Journal of CO_2 Utilization 21 (2017) 191–199

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Three dimensional porous Cu-Zn/Al foam monolithic catalyst for CO_2 hydrogenation to methanol in microreactor

Zhuangdian Liang[a,b,c,1], Peng Gao[a,1], Zhiyong Tang[a], Min Lv[a,*], Yuhan Sun[a,c,**]

[a] CAS Key Lab of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, No. 99 Haike Road, Zhangjiang Hi-Tech Park, Shanghai 201210, China

[b] University of the Chinese Academy of Sciences, Beijing 100049, China

[c] School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

ARTICLE INFO

Keywords:
Carbon dioxide hydrogenation
Copper-based catalyst
Methanol synthesis
Monolithic catalyst
Microreactor

ABSTRACT

CO_2 hydrogenation turns to be an attractive pathway of C1 conversion. For CO_2 hydrogenation to methanol, a novel method was investigated for the preparation of layer structured Cu-Zn/Al foam monolithic catalyst integrated with microreactor. Such a monolithic catalyst could be loaded in a flange-type microreactor in the form of packed bed to intensify the process. As a result, a high copper time yield of methanol, 7.81 g g_{Cu}^{-1} h^{-1}, was obtained at 250 °C, 3 MPa and 20000 mL g_{cat}^{-1} h^{-1} due to the heat/mass-transfer properties with microreactor. Besides, the monolithic catalyst showed a good ability of adhesion.

1. Introduction

Recently, conversion of CO_2 to methanol is considered as an effective way for CO_2 utilization. Both as a green liquid fuel and as a feedstock of many value-added products, methanol plays an increasingly important role in chemical industry [1,2]. The utilization of CO_2 as a feedstock for producing chemicals is an effective method to relieve climate changes caused by increasing CO_2 in the atmosphere, as well as providing a great opportunity in developing new concepts for catalysts and industrial process [3]. Methanol synthesis from CO_2 hydrogenation with the aid of renewable or low-carbon energy sources has already shown industrial viability [4,5].

As a highly exothermic reaction, CO_2 hydrogenation reaction is strongly influenced by the thermal management at the device level. Accumulation of reaction heat will increase the local temperature on the catalyst particle surface as well as the overall temperature of the reaction system, which will consequently lower methanol selectivity, promote side reactions, cause catalyst sintering and degradation [6,7]. Furthermore, other by-products are formed during the hydrogenation of CO_2, such as CO, hydrocarbons, and higher alcohols [8]. Therefore, a highly selective catalyst is required to avoid the formation of undesired byproducts for methanol synthesis. In addition, meso- and macro-pores in catalyst substrate can effectively promote heat and mass transport to intensify progress [9,10]. Tubular fixed bed reactor is commonly used for CO_2 hydrogenation to methanol synthesis. Due to the limitation of heat transfer in fixed bed reactor, it is always challenging to avoid the hotspot and temperature runaway.

The process intensification potential of microreactor has attracted attention in the field of energy technology. The specific features of microreactor mainly include: (1) enhanced heat and mass transfer, (2) narrow residence time distributions due to fast species exchange by diffusion in the small lateral dimensions, and (3) low pressure drop. Therefore, it is a particularly interesting choice for those gas conversion processes in which selectivity and conversion are closely related to the heat/mass transfer properties of reactor and catalyst. However, most existing methods of combining catalyst and microreactor are often constrained to certain disadvantages such as easily crushed layer for washcoating, hotspot and sintering for catalyst particles in fixed bed. Hence, the distinctive feature of heat and mass transfer ability of microreactor could be hindered by directly filling catalyst particles into microchannel [11].

In our previous work, Cu-Zn-Al layer structure compounds were selected as the precursors [12–15]. Small Cu clusters were generated as the active sites for CO_2 hydrogenation to methanol. The Cu-Zn-Al catalyst was synthesized through co-precipitation methods. The atomic level homogeneous dispersion of catalyst brought high stability and activity. In addition, catalyst particles were diluted with quartz sand and then tested in the fixed bed reactor [16]. A good catalytic

* Corresponding author.
** Corresponding author at: CAS Key Lab of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, No.99 Haike Road, Zhangjiang Hi-Tech Park, Shanghai 201210, China.
E-mail addresses: lvmin@sari.ac.cn (M. Lv), sunyh@sari.ac.cn (Y. Sun).
[1] Contributed equally to this work.

http://dx.doi.org/10.1016/j.jcou.2017.05.023
Received 16 February 2017; Received in revised form 24 May 2017; Accepted 25 May 2017
Available online 25 July 2017

performance of 25% CO_2 conversion and 60% methanol selectivity was achieved [17].

Moreover, hydrothermal synthesis is an alternative process to make layered materials. Layer structure compounds on Al substrate can be synthesized via hydrothermal approach, which employs the Al substrate of a trivalent metal instead of its salt and oxide to be catalyst substrate. It has been proved that the monolithic catalyst supported by metal foam presents better performance than the particle catalyst for an exothermic reaction [18]. Monolithic catalyst in microreactor effectively minimizes sintering and stabilizes the coke formation [19,20].

The focus of this paper is to study the new method of preparing monolithic catalyst of CO_2 hydrogenation to methanol and investigate the influence of reaction condition on catalytic performance in microreactor. By efficiently integrating catalyst with microreactor, this method is helpful to fix the most critical problem of microreactor [21,22]. The textural and structural properties of monolithic catalyst were characterized in detail. And the advantage of this method to prepare the catalyst used in microreactor was discussed.

2. Experimental section

2.1. Aluminum foam as catalyst support

Fig. 1A(a) shows the photograph of three dimensional porous aluminum foams (Suzhou Jiashide Metal Foam Co., Ltd., China) used in the present work with 120 Pores Per Linear Inch (PPI). Each block of aluminum foam was sized into 20 × 50 × 1 mm. Aluminum foam not only has meso- and macro-pores in the three dimensional porous structure, but also shows a good property in heat transfer by inheriting metallic characteristics. Prior to the experiment, the aluminum form was degreased in acetone with consecutively ultrasonic shaking for 5 min. Then, the aluminum form was etched with 0.4 mol L^{-1} HCl for 10 min at room temperature. After rinsed with water and consecutively ultrasonic shaking for 10 min, the aluminum support for catalyst preparation was obtained.

2.2. Catalyst preparation

In this study, layer structure attached on aluminum support named Cu-Zn/Al foam was prepared via a hydrothermal method. In a typical procedure to synthesize hydrotalcite nanostructure, 100 mL solution of cupric oxalate (CuC_2O_4, 24 mmol L^{-1}) and zinc acetate ($Zn(CH_3COO)_2$, 46 mmol L^{-1}) was magnetically stirred for 2 h at room temperature. The pH of the solution is approximately 7 detected by pH indicator strips. The obtained solution was transferred into autoclave and ready for the growth of nanostructure. Afterwards, the pre-treated aluminum foam was immersed into the reaction solution. Then the autoclave was sealed and rotated at the rate of 20 r min^{-1} which lasted 24 h at 70 °C for hydrothermal nanostructure growth. After hydrothermal procedure, the autoclave was cooled down to ambient temperature. Dark brown monolithic precursors were taken out and rinsed with distilled water several times. After that, the sample was calcined in the atmosphere at 350 °C for 4 h.

2.3. Characterization

The morphology of the monolithic catalysts was investigated in a ZEISS SUPRA 55 scanning electron microscope (SEM) at 2.00 kV

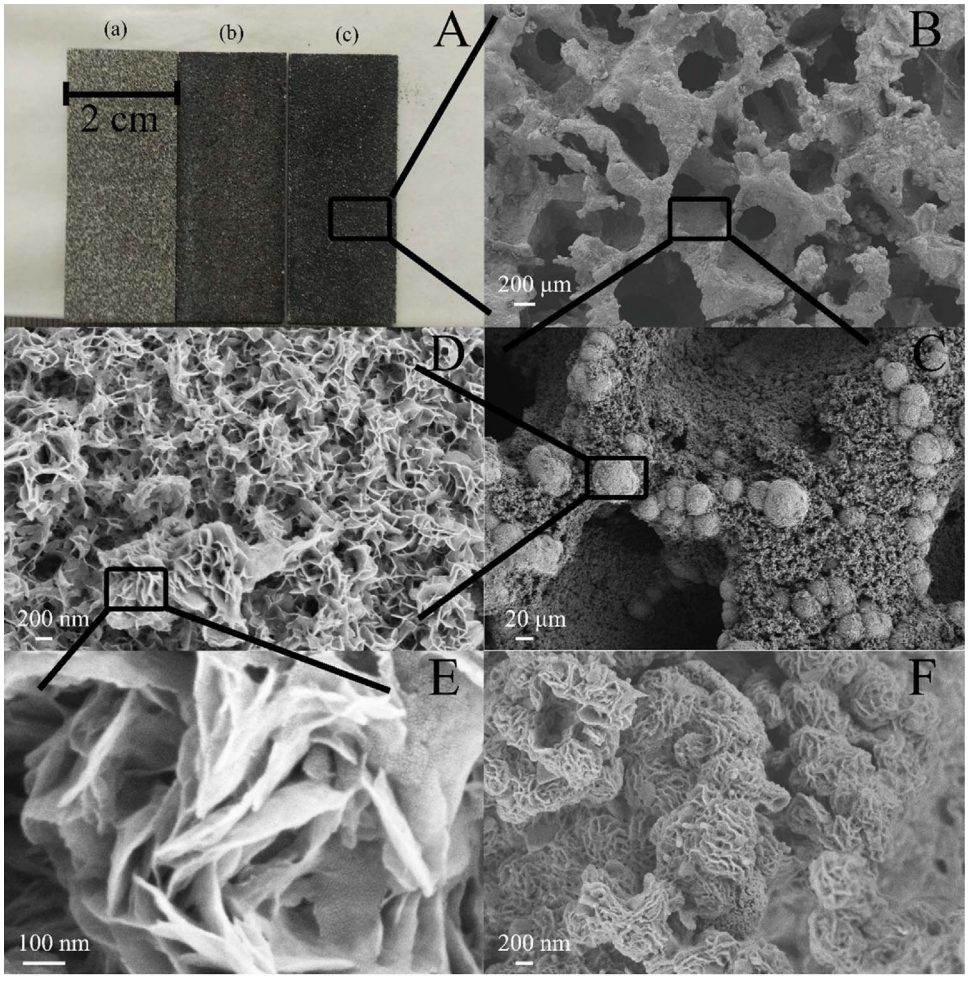

Fig. 1. All-in-one for the monolithic catalysts. A: Photograph of the macroscopic sample, (a) the Al foam (b) the catalyst after hydrothermal method (c) the catalyst of Cu-Zn/Al foam after calcine; B-E: SEM image in different magnifications, showing the three dimensional porous structure and surface morphology of monolithic catalysts; F: SEM image of spent monolithic catalysts.