



Role of zirconium in direct CO₂ hydrogenation to lower olefins on oxide/zeolite bifunctional catalysts



Shanshan Dang^{a,b}, Peng Gao^{a,*}, Ziyu Liu^a, Xinqing Chen^a, Chengguang Yang^a, Hui Wang^a, Liangshu Zhong^{a,c}, Shenggang Li^{a,c,*}, Yuhan Sun^{a,c,*}

^a CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201203, PR China

^b University of the Chinese Academy of Sciences, Beijing 100049, PR China

^c School of Physical Science and Technology, ShanghaiTech University, Shanghai 201203, PR China

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ABSTRACT

Direct production of lower olefins (C₂–C₄: ethylene, propylene and butylene), basic carbon-based building blocks, from carbon dioxide (CO₂) hydrogenation is highly attractive, although the selectivity towards olefins has been too low. Here we present a series of bifunctional catalysts contained indium-zirconium composite oxides with different In:Zr atomic ratios and SAPO-34 zeolite, which can achieve a selectivity for C₂–C₄ as high as 65–80% and that for C₂–C₄ of 96% with only about 2.5% methane among the hydrocarbon products at CO₂ conversion of 15–27%. The selectivity of CO via the reverse water gas shift reaction is lower than 70%. The product distribution is completely different from that obtained via CO₂-based Fischer-Tropsch synthesis and deviates greatly from the classical Anderson-Schulz-Flory distribution. The zirconium component plays a critical role in determining the physicochemical properties and catalytic performance of bifunctional catalysts. Catalyst characterization and density functional theory calculations demonstrate that the incorporation of a certain amount of zirconium can create more oxygen vacancy sites, stabilize the intermediates in CO₂ hydrogenation and prevent the sintering of the active nanoparticles, thus leading to significantly enhanced catalytic activity, selectivity of hydrocarbons and stability for direct CO₂ hydrogenation to lower olefins at the relatively high reaction temperature of 380 °C.

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1. Introduction

As a nontoxic, renewable, readily available, and abundant carbon resource, carbon dioxide (CO₂) can be transformed from a chemical waste into valuable products, which to some extent can further mitigate the global warming caused by excessive CO₂ emissions [1,2]. In addition, due to dwindling fossil fuel resources, the utilization of CO₂ as an alternative carbon feedstock for the production of chemicals and fuels, i.e. CO₂ refineries, becomes increasingly important [3,4]. Many recent studies are mainly focused on the conversion of CO₂ to carbon monoxide, methanol, methane and long-chain alkanes [5–15], whereas few studies are on the direct conversion of CO₂ to olefins. Lower olefins (C₂–C₄), generally referring to ethylene, propylene and butylene, are the most

important bulk petrochemicals used to produce plastics, fibers and other chemicals. The annual worldwide production of lower olefins is about 200 Mt, which are manufactured by the chemical industry through alkane steam cracking or from natural gas via methanol and MTO routes. These processes are energy intensive, not to mention their 180–200 million tons of CO₂ emission [16–18]. Therefore, CO₂ hydrogenation to lower olefins is a more promising route for CO₂ emission reduction especially if renewable hydrogen sources are made available. However, significant technical challenges exist owing to the inherent chemical inertness of CO₂ and the high C–C coupling barrier.

There are several different routes to produce hydrocarbons from CO₂ with renewable H₂ [19]. Generally, modified Fischer-Tropsch synthesis (FTS) catalysts are applied to CO₂ hydrogenation for hydrocarbons synthesis, which usually proceeds via two distinct steps: reverse water gas shift (RWGS) followed by further CO hydrogenation to hydrocarbons via the FTS reaction. Unfortunately in the FTS reaction, product selectivity is controlled by the Anderson-Schulz-Flory (ASF) distribution, which predicts a maximum C₂–C₄ hydrocarbon fraction (including C₂–C₄ and C₂–C₄)

* Corresponding authors at: CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201203, PR China (S. Li and Y. Sun).

E-mail addresses: gaopeng@sari.ac.cn (P. Gao), liscg@sari.ac.cn (S. Li), sunyh@sari.ac.cn (Y. Sun).

paraffins) of about 56.7% and an undesired methane fraction of about 29.2% [20,21]. Alternatively, the conversion of CO_2 to $\text{C}_2\text{--C}_4$ can also be accomplished via methanol- or dimethyl ether (DME)-mediated reactions, which can overcome the limitation on the selectivity imposed by the above FTS mechanism [22,23]. Traditionally, this latter route requires two separate reactors, where methanol or DME is obtained from CO_2 hydrogenation in the first reactor, and lower olefins can be synthesized from methanol or DME over zeolite in the second reactor. For process intensification and operational cost reduction, it is highly desirable to develop an efficient multifunctional catalyst for direct CO_2 conversion to $\text{C}_2\text{--C}_4$ with high selectivity. This approach has recently been used to convert synthesis gas to $\text{C}_2\text{--C}_4$ over oxide/zeolite bifunctional catalysts to achieve the high selectivity of >70% among all hydrocarbons [24–26]. In our recent works, we also adopted this approach by designing and synthesizing a series of bifunctional catalysts composed of reducible indium oxide and zeolite, which can realize the direct synthesis of gasoline-range hydrocarbons ($\text{C}_5\text{--C}_{11}$) and $\text{C}_2\text{--C}_4$ from CO_2 hydrogenation with excellent selectivity [27,28]. This approach was also utilized by other researchers for direct CO_2 hydrogenation using bifunctional catalysts [29–31], although there remain significant challenges. Different from CO hydrogenation, CO_2 hydrogenation via methanol-mediated reaction over a bifunctional catalyst has the additional necessity for suppressing CO formation via the RWGS reaction, which is thermodynamically and kinetically favored at the higher reaction temperature. In addition, a larger amount of H_2O formed in CO_2 hydrogenation to hydrocarbons can strongly inhibit the reaction and greatly reduce the stability of the catalysts.

In_2O_3 with oxygen vacancy sites proves to have superior catalytic activity for CO_2 hydrogenation to methanol even at the high temperature above 300 °C. The methanol formation mechanism at the oxygen vacancy sites was found to be distinct from that over traditional Cu-based catalysts, which can stabilize the key intermediates involved in methanol formation [32–35]. Additionally, the reaction rate over In_2O_3 decreased moderately in an H_2O co-feeding CO_2 hydrogenation experiment at 300 °C, while the conventional Cu/ZnO/ Al_2O_3 catalyst experienced rapid deactivation [36,37]. However, C–C coupling from methanol over zeolites is thermodynamically favorable at the high temperature of above 350 °C [38–40]. Therefore, more efficient bifunctional catalysts need be developed. Zirconia has received considerable attention as a promoter and support due to its unique properties, for example, the presence of both acid and basic sites, as well as the high thermal stability [41]. Recently, Wang et al. [42] found that the strong synergetic effect between Zn and Zr sites resulted in the excellent performance for CO_2 hydrogenation to methanol at 320 °C. Using ZrO_2 as a carrier for In_2O_3 , the $\text{In}_2\text{O}_3/\text{ZrO}_2$ mixed oxide catalyst exhibited excellent stability for 1000 h on stream during methanol synthesis from CO_2 hydrogenation [37]. For Cu-based catalysts, it was proposed that the enhanced Cu/ ZrO_2 interaction led to the improved catalytic performance for methanol formation from CO_2 [43,44].

In this work, more efficient bifunctional catalysts for direct CO_2 hydrogenation to lower olefins were developed to further suppress CO formation and improve catalyst stability. Zirconia was introduced into In_2O_3 to synthesize In-Zr composite oxides with different In:Zr atomic ratios. The bifunctional catalysts were prepared by mechanically mixing the In-Zr composite oxides with the SAPO-34 zeolite, which were optimized for direct production of $\text{C}_2\text{--C}_4$ from CO_2 hydrogenation. Further experimental characterizations and density functional theory (DFT) calculations revealed that the incorporation of an optimal amount of zirconium resulted in create more oxygen vacancy sites with proper formation energies, which further stabilized the intermediates in the CO_2 hydrogenation reaction. The zirconium component also helped to prevent the

sintering of the active nanoparticles, thus leading to significantly enhanced catalytic activity, selectivity of hydrocarbons and stability for direct CO_2 hydrogenation to lower olefins at the relatively high reaction temperature of 380 °C.

2. Experimental

2.1. Catalyst preparation

A series of $\text{In}_2\text{O}_3/\text{ZrO}_2$ catalysts with different In:Zr atomic ratios (1:0, 16:1, 4:1, 1:1, 1:4, 0:1) were prepared through the controlled calcination of hydroxides. The mixture of NH_4OH (28–30 wt% in H_2O) and ethanol was added under vigorous stirring to an aqueous solution of the $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$. The product was aged at 80 °C for 10 min and then filtered and washed with deionized water. The filter cakes were dried overnight at 60 °C and calcined in air at 500 °C for 5 h. The obtained composite oxides were denoted as In:Zr(X) (X is the In:Zr atomic ratio in the synthesis mixture).

Parent SAPO-34 crystals were prepared by a hydrothermal route. The synthesis gel recipe in molar composition is 1 Al_2O_3 :0.44 SiO_2 : 1.1 P_2O_5 :2.25 triethyl-amine: 35 H_2O , and SAPO-34 crystal seeds with a mass ratio of 1:500 to the gel were mixed in a closed autoclave. Then the mixture was heated from room temperature to 165 °C in 7 h and kept at 165 °C for 33 h before cooling down. The solid product was filtered, washed and dried, followed by calcination at 600 °C for 6 h.

For the preparation of the bifunctional catalysts, the In_2O_3 , In-Zr oxides or ZrO_2 and the SAPO-34 were pressed, crushed and sieved to granules in the range of 40–60 mesh (granule sizes of 250–400 μm), respectively. Then, the granules of the two samples (oxides and SAPO-34) were mixed together by shaking in a vessel.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) was analyzed in the 2θ range 5–90° using a Rigaku Ultima 4 X-ray diffractometer with Cu K α radiation, operating at 40 kV and 40 mA and in the step mode (0.0167°).

The surface area (BET), pore volume and the pore size (BJH) were determined from the nitrogen adsorption/desorption isotherms at 77 K, using a TriStar II 3020 instrument. Prior to the measurements, the samples were outgassed at 473 K under vacuum for 10 h.

Raman spectra measurements were performed using a 532 nm line of He-Ne laser by the Thermo Scientific DXR Raman microscope.

The morphology of the samples was observed by a Tecnai G²20 S-Twin high-resolution transmission electron microscope (HR-TEM) and TEM operated at 200 kV. The morphology of the samples was observed by a SUPRRATM 55 Scanning electron microscopy (SEM) with an accelerating voltage of 2.0 kV.

The X-ray photoelectron spectroscopy (XPS) measurements were manufactured by a Thermo Scientific K-Alpha spectrometer equipped with Al K α radiation (150 W, $h\nu = 1486.6$ eV) under ultrahigh vacuum (10^{-7} bar). The binding energies were calibrated by adventitious carbon deposit C (1s) with $E_b = 284.9$ eV.

CO_2 temperature-programmed desorption (CO_2 -TPD) experiments were performed on an OmniStar GSD320 02 mass spectrometer to monitor the desorption of CO_2 . All the samples were reduced at 400 °C for 1 h with pure Ar in a flow of 60 mL min^{-1} . After cooling to 50 °C, the catalysts were saturated in CO_2 flow with 30 mL min^{-1} for 1 h and then flushed with Ar for 3 h to remove any physisorbed molecules. The CO_2 -TPD measurement was carried out at 50–750 °C with a heating rate of 10 °C min^{-1} under continuous flow of Ar with 35 mL min^{-1} and was recorded by the mass spectrometer. The CO_2 peak area was quantitatively calibrated by injecting CO_2 pulses.

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