



Sorption-enhanced methanol steam reforming for hydrogen production by combined copper-based catalysts with hydrotalcites

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ABSTRACT

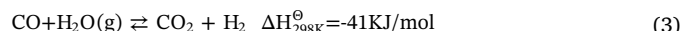
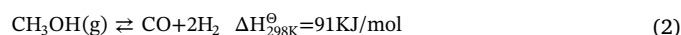
Hydrogen is stored in liquid methanol to ensure safe transportation, and when needed, hydrogen is produced in situ through methanol steam reforming at a relatively low temperature (about 473 K–573 K), which is considered as a significant breakthrough in the storage and transport system of hydrogen energy. To improve methanol conversion, the process intensification technology, called as sorption enhanced methanol steam reforming, is developed, where the configuration between catalyst and sorbent is investigated experimentally in this work. Catalyst is commercial CuO/ZnO/Al₂O₃ catalyst, and sorbent is K₂CO₃ promoted hydrotalcite (K-hydrotalcite). Two kinds of packed modes in the reactor are tested and compared with each other, one packed mode with the mixture of catalyst particles and sorbent particles, and the other packed mode with composite sorbent-catalyst particles pelleted with the mixture of catalyst powders and sorbent powders. According to the experimental results, it is found that CO₂ adsorption by K-hydrotalcites enhances significantly methanol steam reforming in both packing modes. When combined CuO/ZnO/Al₂O₃ catalyst with K-hydrotalcite into one-body composite pellet, the methanol conversion reduces due to the loss of catalytic activities under the alkaline atmosphere of K-hydrotalcites. Therefore, attention should be paid on the synergic relationship between catalysts and sorbents for sorption enhanced reaction.

1. Introduction

Hydrogen energy is known as the next generation of secondary clean energy, but the efficient preparation, safe storage and transportation of hydrogen have been the bottlenecks to the large-scale application of hydrogen energy. Because methanol can be safely transported, hydrogen may be stored in liquid methanol for the safe transportation. When needed, hydrogen is produced in situ by methanol steam reforming at a relatively low temperature to release hydrogen stored in methanol. It is considered as a feasible way to utilize hydrogen energy, low energy consumption, easy integration with on-board or fixed polymer electrolyte membrane fuel cells (PEMFCs) [1,2]. Moreover, with the successful development of the highly active catalytic system, the concept of hydrogen storage in methanol and reforming release when needed may be applied in practice, which will be a significant breakthrough in the storage and transport system of hydrogen energy [1–3].

From the stoichiometry of the overall reaction for methanol steam reforming (MSR), as shown in Eq. (1), no carbon monoxide and methane are produced in H₂ rich stream. However, methanol steam

reforming is frequently accompanied with side reactions, such as Eqs. (2)–(6). Methanol decomposition Eq. (2) and water-gas shift reaction Eq. (3), will result in the formation of CO as by-product in H₂ rich stream, which would be controlled as small as possible in order to avoid poisoning of the Pt anode of the fuel cell. The limitation of CO concentration for PEMFC application is in the range of 10 ppm–50 ppm. From side reactions Eqs. (4)–(6), by-product CH₄ also appears probably in H₂ rich stream.



A large number of research works can be found in the literature regarding the preparation of high-effect catalysts for methanol steam

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reforming [4]. It is expected that catalysts have a high methanol conversion with high hydrogen yield and low concentration of CO as the undesired byproduct at a relative lower temperature. According to the published works, catalysts are divided mainly in three groups: copper-based catalysts [5–8], palladium-based catalysts [9–11] and nickel-based catalysts [12–14]. Copper-based catalysts are the most active ones, and the most common catalysts for methanol steam reforming. Both palladium-based catalysts and nickel-based catalysts present better results in terms of thermal stability and long-term stability, but the preparation cost and the reforming temperatures are relatively higher. Some authors tried to synthesize catalysts based on different alloy species, such as nickel and studied the effect of Zn addition on bimetallic catalysts to overcome these difficulties.

To improve the methanol conversion for H₂ production at a relatively low temperature, a few researchers tried to develop the process intensification of sorption-enhanced methanol steam reforming for hydrogen production in order to obtain high-purity H₂ with low CO₂ and CO contents [15,16]. Their research works were focused on the thermodynamic analysis, and the experimental researches were scarce. Similar research works, sorption-enhanced water gas shift reaction for high-purity hydrogen production, have attracted the attention of many scholars [17–20], and there were also many reports on the development of high temperature CO₂ sorbents and their application for hydrogen production by sorption enhanced methane steam reforming, sorption enhanced ethanol steam reforming et al. [21–25].

In the sorption-enhanced reaction, the preparation of the high temperature CO₂ sorbents is very important. Usually, hydrotalcite and K₂CO₃ promoted hydrotalcite have good CO₂ adsorption capacities at high temperature, easy regeneration and low preparation cost, which is suitable for sorption enhanced hydrocarbon steam reforming for hydrogen production [26–33]. When the steam reforming is at a relatively low temperature, such as water gas shift reaction in range of 423 K–573 K, 13X zeolite and Na-Mg double salt-based sorbent have been also recommended as CO₂ sorbents [18,20]. The uniform packing of catalyst and sorbent mixture is also very important for sorption enhanced reaction, several kinds of packing configurations have been investigated for sorption-enhanced water gas shift reaction [18–20], including the mixture packing with catalyst-only pellets and sorbent-only pellets, catalyst-sorbent pellets packing and multilayer-pattern packing. In this work, we shall investigate experimentally the configuration between CuO/ZnO/Al₂O₃ catalyst and K₂CO₃ promoted hydrotalcite packed in reactor for sorption-enhanced methanol steam reforming.

2. Experimental details

2.1. Materials

Copper-based catalysts for methanol steam reforming were purchased from Alfa Aesar Company, CuO/ZnO/Al₂O₃ catalysts with the mass ratio of 50%/30%/20%. Catalysts were crushed into 2 mm particle size for experiments. The key microstructure parameters of catalysts are BET surface area 76.31 m²/g, micropore volume 0.209 cm³/g, micropore average diameter 10.95 nm. Fig. 1a showed CuO and ZnO crystalline phases in copper-based catalysts by XRD characterization.

Hydrotalcites (HTlc) were used to adsorb CO₂ gas, which were purchased from SIFGMA-ALDRICH Company. The main compositions of hydrotalcite were MgO (58.89%, mass fraction) and Al₂O₃ (39.43%, mass fraction). The key microstructure parameters of hydrotalcite were BET surface area 22.01 m²/g, micropore volume 0.098 cm³/g, micropore average diameter 16.17 nm. Fig. 1b showed the hydrotalcite crystalline phase by XRD characterization.

Methanol and K₂CO₃ were analytical-reagent grade, supplied by Sinopharm Chemical Reagent Co. Ltd. CO₂ and N₂ used in experiments were supplied by Jiajie Gas company (Shanghai, China) with purity of CO₂ > 99.99%, N₂ > 99.995%. Helium was from Air Liquide company

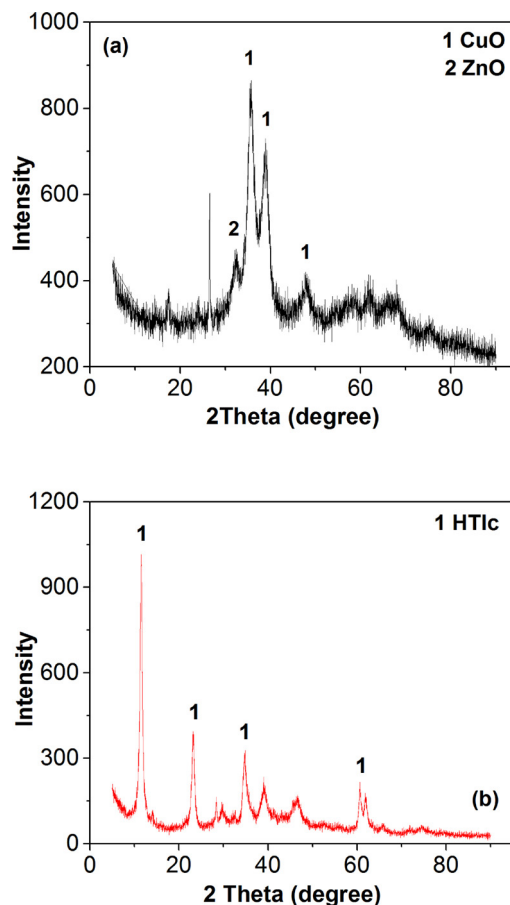


Fig. 1. XRD images of hydrotalcite and CuO/ZnO/Al₂O₃ catalyst. (a) CuO/ZnO/Al₂O₃ catalyst (b) hydrotalcite.

(China) with purity of He > 99.999%.

2.2. Preparation of K-hydrotalcite and composite sorbent-catalyst pellets

To improve CO₂ adsorption amount on hydrotalcite, the commercial hydrotalcite powders were modified with K₂CO₃ impregnation. The fresh hydrotalcite powders underwent calcination at 673 K for four hours to remove volatile impurities. And then, K₂CO₃ solution was used to leach the calcinated HTlc powders at 303 K, where K₂CO₃ amount was added as 20% of hydrotalcite weight. After the ultrasonic dispersion of samples, K₂CO₃ impregnation continued for 4 h to keep alkali metal into the interlayer space of hydrotalcite. The impregnated slurries were extruded with a syringe, dried at 473 K, and crushed as cylinder shape (diameter 2 mm, length 2 mm). Hydrotalcite after K₂CO₃ modification was marked as K₂CO₃ promoted hydrotalcite (K-hydrotalcite) for CO₂ adsorption.

Composite sorbent-catalyst pellets were prepared with the uniform mixture of K-hydrotalcite powders and CuO/ZnO/Al₂O₃ catalyst powders. The commercial copper-based catalyst particles were crushed into powders, and mixed with the prepared K-hydrotalcite powders. And then, the mixed slurries were extruded with a syringe, dried at 473 K, and crushed as cylinder shape (diameter 2 mm, length 2 mm) for experiments.

2.3. Experiments for sorption enhanced methanol steam reforming in the fixed bed reactor

The experiments of sorption enhanced methanol steam reforming were carried out in a fixed bed reactor, as shown in Fig. 2, where a quartz tube with 16 mm inner diameter was packed with the mixture of

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