed desorption (TPD) and N$_2$O chemisorption.

2. Experimental

2.1. Catalyst preparation

Several CuZnGaOx catalysts with the molar ratio Cu:Zn:Ga = 5:3:2 (48.7:31.3:20 precisely) were synthesized using the co-precipitation method at different constant pH values i.e. 5.4, 6.5, 6.8, 6.9 and 7.4. The solutions of metal nitrate salts (Aldrich), Cu(NO$_3$)$_2$ ∗ 3H$_2$O, Zn (NO$_3$)$_2$ ∗ 6H$_2$O and Ga(NO$_3$)$_3$ ∗ 9H$_2$O, were dissolved in 100 mL of distilled water, and also sodium carbonate (Aldrich), Na$_2$CO$_3$, was dissolved in 100 mL distilled water. Both solutions were dispensed with 60 mL plastic syringes (diameter 28.95 mm) to a 500 mL Erlenmeyer flask filled with 300 mL distilled water, which was preheated to 85 °C. The flow rate of the nitrate solution was kept constant at 0.42 mL/min, while the carbonate solution flow rate was initially set to the selected 0.5 mL/min, and it was subsequently varied to maintain the desired pH, which was controlled by a pH electrode. The resulting co-precipitate was aged at the same temperature for 24 h. After ageing, the cryoprecipitate was washed with distilled water, followed by the separation of the co-precipitate. The co-precipitate was separated from the solution by centrifugation using a laboratory centrifuge (Sigma 4–15C). Every