Fuel 217 (2018) 21–30

Contents lists available at ScienceDirect

Fuel

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

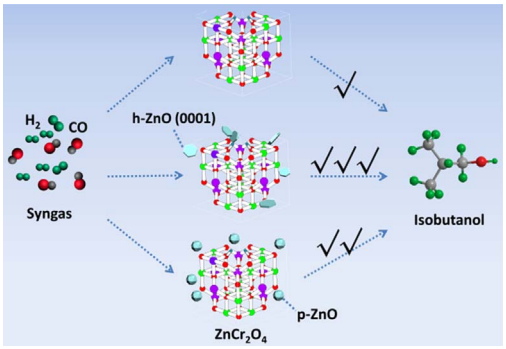
Full Length Article

Isobutanol synthesis from syngas on Zn-Cr based catalysts: New insights into the effect of morphology and facet of ZnO nanocrystal

Xiaofeng Gao[a,b], Tao Zhang[a], Yingquan Wu[a], Guohui Yang[a], Minghui Tan[a], Xiaoli Li[a,b], Hongjuan Xie[a], Junxuan Pan[a], Yisheng Tan[a,c,*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] National Engineering Research Center for Coal-Based Synthesis, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
ZnO
$ZnCr_2O_4$
Interaction
Hexagonal
(0 0 0 1) Facet

ABSTRACT

Isobutanol synthesis from syngas could be realized on Zn-Cr based catalysts with high activity and selectivity. The ZnO crystal morphology may play an important role on the catalytic performance of Zn-Cr based catalyst for isobutanol synthesis. In this study, a series of Zn-Cr based catalysts with polyhedral or hexagonal ZnO nanocrystal were prepared to explore the effect of morphology and facet of ZnO on direct synthesis of isobutanol from syngas. We find that the interaction between ZnO and $ZnCr_2O_4$ phases poses a crucial factor for the catalytic performance. Compared with sole ZnO or Zn-Cr catalyst, Zn-Cr/p-ZnO and Zn-Cr/h-ZnO catalysts with a binary crystal structure of ZnO and $ZnCr_2O_4$ show higher total alcohol and isobutanol selectivity. Furthermore, the hexagonal ZnO of Zn-Cr/h-ZnO catalyst exposes more (0 0 0 1) facets compared to the polyhedral ZnO of Zn-Cr/p-ZnO catalyst, resulting in stronger interaction between ZnO and $ZnCr_2O_4$ phases for Zn-Cr/h-ZnO catalyst. The most excellent catalytic performance could be obtained on Zn-Cr/h-ZnO catalyst with the highest CO conversion (22.1%) as well as isobutanol selectivity (24.4 wt%). Thus, exposing more (0 0 0 1) facets of h-ZnO could significantly improve the catalytic performance for isobutanol synthesis from syngas, which provides a new perspective of the face-activity relationship on Zn-Cr based catalyst.

* Corresponding author at: State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China.
E-mail address: tan@sxicc.ac.cn (Y. Tan).

https://doi.org/10.1016/j.fuel.2017.12.065
Received 19 October 2017; Received in revised form 23 November 2017; Accepted 17 December 2017

1. Introduction

With crude oil resource depleting and the price of petroleum increasing, non-oil and environment-friendly route for value-added chemicals synthesis has attracted extensive attention. Syngas (a mixture of CO and H_2), a coal-based clean synthetic fuel and an important industrial chemical product, is used widely as raw material for other chemicals synthesis or directly as fuel [1–4]. Nowadays, the conversion of syngas to higher alcohols has roused great interests due to its broader prospects in a wide range of fields [5–9]. Among these alcohols from the conversion of syngas, isobutanol is one important product which is widely utilized to produce rubber, flavors, paint solvents, antioxidants, etc. [10–12] In addition, isobutanol could be used as an additive to improve the quality of gasoline and is also expected as a potential precursor for obtaining methyl tertiary-buty ether (MTBE) [13–14], which could act as an additive for the unleaded gasoline and as an emission-reducing agent. Until now, isobutanol is mainly obtained as the by-product of butanol synthesis during propylene carbonyl reaction. In order to meet the increasing demand, it is essential to explore a low-cost and non-oil route for isobutanol synthesis.

The Zn-Cr based catalyst has been studied extensively since 1980s due to its high selectivity and activity for the isobutanol synthesis from syngas at high temperature and pressure [14–18]. Because the products obtained over Zn-Cr catalysts are mainly composed of methanol and isobutanol, the separation operation of isobutanol from products could be simplified, in the long term, making the industrial production of isobutanol on a large scale via syngas possible. In our previous studies, a lot of works have been performed on the investigation of active sites and reaction mechanism for isobutanol synthesis. However, there are still many severe challenges that force us to present detailed investigations. Wu et al. [19–21] indicated that COH → CCOH was rate-determining-step for isobutanol synthesis on ZrO_2-based catalyst based on chemical enrichment method. After the C_2 alcohol formed, the isobutanol could quickly generate by aldo-condensation reaction of C_{2+} alcohols. Tian [22–25] demonstrated that the non-stoichiometric Zn-Cr spinel ($Zn_xCr_{2/3(1-x)}O$), presenting variation of cations on the tetrahedral and octahedral coordination sites, was the catalytic active phase for isobutanol formation. Meanwhile, although the ZnO catalyst shows only negligible catalytic activity, the presence of ZnO could improve the catalytic performance of Zn-Cr based catalyst. Kuld [26] and Kattel [27] had reported that the ZnO coverage degree and the ZnO-Cu interfacial sites were closely related to the catalytic performance in both CO hydrogenation and CO_2 hydrogenation to methanol. Therefore, for isobutanol synthesis from syngas, the interaction between ZnO and $ZnCr_2O_4$ spinel could play a crucial role, but the effect of ZnO is still not explicitly established.

Znic oxide, a typical N-type semiconductor with a large exciton binding energy and a wide band gap, is widely used in a range of optical and electronic applications. ZnO spinel serves as a good catalyst candidate for photocatalysis, transition metal catalysis, hydrogenation and oxidation-reduction catalysis due to its high mechanical strength, thermal and chemical stability as well as high activity [28–31]. Furthermore, the physicochemical properties of ZnO crystal, like the particle size, crystallization, and morphology, could significantly affect its catalytic performance. Among these properties, the morphology and facet of ZnO may play an important role in affecting its catalytic activity. Some studies have reported that tailoring the degree of extended growth of ZnO nanoparticles along the (0 0 0 1) axis gave regular hexagonal plate-like nanocrystals, exposing more polar (0 0 0 1) and (0 0 0 $\bar{1}$) facets [32–34]. Mclaren et al. [32] showed that the terminal polar (0 0 0 1) facets were more active surfaces for photocatalysis than the nonpolar surfaces perpendicular to them (i.e., 1 1 0 0, 1 0 1 0). Because the surface energy of (0 0 0 1) facets is high, the ZnO catalysts with more (0 0 0 1) facets exhibit excellent photocatalysis efficiency [32–34]. As a typical polar crystal, the hexagonal ZnO shows a positive polar plane in Zn (0 0 0 1), a negative polar plan in O (0 0 0 $\bar{1}$), and lateral facets consisting of a nonpolar (1 1 0 0), (0 1 1 0) and (1 0 1 0) facets. To our knowledge, for the isobutanol synthesis from syngas over Zn-Cr based catalysts, the effect of morphology and facet of ZnO crystal on the catalytic performance has not been studied in the previous articles. In this study, a series of polyhedral ZnO (p-ZnO), hexagonal ZnO (h-ZnO), $ZnCr_2O_4$ (Zn-Cr), Zn-Cr/p-ZnO, Zn-Cr/h-ZnO, Zn-Cr&p-ZnO and Zn-Cr&h-ZnO catalysts were employed to synthesize isobutanol from syngas, during which the relationship between the (0 0 0 1) facet of ZnO and catalytic performance for isobutanol synthesis was investigated. The face-activity relationship studied on this work could help to provide a significant avenue to develop more effective Zn-Cr based catalyst for isobutanol synthesis or any other reactions based on Zn-Cr catalyst.

2. Materials and methods

2.1. Material

$Zn(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ and $Zn(CH_3COO)_2{\cdot}2H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) Oxalic acid and ammonia solution ($NH_3{\cdot}H_2O$, 25 wt%) were purchased from Beichen Fangzheng Chemical Reagent Co. Ltd. (China) Dimethyl sulfoxide (DMSO) was purchased from Fengchuan Reagent Co. Ltd. (China) Cetyltrimethyl ammonium bromide (CTAB) was purchased from Tianjin Guangfu Fine Chemical Research Institute. (China) All the chemicals were of analytic grade, which were used as received.

2.2. Preparation

p-ZnO: The p-ZnO catalyst was prepared by sol-gel method, using $Zn(NO_3)_2{\cdot}6H_2O$ as precursor and oxalic acid as complexing agent. Typicality, 200 mL of an ethanol solution of $Zn(NO_3)_2{\cdot}6H_2O$ (1.0 M) was heated to 50 °C. Then, 200 mL of an ethanol solution of oxalic acid (1.15 M) was added into the above ethanol solution by peristaltic pump with the flow rate of 20 mL/min under vigorous stirring. The obtained solution was aged for 2 h at room temperature to form a sol, after that, evaporation was performed at 65 °C for 3 h. Subsequently, the mixture was transferred into an oven at 75 °C for 3 h and 120 °C for another 10 h to evaporate the ethanol solvent to form a gel. Finally, the gel was calcined at 250 °C for 2 h to decompose the organic chemicals completely, followed by calcination at 400 °C for 6 h to obtain the p-ZnO sample. h-ZnO: 0.22 g $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.40 g CTAB were added to a mixture of DMSO (58.4 mL) and H_2O (41.6 mL) in a beaker at room temperature. Then, the obtained solution was stirred for 30 min at room temperature and heated at 70 °C for 40 min in an oven. The sample was separated by centrifugation, washed several times with absolute ethanol. Finally, the sample was dried in a vacuum oven at 60 °C for 2 h and calcinated at 400 °C for 6 h.

Zn-Cr: The Zn-Cr spinel ($ZnCr_2O_4$) catalyst was prepared by sol-gel method. 17.8 g $Zn(NO_3)_2{\cdot}6H_2O$ and 48.0 g $Cr(NO_3)_3{\cdot}9H_2O$ (Zn/Cr molar ratio = 0.5) were dissolved in 200 mL ethanol under vigorous stirring at 50 °C, followed by adding 200 mL oxalic acid ethanol solution. The amount of oxalic acid was excess 15 mol% in order to ensure all the metal ions being chelated completely with oxalic anion. Then, the mixture solution was aged for 2 h at room temperature and then kept at 75 °C for 2 h and 120 °C for another 10 h in an oven to evaporate the ethanol solvent. The final gel was first calcined at 250 °C for 2 h, followed by being calcinated at 400 °C for 6 h to obtain the Zn-Cr sample.

Zn-Cr/p-ZnO: The Zn-Cr/p-ZnO was prepared by the similar method to the above Zn-Cr spinel catalyst preparation, where the Zn/Cr molar ratio was adjusted to 1.0.

Zn-Cr/h-ZnO: The Zn-Cr/p-ZnO (Zn/Cr molar ratio = 1.0) was prepared by the similar method to the above Zn-Cr spinel catalyst preparation, except that after the addition of oxalic acid solution, a certain amount of $NH_3{\cdot}H_2O$ (25 wt%) was added to obtain a solution with 0.02 M NH^{4+}. After evaporation of the ethanol solvent and