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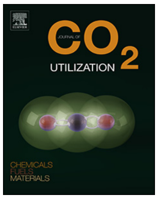

Highly selective conversion of CO_2 to lower hydrocarbons (C_2-C_4) over bifunctional catalysts composed of In_2O_3-ZrO_2 and zeolite

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ABSTRACT

Although many researchers have reported CO_2 hydrogenation to various C1 chemicals, it is still challenging to directly and selectively convert CO_2 to C_2-C_4 hydrocarbons in terms of overcoming the extreme inertness of CO_2 and a high C—C coupling barrier. In the present work, we report an efficient integration of methanol-synthesis and the methanol-to-hydrocarbons with the bifunctional catalyst component of In_2O_3-ZrO_2 and SAPO-5. These tandem reactions exhibit an excellent relative selectivity of C_2-C_4 (83%) with a suppressed CH_4 relative selectivity less than 3% at $T = 300\,^\circ C$. A detailed analysis indicates that the partially reduced indium oxide surface (In_2O_3-ZrO_2) can better activate CO_2 and promote the synthesis of methanol than In_2O_3 alone, and C—C coupling is subsequently manipulated within the confined acidic pores of SAPO-5 according to XRD, H_2-TPR, CO_2-TPD, SEM and TEM. Furthermore, the proximity of two components and the content of Si also play an important role in such outstanding selectivity to C_2-C_4. Our study paves a new path for the direct synthesis of lower hydrocarbons.

1. Introduction

In recent years, with the growth of the energy demand and the burning of fossil fuel, a considerable amount of CO_2 is emitted into the atmosphere and causes damage to the environment. On the other hand, lower hydrocarbons, as the basic chemicals that have largely required in market, are still produced mainly from oil reserves, the consumption of which produces a large amount of CO_2 in the meantime. In this case, the growing demand of lower hydrocarbons and the continually increased CO_2 emission becomes contradictory, and the solution to this issue is urgent. Alternatively, CO_2 hydrogenation to lower hydrocarbons is one of the approaches that attracts great attention nowadays, because it can not only decrease the CO_2 emission, but also possess the potential to reduce the dependence on nonrenewable fossil fuels [1–3].

Now, there are lots of catalysts reported can catalyze conversion of CO_2 to various C1 feedstocks with the high selectivity, such as CO, CH_4, CH_3OH, HCOOH [4–18]. However, it is still difficult to control the content of lower hydrocarbons and gasoline because of the CO_2 chemical stability and the high barriers for the C—C bond formation [19,20]. CO_2 hydrogenation is often described as the combination of reverse water gas shift with Fischer-Tropsch synthesis [21]. So, traditional Fe-based and Co-based catalysts have been used to the CO_2 hydrogenation [22–26]. Compared to the latter, which methane is the main product, Fe-based catalysts display high activity in CO_2 hydrogenation to lower olefins and higher hydrocarbons, since it can catalysis both reverse water gas shift and Fischer-Tropsch synthesis [27–30]. While, the selectivity of lower hydrocarbons on the modified FT catalysts is generally lower than 60 C-mol% because of the limitation by the Anderson-Schulz-Flory distribution [31]. So, it is still a challenge to both active the CO_2 and control the formation of C—C bonds.

It was reported that synthesis gas can be directly transformed into lower olefins with bifunctional catalyst, combining methanol synthesis and methanol to olefins which can overcome the limitation of Anderson–Schulz–Flory (ASF) distribution [32,33]. Some researchers have also achieved that hydrogenation of CO_2 to hydrocarbon over metal oxide/zeolite long before, including using surface modified zeolite and combining core (metal-oxide)-shell (zeolite) catalyst [34–42]. While, compared with hydrogenation of CO to lower olefins, it is more

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difficult to do CO_2 hydrogenation over bifunctional catalysts (methanol synthesis catalyst/zeolite) because of the inertness of CO_2. It is well-known that the C—C bond formation can take place on the zeolite in methanol conversion, such as HZSM-5 and SAPO-34 [43,44]. As for the hydrogenation of CO_2 to methanol, traditional catalysts such as Cu-based, their activity and selectivity still need to improve. Actually, under the DFT studies over the Al_2O_3, Ga_2O_3, and In_2O_3, In_2O_3 theoretically possesses high activity for CO_2 hydrogenation to methanol [45–49], and their studies on CO_2 hydrogenation over non-defective and defective In_2O_3 (110) surface suggested that methanol is the favorable product [48,49]. Futhermore in experimental, In_2O_3 or In-based catalyst have been also used for CO_2 hydrogenation with high methanol selectivity [50,51] Recently, CO_2 hydrogenation made experimental breakthrough to higher hydrocarbons through mixing metal oxide (Fe_3O_4, In_2O_3) and HZSM-5 [36,40]. While, it is still a challenge that CO_2 directly hydrogenation to short-chain carbon (C_2-C_4), because it is difficult to find the suitable conditions that apply to both the methanol catalyst and MTH catalyst, as well as the integration of components.

Inspired by that, here we demonstrate a bifunctional catalyst comprised of metal oxide supported-In_2O_3-ZrO_2 and zeolite (SAPO-5) exhibited an excellent performance for the C_2-C_4 selectivity reaches around 83% in hydrocarbons, as well as only less than 3 C-mol% CH_4 selectivity at CO_2 conversion of 6.7% under the relatively low temperature (573 K). It was also discovered the silicon content of SAPO-5 and integration of the components have impact on the product distribution.

2. Experimental

2.1. Catalyst preparation

In_2O_3 was prepared through the controlled calcination of $In(OH)_3$, wherein the precipitate was obtained by dissolving 0.5 g $In(NO_3)_3 \cdot 5H_2O$ in 100 ml deionized water, followed by the addition of NH_4OH (50 ml, 1 wt.% in H_2O). After centrifugation and decantation, the precipitate was collected and washed with deionized water. Prior to calcination, the sample was dried at 353 K for 12 h, and then calcined at 773 K (5 K min^{-1}) for 4 h in air.

In_2O_3-ZrO_2 (In: 9 wt%), containing Indium nitrate hydrate loading ($In(NO_3)_3 \cdot 5H_2O$, 99.9%, metals basis), was prepared by incipient-wetness impregnation of commercial ZrO_2 (monoclinic phase, Aladdin, 99.99%, metals basis), then dried at 373 K for 12 h. The sample was then calcined using a similar temperature program as In_2O_3.

The Cu-Zn-Al_2O_3 (the ratio of Cu:Zn:Al = 6:3:1) catalyst was prepared by co-precipitation, which was performed at PH = 8 and aged at 343 K for 3 h. After filtering and wishing by deionized water, the obtained product was dried overnight at 353 K and then calcined in air at 773 K for 3 h.

SAPO-5 samples were synthesized by a hydrothermal method from a gel with a ratio of Al:Si:P:TEA:H_2O = 1:x:1.2:0.9:20, wherein the x varied from 0 to 0.3. Pseudoboehmite (82% AlOOH), orthophosphoric acid (85 wt% H_3PO_4), silica sol (30 wt% SiO_2) and triethylamine (TEA) were used as the source materials. Pseudoboehmite was dissolved in deionized water to form alumina sol, and then silica sol was added to the alumina sol under stirring for 1 h. Trimethylamine was then added slowly under continual stirring for 2 h. After that, orthophosphoric acid was added to the mixture, and stirred for 10 h until a homogeneous gel mixture was obtained. The gel mixture was sealed in a 100 ml Teflon-lined stainless-steel vessel and was heated from room temperature to 573 K. The crystallization was carried out at 573 K under autogenic pressure for 48 h. After crystallization, the as-synthesized sample was obtained by centrifugation, washing, and drying at 373 K for 10 h. Finally, the sample was calcined at 823 K (5 K min^{-1}) for 6 h to remove the organic template.

SAPO-34 was synthesized using a hydrothermal method. Typically, 82% AlOOH, 85% phosphoric acid, 30% silica sol and triethylamine (TEA) were well dispersed in distilled water with a ratio of Al:Si:P:TEA:H_2O = 1:0.15:1:1.5:25. The reactants were mixed with vigorous stirring at 303 K, and the resultant mixed gel was transferred to a stainless-steel autoclave lined with Teflon and heated at 573 K for 72 h. The product was washed with deionized water and dried at 373 K. The SAPO-34 precursors were calcined at 823 K (5 K min^{-1}) for 6 h.

The synthesized ZSM-5 was prepared by hydrothermal crystallization, 17.75 g TPABr was added into 66.67 g colloidal silica (30%) solution that was labelled as solution A, then 1.04 g suspension comprised 0.5 wt% nano Silicate-1 (with uniform particle size at around 60–70 nm) was poured into. After 30 min's hydrolysis at 308 K, a solution contained 2.07 g $AlCl_3 \cdot 6H2O$ and 45 g H_2O was dropwise added into solution A. Finally, 22.26 g ethylamine aqueous solution (65%) was poured into silica-aluminium sol. The mother gel was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 443 K for 72 h. The molar composition of the final gel was 1 SiO_2 : 0.0125 Al_2O_3 : 0.20 TPABr : 1 Ethylamine : 17 H_2O. The product was collected by centrifugation and drying overnight at 373 K, a following calcination at 813 K for 6 h was used to remove template.

The synthesized ZSM-11 was prepared by hydrothermal crystallization, the reagents used were silica sol, aluminum sulfate, NaOH, and as structure directing agents were tetrabutyl ammonium bromide. The molar composition of the synthesis gel was 1SiO_2 : 0.03$Al_2(SO_4)_3$: 0.1TPABr: 70H_2O: 0.35NaOH. Aluminum sulfate was dissolved under magnetic stirring in a solution consisting of silica sol and TPABr, later on NaOH was slowly added. The mixture were placed in a Teflon-lined stainless steel autoclave at 433 K for 96 h while stirring. After cooling to room temperature, the zeolite product was filtered and thoroughly washed with deionized water, dried for 12 h at 373 K, and subsequently calcined in air for 2 h at 813 K. To get the H-form zeolite the obtained powder was treated with 5 ml /g zeolite of a 1 M NH_4NO_3 solution for three times and calcined at 813 K. After that the catalyst was extruded with aluminum compound, cementing material, 10% HNO_3 with the ratio of 1: 0.25: 0.05: 0.6. It subsequently placed for 48 h at room temperature, dried for 12 h at 373 K and calcined 4 h at 813 K. The obtained zeolite was denoted as ZSM-11.

2.2. Catalytic test

CO_2 hydrogenation to hydrocarbons was conducted using a pressurized fixed-bed flow reactor. 0.9 g composite catalyst (In_2O_3-ZrO_2/SAPO-5 mass ratio = 1:2) was mounted in a stainless-steel tube reactor (inner diameter, 9 mm). Prior to reaction, catalyst was reduced in H_2 at 573 K for 1 h with a flow rate of 45 ml min^{-1}. Then, the feed gas was switched to the CO_2 and H_2 mixture gas (H_2/CO_2 = 75:25) under the reaction conditions of P = 3 MPa, T = 573 K, and GHSV = 4000 ml g^{-1} h^{-1}.

The products were analyzed on-line by a gas chromatograph (FULI GC 97). Carbon monoxide, carbon dioxide and methane were analyzed on a carbon molecular sieve column with a thermal conductivity detector (TCD) while methane and C_2–C_8 hydrocarbons (C_2^+) were analyzed with a flame ionization detector (FID) with a HayeSep Q column. Chromatograms of FID and TCD were correlated through methane and product selectivity was obtained based on carbon. The conversion percentage of CO_2 was based on the fraction of CO_2 that formed carbon-containing products according to:

$$\mathrm{CO_2 conversion}(\%) = \frac{\Sigma \mathrm{n_i M_i}}{\mathrm{M_{CO2}}} \times 100$$

where n_i is the number of carbon atoms in product i, M_i is the percentage of product i and M_{CO2} is the percentage of CO_2 in the mixed feed. The selectivity of the carbon-containing product i (S_i, C-mol%) is based on the total number of carbon atoms in the product and is therefore defined as: