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Article

Direct conversion of syngas into hydrocarbons over a core-shell Cr-Zn@SiO₂@SAPO-34 catalyst

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ABSTRACT

Direct conversion of syngas into hydrocarbons with high selectivity remains a challenge. Herein, we report the synthesis of a core-shell-structured catalyst constituting Cr-Zn oxide as the core and SAPO-34 as the shell for the conversion of syngas into hydrocarbons with high selectivity. A SiO₂ layer was sandwiched between the core and the shell to prevent damage to the core during shell synthesis. Furthermore, the intermediate SiO₂ layer acted as a Si source for the formation of the shell. The prepared catalyst displayed considerably higher selectivity toward the production of C₂–C₄ hydrocarbons (66.9%) than that of methanol and methane. The findings show the potential of the prepared core-shell-structured catalyst in the one-step production of hydrocarbons, such as liquefied petroleum gas, from syngas. However, further optimization of the catalyst is necessary to achieve higher performance.

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1. Introduction

Hydrocarbons, such as light olefins, liquefied petroleum gas, and gasoline, are important chemicals that are mainly produced from oil cracking in industry. Owing to the decreasing oil reserves and increasing demands for hydrocarbons, the development and use of alternative resources has become highly desirable. Particularly in China, coal chemistry generates widespread attention because of the larger reserve of coal when compared with that of oil and natural gas. Hydrocarbons can be produced from coal via syngas (CO+H₂) using either the Fischer-Tropsch synthesis (FTS) technology or a multi-stage process. The latter process involves the conversion of syngas into methanol that is subsequently converted into desired hydrocarbons. The conventional FTS process is characterized by a wide distribution of hydrocarbons with different chain lengths that generally follows the Anderson-Schulz-Flory (ASF) rule [1]. In contrast, the multi-stage process (via methanol) generates a

considerably narrower product distribution because the two independent processes, i.e., syngas-to-methanol [2] and methanol-to-hydrocarbons (MTH) [3], are operated under their respective optimal conditions, which are significantly different. The first syngas-to-methanol process relies on mixed oxide catalysts, whereas the second MTH process is catalyzed by zeolites. From an economic standpoint, combining these two independent processes into one operation unit is highly attractive. In addition, another beneficial effect may be expected for promoted syngas conversion into methanol because of methanol conversion into hydrocarbons. Therefore, wide efforts have been made to develop a single process and an associated efficient catalyst to achieve one-step syngas conversion into hydrocarbons.

An important strategic step to address this issue is the development of a bi-functional catalyst that is capable of catalyzing both the syngas-to-methanol and MTH reactions. The widely studied syngas-to-methanol conversion catalysts in-

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clude mixed metal oxides containing more than one of the following oxides CuO, ZnO, Al₂O₃, and Cr₂O₃ [4–7], whereas the MTH conversion catalysts are zeolites such as HZSM-5 and SAPO-34 [8,9]. The most direct and simplest approach to generate a bi-functional catalyst is to physically mix these two types of catalysts; this method has been frequently studied [10–12]. The effects of the relative ratio of the two catalyst types, the method of mixing, and the arrangement of the two catalyst types in the reactor, as well as the effects of the reaction conditions have been investigated on the catalyst activity and life time [10–12]. Another method to generate bi-function catalysts is through the development of core-shell structures: such types of catalysts have been demonstrated to be efficient in consecutive reactions [13–15]. For example, Yang et al. [16,17] and Pinkaew et al. [18] prepared a series of core-shell catalysts constituting millimeter-sized metal oxides as the core and micrometer-sized zeolite as the shell. Such structured catalyst exhibited a considerably higher activity and selectivity in the one-step conversion of syngas into dimethyl ether than the physically mixed catalysts. Chen et al. [19,20] reported the synthesis of core-shell Cu-Zn-Al@SAPO-34 catalyst and its application in syngas transformation reactions. Likewise, the authors demonstrated that the core-shell-structured catalyst displayed better performance than the physically mixed catalyst consisting of Cu-Zn-Al and SAPO-34. They proposed that small molecules of syngas first diffuse into the metal oxide core, where syngas is converted into methanol, which subsequently diffuses through the pores of the zeolite shell and transforms into dimethyl ether or hydrocarbons over the acidic sites in the pores.

In this paper, we report the synthesis of core-shell Cr-Zn@SiO₂@SAPO-34 catalyst for the one-step conversion of syngas into hydrocarbons. Cr-Zn oxides constituted the core of the catalyst for catalyzing the methanol synthesis reaction. A layer of SiO₂ membrane was grown over the Cr-Zn core to prevent damage to the core oxide while the SAPO-34 shell was grown onto the intermediate SiO₂ layer. Moreover, the SiO₂ layer served as Si source for the synthesis of the SAPO-34 shell.

2. Experimental

2.1. Catalyst preparation

Cr₂O₃-ZnO catalyst with a Cr/Zn molar ratio of 1:2 was prepared by the co-precipitation method, described as following. Chromium nitrate and zinc nitrate (Sinopharm Chemical Reagent Co., Ltd.) were used as the precursors, which were added together with ammonium carbonate to deionized water at 70 °C. The mixture was aged for 3 h under continuous stirring. The precipitate was filtered and washed with deionized water until the filtrate exhibited pH = 7. The product was dried at 110 °C for 12 h followed by calcination at 500 °C for 1 h in static air. The resulting catalyst was denoted as Cr-Zn. It was granulated into 20–40 mesh for subsequent experiments.

Silica sol (30 wt% SiO₂; Qingdao Haiyang Chemical Co., Ltd.) was mixed with the same volume of deionized water. Then, the Cr-Zn granules were added to the silica sol and allowed soak

for 2 h before filtration. Subsequently, the granules were dried at 120 °C for 12 h followed by calcination at 500 °C for 2 h in static air. The resulting catalyst was sieved to 20–40 mesh and denoted as Cr-Zn@SiO₂.

A layer of SAPO-34 was then grown onto Cr-Zn@SiO₂. First, the precursors were mixed following a recipe 1 Al₂O₃:2 H₃PO₄:0.6 SiO₂:2.5 triethylamine (TEA):30 H₂O, which was stirred at room temperature for 24 h. Then, the Cr-Zn@SiO₂ granules were added to the above solution and transferred to a stainless steel autoclave. Hydrothermal reactions were allowed at 200 °C for 24 h. Upon completion of the reaction, the sample was filtered, washed with deionized water until the filtrate reached pH = 7, and further dried at 60 °C for 12 h, followed by calcination at 550 °C for 3 h in static air. The resulting catalyst is denoted as Cr-Zn@SiO₂@SAPO-34. For comparison, pure SAPO-34 zeolite was synthesized using the same recipe and procedures as described above.

2.2. Catalytic reaction tests

Catalytic reactions were carried out in a fixed-bed reactor with an inner diameter of 5 mm. Prior to the tests, the catalysts were reduced in the reactor for 2 h at 400 °C in a flowing H₂ stream. After cooling to room temperature, syngas with a H₂/CO molar ratio of 2 was introduced into the reactor. The catalytic reactions were conducted at 400 °C, 2.0 MPa, and space velocity of 1000 h⁻¹. The effluents were analyzed using an online Agilent 7890 gas chromatograph, which was equipped with FFAP and Plot Al₂O₃ S columns for the flame ionization detector (FID), and Porapark Q and 5A zeolite columns for the thermal conductivity detector (TCD).

2.3. Characterization of the catalysts

X-ray diffraction (XRD) was conducted on a Rigaku D/max-rb diffractometer with Cu K_α radiation ($\lambda = 0.154056$ nm) at 40 kV and 200 mA. The spectra were recorded at a scanning rate of 5°/min within a range of $2\theta = 5^\circ$ – 80° .

The physical morphology of the catalysts was characterized by scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) unit (FEI, Quanta 200F). Before analysis, the catalysts were coated with a layer of gold to improve conductivity of the samples.

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the XRD patterns of Cr-Zn, Cr-Zn@SiO₂@SAPO-34, and pure SAPO-34 zeolite. The pattern of Cr-Zn exhibits both ZnO and ZnCr₂O₄ characteristic peaks [6]. The diffraction peaks of SAPO-34 observed at $2\theta = 9.5^\circ$ and 20.5° were attributed to the CHA structured SAPO-34. The additional peak observed at $2\theta = 7.5^\circ$ was attributed to SAPO-5 [21]. Cr-Zn@SiO₂@SAPO-34 displayed characteristic diffraction peaks of SAPO-34, ZnO, and ZnCr₂O₄. This finding suggests that the structure of Cr-Zn oxide is mostly retained and that the SiO₂

Fig. 1. XRD patterns of Cr-Zn, Cr-Zn@SiO₂@SAPO-34, and pure SAPO-34 zeolite.

layer provides sufficient protection for the Cr-Zn oxide core during hydrothermal synthesis of the SAPO-34 shell. Moreover, the silicon in this layer acts as a silicon source for the growth of SAPO-34 shell. In contrast, in the absence of the SiO₂ layer, SAPO-34 did not grow well on the surface of Cr-Zn. Interestingly, no diffraction peaks of SAPO-5 were observed. According to the Scherrer equation, the crystallite size of Cr-Zn was estimated to be about 5–10 nm and that of SAPO-34 was about 50 nm.

The morphology and composition of Cr-Zn catalyst were characterized by SEM and EDS (Fig. 2). As shown in Fig. 2(a), Cr-Zn catalyst displayed a relatively rough surface. Only characteristic Cr K_{α} and Zn K_{α} signals were detected in the EDS pattern (Fig. 2(b)), and the composition of the catalyst was esti-

mated at 41.1% Cr and 58.9% Zn (mole percentage).

Figure 3 shows the SEM and EDS results of Cr-Zn@SiO₂. Unlike Cr-Zn discussed above, Cr-Zn@SiO₂ featured a relatively smoother surface. This suggests the successful formation of the SiO₂ layer on the Cr-Zn surface. However, regions of rough surface textures were occasionally observed that may be attributed to incomplete SiO₂ coating in these regions. Furthermore, irregular cracks on the SiO₂ layer were observed (Fig. 3(b)) that likely formed during gel formation from the SiO₂ sol and calcination as no polymer was used during gelation. EDS analysis showed that Cr-Zn@SiO₂ featured a high silicon content (65.6%), also suggesting the presence of a SiO₂ layer on the Cr-Zn core. The inclusion of the SiO₂ intermediate shell, which will act as a Si source for the hydrothermal synthesis of the SAPO-34 shell, is beneficial for growing zeolite layer, while avoiding damage of the Cr-Zn oxide core during the hydrothermal process [17].

Following hydrothermal synthesis, the color of the granules turned from black to white, indicating coverage of the SAPO-34 layer on Cr-Zn@SiO₂ though some small defects were observed (Fig. 4(a)). Based on the defect region in Fig. 4(b), SAPO-34 zeolite shell displayed an estimated thickness of 20–50 μ m, whereas SiO₂ intermediate layer was estimated to have a thickness of 2–3 μ m. In the absence of this intermediate layer, many defects and regions of uncoated metal oxide core were observed, thereby revealing the importance of the SiO₂ layer. SEM and EDS analyses of a region consisting of a SAPO-34-well-coated area (Fig. 4(c) and (d)) showed lower concentrations of Cr and Zn, suggesting that the Cr-Zn surface was well coated.

Fig. 2. SEM image (a) and EDS analysis (b) of Cr-Zn catalyst.

Fig. 3. SEM images (a, b) and EDS analysis (c) of Cr-Zn@SiO₂.

Fig. 4. SEM images showing the surface morphology of Cr-Zn@SiO₂@SAPO-34 catalyst. (a) Granule; (b) Cross-section; (c) Surface morphology; (d) EDS surface analysis of a well-coated area.

3.2. Catalytic performance of the one-step syngas conversion

The catalytic activity of the prepared catalysts was assessed towards the one-step syngas conversion process. Table 1 lists the reaction results obtained using Cr-Zn and Cr-Zn@SiO₂@SAPO-34 catalysts. Figure 5 further illustrates the product distribution obtained using the two types of catalysts. The main products obtained using Cr-Zn catalyst were CO₂ (selectivity of 47.5%, Table 1), CH₄ (selectivity of 30.7%, Fig. 5), C₂–C₄ hydrocarbons (selectivity of 16.4%, Fig. 5), and a small amount of methanol. Although Cr-Zn is a good methanol synthesis catalyst, temperatures of 400 °C and above do not favor the formation of methanol because the reaction is a thermodynamically controlled process [22]. Instead, large amounts of methane are obtained, as observed herein. However, coverage of the Cr-Zn surface with SAPO-34 resulted in a shift in the formation of products. Methanol selectivity decreased to 0.9% (Table 1) and CH₄ selectivity decreased to 17.5% (Fig. 5), which is almost half of that obtained using Cr-Zn catalyst. In contrast, the selectivity of C₂–C₄ hydrocarbons increased significantly to 38.2% (Fig. 5). Among C₂–C₄, alkanes were the dominant products (58.1%). Thus, the findings clearly show the effectiveness of the SAPO-34 coating. Under the reaction conditions employed, methanol formed over the Cr-Zn surface is presumably converted into hydrocarbons upon diffusion through the pores of the SAPO-34 layer. Surprisingly, Cr-Zn@SiO₂@SAPO-34 displayed a lower CO conversion of 4.2% when compared with that achieved over Cr-Zn (11.6%). The lower CO conversion is likely because of the rather dense SiO₂ intermediate layer, which may hinder the transport of methanol out of the core and

Fig. 5. Product distribution of syngas conversion catalyzed by Cr-Zn and Cr-Zn@SiO₂@SAPO-34 catalysts.

subsequent conversion. We speculate that applying a mesoporous intermediate layer may improve the reaction activity and increase the CO conversion.

4. Conclusions

A core-shell-structured catalyst Cr-Zn@SiO₂@SAPO-34 was synthesized with Cr-Zn oxide as the core and SAPO-34 as the shell, which was grown using a hydrothermal method. A SiO₂ intermediate layer was applied that acted as a Si source for the hydrothermal growth of the shell. SEM and EDS analyses confirmed the formation of a core-shell structure, with some small defects. Such a core-shell-type catalyst afforded a shift in the product distribution from methanol and methane to light hydrocarbons C₂–C₄ with respect to Cr-Zn reference catalyst. The results indicate that such core-shell-structured catalysts provide a feasible approach for converting syngas directly into hydrocarbons such as LPG. However, further optimization of the catalyst and its synthesis process is necessary to achieve higher performance.

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Table 1

Catalytic activity and product distribution of the prepared catalysts.

Catalyst	Cr-Zn	Cr-Zn@SiO ₂ @SAPO-34
CO conversion (%)	11.6	4.2
Selectivity (%)		
Hydrocarbons	49.1	57.1
CO ₂	47.5	42.0
C _x OH	3.4	0.9
Distribution of hydrocarbons (%)		
CH ₄	62.6	30.7
C ₂ –C ₄	10.9	8.8
C ₂ –C ₄	22.6	58.1
C ₅ +	3.9	2.5

Reactions conditions: 400 °C, 2 MPa, 1000 h⁻¹, H₂/CO = 2.

Graphical Abstract

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An alternative route to the Fischer-Tropsch process for the one-step conversion of syngas into hydrocarbons is proposed using core-shell Cr-Zn@SiO₂@SAPO-34 catalyst that enabled selective formation of C₂–C₄ hydrocarbons.

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核壳结构催化剂Cr-Zn@SiO₂@SAPO-34催化合成气直接转化制低碳烃的性能

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摘要: 合成气直接转化高选择性制烃类产物仍是巨大的挑战. 本文合成了以Cr-Zn氧化物为核, SiO₂为中间过渡层, 再通过原位水热合成覆盖一层SAPO-34分子筛为壳的核壳结构催化剂. 合成气转化反应结果显示, 与纯Cr-Zn金属氧化物相比, 核壳结构催化剂将产物分布由甲醇和甲烷移动至C₂–C₄烃(所有烃类产物中占66.9%). 这表明核壳结构催化剂用于合成气一步法直接转化制液化石油气的反应具有可行性, 但是催化剂结构和组成有待于进一步优化, 以提高其催化反应性能.

关键词: 铬锌金属氧化物; 分子筛; 核壳结构; C₂–C₄烃; 合成气直接转化

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