Short Communication

Cu supported on ZnAl-LDHs precursor prepared by in-situ synthesis method on γ-Al$_2$O$_3$ as catalytic material with high catalytic activity for methanol steam reforming

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ABSTRACT

A novel catalyst precursor ZnAl-LDHs/γ-Al$_2$O$_3$ was prepared by in-situ synthesis method, and the copper was supported on calcined hydrotalcite catalyst precursor by wet impregnation. The correlation between the structure and the catalytic activity for methanol steam reforming was studied by XRD, SEM, TPR, chemisorption N$_2$O, IR and N$_2$ adsorption techniques. The results showed that the ZnAl-LDHs was successfully synthesized by in-situ synthesis method on γ-Al$_2$O$_3$ and the copper mass fraction had a great effect on the interactions between support and copper species. Furthermore, the catalyst reducibility and copper surface area evidently influenced catalytic activity for methanol steam reforming. The 10% Cu/γ-Al@MMO exhibited the best catalytic activity, that was, the methanol conversion was 99.98% and the CO concentration was only 0.92% at 300 °C in hydrogen production by methanol steam reforming.

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Introduction

As we know, the use of fossil fuels causes more and more serious environment pollution. It is imperative to seek for alternative clean energy. Hydrogen is particularly attractive as one of many fuel options in the future since it can be stored and transported efficiently. It burns cleanly producing only water as a byproduct [1].

Conventional hydrogen production includes natural gas, petrol and alcohols reforming [2—4]. Among them, methanol is considered effective source of hydrogen production due to its advantages of high C—H ratio, low cost and no NO$_x$, SO$_x$ emission in the reaction [5]. Besides, steam reforming (SRM) [6—10], partial oxidation (POM) [11] and autothermal reforming (ATM) [12,13] are widely known reaction applied for hydrogen production. Among them, the steam reforming is considered

the most effective method of producing hydrogen [14]. So, the following question is finding the efficient catalysts for hydrogen production technology. Nowadays, Copper catalysts are widely used in SRM reaction [15—20]. Among them, the $CuO/ZnO/Al_2O_3$ systems is widely known catalysts for SRM, with high copper content (30—50% wt%) [21]. However, the traditional Cu-based catalysts have poor copper dispersion and high CO yield. Therefore, it is necessary that great attention should be paid to the research on the catalytic materials which have low CO emission and high catalytic activity in the SRM reaction.

In this paper, the Cu/Zn—Al catalysts were prepared by using ZnAl-LDHs which was synthesized by in-situ co-precipitation on the surface of γ-Al_2O_3. Then the aqueous solutions of copper nitrate with different percentage weight were penetrated in the calcination of γ-Al_2O_3@ZnAl-LDHs material. ZnAl-LDHs on γ-Al_2O_3 by in-situ synthesis method has a more uniform distribution of zinc cations on the surface of γ-Al_2O_3 than that can be obtained by conventional methods, which can overcome drawbacks of co-precipitation method and increase activity and specific surface area. Hydrotalcite, also known as layered double hydroxides (LDHs), is a class of two-dimensional (2D) anionic clay materials [22,23]. In addition, LDHs can be transformed topotactically into highly active mixed metal oxides (MMOs) by controlled thermal decomposition [24—27]. Here this study focuses on the function of γ-Al_2O_3@ZnAl-LDHs prepared by in-situ synthesis method, and the correlation between the catalyst structure and performance.

Experimental

Preparation of catalysts

ZnAl-LDHs/γ-Al_2O_3 precursor was prepared by in-situ synthesis method. 5.0 g γ-Al_2O_3 support was firstly put into the muffle furnace and calcined at 600 °C for 4 h, and dipped in a 150 mL aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M) and NH_4NO_3 (0.1 M) by string at 70 °C for 24 h, followed by adjusting the pH value of solution to 7 by adding diluted ammonia (1% NH_4OH). Then the precipitation was washed with 300 mL mixed solution of NH_4NO_3 and ammonia water at the same pH value of the end of the reaction solution by Buchner filter. After being aged for 1 h in air, the wet sample was washed with deionized water until pH = 7. After washing, the precipitate was dried at 60 °C for 24 h, and the obtained γ-Al_2O_3@ZnAl-LDHs precursor was denoted as γ-Al@LDHs. Finally, the γ-Al@LDHs was calcined at 400 °C for 4 h (the γ-Al@LDHs has been completely converted to mixed metal oxide at 400 °C shown by the TG-DTA profile in Fig. S1, So we chose 400 °C for the calcination temperature), which denoted as γ-Al@MMO.

4.0 g of the powder γ-Al@MMO was dipped in 100 mL of aqueous solution of copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$ with different percentage weight x (x = 5, 10, 20, 30) for 4 h under agitation at room temperature. Then the obtained slurry was dried at 100 °C overnight. The sample were finally calcined at 500 °C for 3 h and were denoted x% Cu/γ-Al@MMO (x = 5, 10, 20, 30). The obtained powders were pelletized, crushed, sieved

to a particle of 0.28—0.45 mm, which was then used as catalysts for SRM.

Characterization of catalysts

The phase structure of the samples was studied by X-ray diffractometer (Bruker D8) with Cu-Kα radiation operated at 40 kV and 40 mA. The CuO particle sizes (d_{CuO}) were obtained by the Scherrer equation.

The morphology of powder was observed by scanning electron microscope (Hitachi SU 8010) operated at 15 kV.

FT-IR spectra were collected on an FT-IR-660 spectrometer (Agilent Technologies) in the range 4000—400 cm^{-1} at 4 cm^{-1} resolution.

BET surfaces of all the samples were measured by N_2 adsorption—desorption at −196 °C with a Quantachrome NOVA 2200E instrument and the specific surface areas were obtained by method of Brunauer, Emmet, and Teller (BET).

Temperature Programmed Reduction (TPR) was measured on a Quantachrome ChemBET Pulsar instrument with a thermal-conductivity detector during the reduction. 50.0 mg catalyst was heated under an Ar flow (40 mL min^{-1}) from room temperature to 300 °C to remove the water. TPR measurement was carried out by heating the sample in a stream of 5% H_2/Ar (40 mL min^{-1}) from 20 to 800 °C at a rate of 10 °C min^{-1}.

The N_2O measurements were measured on a Quantachrome ChemBET Pulsar instrument and the copper surface area was calculated by the N_2O titration method [28]. Prior to the measurement, the sample was pretreated with argon at 300 °C and then pre-reduced at 300 °C with 5% H_2/Ar for 90 min. After that, the reactor was cooled to room temperature with Ar for the N_2O reaction. A measurement was carried out in 5.01% N_2O at 90 °C for 1 h to obtain the Cu_2O and then switched to 5% H_2/Ar from 90 to 600 °C to reduce the Cu_2O at the surface. The dispersion can be computed from the H_2-back-titration.

Catalytic performance

SRM was carried out in a fixed-bed reactor (8 mm internal diameter). Firstly, the catalyst was pre-reduced at 280 °C for 2 h by 5% H_2/N_2 and then the temperature was stabilized at the reaction temperature. Following a solution of methanol and water (water/methanol = 1.2 molar ratio) was fed to the reactor at methanol gas hourly space velocity of 800 h^{-1} through the evaporator. The produced gas was analysed by on-line gas chromatograph (GC, SP1000) equipped with a thermal conductivity detector (TCD).

The methanol conversion is defined as

$$X(\%) = F_R \times (C_{CO} + C_{CO_2}) \times (32 + 18w)/(F \times \rho \times 22.4 \times 1000) \times 100\%$$

The CO selectivity is defined as

$$S_{CO}(\%) = C_{CO}/(C_{CO} + C_{CO_2}) \times 100\%$$

Here F_R is the flow of reforming gas (cm^3/min); F is the flow of methanol and water solution (cm^3/min); ρ is the density of methanol and water solution (g/cm^3); w is the molar ratio of water to methanol; C_{CO} and C_{CO_2} are the molar concentrations of CO and CO_2 in the reaction products.