

Catalytic conversion of CO₂-rich syngas to high-quality gasoline hydrocarbons over In₂O₃-ZrO₂/SAPO-11 catalysts

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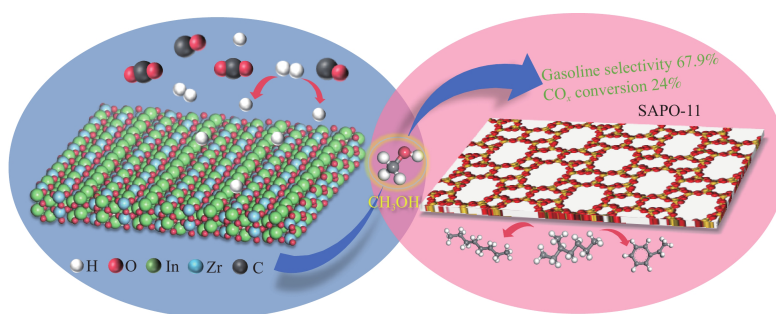
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Abstract: The conversion of CO₂ into gasoline-range hydrocarbons represents a sustainable pathway to achieve deep decarbonization in the transportation sector. Nevertheless, the traditional Fischer-Tropsch synthesis (FTS) suffers from a broad product distribution, which restricts the achievable selectivity toward C₅–C₁₁ gasoline-range hydrocarbons to roughly 45%. This

study presents the development of a bifunctional catalyst that integrates In₂O₃/ZrO₂ metal oxides with SAPO-11 molecular sieves, aiming at efficiently converting CO₂/CO mixtures into C₅–C₁₁ gasoline hydrocarbons. Catalysts with varying In/Zr ratios were prepared *via* co-precipitation. By employing a CO_x (CO/CO₂) co-feeding strategy (CO/CO_x = 0.5), the formation of by-product CO was significantly suppressed, thereby enabling the selectivity for gasoline hydrocarbons to exceed the maximum predicted by the Anderson-Schulz-Flory (ASF) model. Notably, under identical reaction conditions, the In₂ZrO_x/SAPO-11 catalyst exhibited higher performance compared with In₂O₃/SAPO-11 and ZrO₂/SAPO-11. The CO_x conversion was elevated by 1.7% and 0.2%, while the selectivity toward C₅–C₁₁ hydrocarbons was enhanced by 8.0% and 16.0%, respectively. Furthermore, the In₂ZrO_x/SAPO-11 catalyst delivered a single-pass performance of 24% CO_x conversion and 68% selectivity for C₅–C₁₁ hydrocarbons at 380 °C, 3 MPa and a gas hourly space velocity (GHSV) of 2400 mL/(min·g). Within this product distribution, isoparaffins accounted for 32.6% of the total components, corresponding to an isoparaffin/neoparaffin ratio of 12.3. After 150 h of stability testing, the catalyst maintained a single-pass CO_x conversion of 23% and a C₅–C₁₁ selectivity of ~65%, demonstrating excellent catalytic activity and promising potential for industrial application.

Key words: CO₂-rich syngas; OX-ZEO; In₂O₃-ZrO₂/SAPO-11; gasoline-range hydrocarbons



The rapid expansion of the transportation industry has resulted in an extensive consumption of fossil fuels, which in turn has caused the continuous increase in atmospheric CO₂ levels, intensifying the greenhouse effect and posing a serious challenge to the human living environment. By utilizing renewable hydrogen, the efficient transformation of CO₂ into chemical feedstocks and valuable fuels has become an important pathway for achieving a low-carbon

transition and CO₂ resource utilization in the transportation sector^[1–5]. As one of the main transportation fuels, the production capacity and technology level of gasoline directly reflect the progress of a nation's energy sector. However, the traditional gasoline heavily relies on fossil resources, and due to resource depletion and environmental pressures, there is an urgent need to explore green and sustainable alternative production strategies. In this context,

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synthesizing gasoline from CO₂ has been considered a crucial approach to achieving a green, low-carbon energy system.

Currently, two primary methods exist for converting CO₂ into liquid hydrocarbons. One is the traditional FTS route, where CO₂ is first transformed into CO *via* the reverse water-gas shift (RWGS) reaction, and then gasoline hydrocarbons are synthesized using FTS technology^[6]. However, the product distribution of FTS strictly follows the ASF model, resulting in a broad hydrocarbon spectrum and the restricted selectivity for gasoline fractions. The other method involves using OX/ZEO (metal oxide/molecular sieve) bifunctional catalysts, which exhibit significant advantages in selectively producing olefins, aromatics, or gasoline. In this process, metal oxides first catalyze the formation of oxygenated intermediates (e.g., methanol or dimethyl ether), which are then selectively converted into gasoline hydrocarbons over the molecular sieve^[7–9]. However, the reaction temperature in the second stage is typically higher than the optimal temperature required for intermediate synthesis (>375 °C), which suppresses the formation of methanol or dimethyl ether^[10]. In addressing the temperature mismatch issue between the two stages, In₂O₃-based catalysts have shown outstanding advantages, especially maintaining high stability in the second stage at temperatures higher than 375 °C. Recent studies have shown that these catalysts not only have strong CO₂ adsorption capacity, leading to high activity in methanol synthesis, but also effectively suppress the RWGS reaction^[11–14]. Ramirez et al.^[15–19] further found that introducing ZrO₂ as a support in methanol synthesis not only promotes the high dispersion of In₂O₃ but also facilitates controlled growth or the formation of In₂O₃-ZrO₂ solid solution structures on its surface, effectively inhibiting In₂O₃ sintering, thereby enhancing its overall stability. In the bifunctional catalytic reaction system, CO₂/CO and other reactant molecules are first converted into oxygenated intermediates on metal oxides, and these intermediates then undergo C–C coupling reactions in the acidic sites of the molecular sieve to form hydrocarbon products^[20]. Furthermore, the quality of the produced gasoline depends not only on the conversion efficiency of the intermediates but is also significantly influenced by the specific pore structure of zeolite, which directly affects the gasoline's octane rating. Li et al.^[21] showed that SAPO-11, with its 10-membered ring (10-MR) pore structure, is more favorable for reducing aromatic content and achieving high selectivity in gasoline hydrocarbon production compared to other molecular sieves, such as ZSM-12 (12-MR), ZSM-5, ZSM-11 and ZSM-22 with 10-MR. SAPO-11, with its unique non-crossing elliptical pore structure, effectively inhibits the hydrogen cracking of branched alkanes during the isomerization of *n*-alkanes, thereby efficiently promoting the isomerization of long-chain alkanes^[22–24]. Additionally, choosing SAPO-11 is due to its higher external surface area and greater accessibility of active sites, which enhance the

catalytic efficiency of alkane hydrogenation isomerization. Its shorter diffusion path also helps the timely removal of coke precursors, reducing the risk of pore blockage and extending catalyst life^[22].

Previous studies on CO₂ catalytic hydrogenation commonly employ high-purity CO₂ and H₂ as feedstocks. However, the efficiency of methanol/DME (dimethyl ether) synthesis is weakened by the excessive generation of CO in the competing reaction pathway due to the presence of the RWGS reaction. Additionally, CO₂ from biomass gasification usually contains a certain amount of CO^[8]. To address these issues, a CO_x co-feeding strategy has been adopted. This strategy not only reduces the driving force for the CO₂ → CO reaction by introducing external CO, thus partially inhibiting the RWGS reaction, but also allows CO to directly participate in methanol synthesis, providing a more direct and thermodynamically favorable reaction pathway than the CO₂ route, leading to more efficient catalytic conversion^[25]. Furthermore, the co-feeding of CO₂ and CO not only avoids separation costs but also meets the practical need for the recycling of unreacted gases in methanol synthesis processes. In summary, the synergistic utilization of CO_x provides a new research approach for the efficient use of non-petroleum-based carbon sources^[19].

In this context, various OX/SAPO-11 bifunctional catalysts (OX = In₂O₃, ZrO₂, In₂O₃-ZrO₂) were prepared, with systematic control over the In/Zr ratios. Meanwhile, the structure and surface characteristics of the catalysts were analyzed and assessed using a range of characterization techniques. A CO₂ and CO co-feeding strategy was employed, with a focus on investigating the effects of reaction parameters (temperature, pressure, CO/CO_x ratio and time) on the CO_x conversion rates and selective synthesis of high-quality gasoline hydrocarbons. This study aims to reveal the catalyst structure-performance relationship, offering insights into the optimization design of novel STG (syngas-to-gasoline) bifunctional catalysts.

1 Experimental

1.1 Materials

Indium nitrate (InN₃O₉, 99%) was acquired from Beijing Mreda Technology Co., Ltd. *N*-propyl alcohol (C₃H₈O, 99%), aluminum isopropyl alcohol (C₉H₂₁AlO₃, 98%), di-n-propylamine (DPA, 99%), zirconium nitrate (Zr(NO₃)₄·5H₂O, 99%), dodecyl trimethyl ammonium bromide (DTAB, 99%) and diisopropylamine (DIPA, 99%) were obtained from Shanghai Aladdin Biochemical Co. Phosphoric acid (H₃PO₄, 85%) and silicic acid (SiO₂, 95%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ammonium carbonate ((NH₄)₂CO₃, AR), *n*-butanol (C₄H₁₀O, 99.5%) and ethanol (CH₃CH₂OH, 99%) were purchased from Tianjin Yongda Chemical Reagent Co., Ltd.

1.2 Catalyst synthesis

The In₂O₃-ZrO₂ catalyst was synthesized using the coprecipitation method. A solution was prepared by dissolving In(NO₃)₃ and Zr(NO₃)₄·5H₂O with specified ratios in deionized water under stirring to prepare solution A. Meanwhile, a 1 mol/L (NH₄)₂CO₃ solution was prepared as the precipitant, referred to as solution B. The resulting mixture was left for 2 h to ensure complete coprecipitation, followed by vacuum filtration and repeated washing with deionized water. The obtained precipitate was dried at 110 °C for 12 h and then calcined at 500 °C in a muffle furnace for 3 h to obtain the In₂O₃-ZrO₂ metal oxide.

The SAPO-11 molecular sieve was synthesized using a typical hydrothermal synthesis method. The specific steps are as follows: The procedure begins with mixing phosphoric acid, *n*-propyl alcohol and deionized water, which were then stirred for 3 h. Next, the predetermined amount of isopropylaluminum was introduced, followed by stirring the mixture for 12 h. Then, the precise quantities of dipropylamine (DPA) and diisopropylamine (DIPA) were introduced, with continuous agitation maintained for another 3 h. Afterward, a certain amount of silica sol was incorporated, and the mixture was stirred for 2 h. Then, dodecyltrimethylammonium bromide (DTAB) was added, and stirring continued for an additional 2 h to form the initial gel. The resulting gel had a composition of 1.0 P₂O₅:2.0 C₃H₈O:60.0 H₂O:1.0 Al₂O₃:0.6 DIPA:0.6 DPA:0.4 SiO₂:0.1 DTAB. This gel was subsequently transferred to a high-pressure reactor lined with polytetrafluoroethylene, where it was hydrothermally crystallized at 190 °C for 24 h. The crystalline product was collected, vacuum filtered and repeatedly washed several times with anhydrous ethanol and deionized water. Finally, the product was dried at 110 °C for 12 h, followed by calcination at 550 °C in a muffle furnace for 6 h to obtain the SAPO-11 molecular sieve.

The synthesized In₂O₃-ZrO₂ metal oxide and SAPO-11 acidic catalyst were physically combined in a 2:1 mass ratio to obtain the composite catalyst, In₂O₃-ZrO₂/SAPO-11.

1.3 Characterization

The N₂ adsorption-desorption curves of the catalyst were determined at -196 °C using the BSD-PS2 instrument for physical adsorption-desorption, produced by Bessay Instruments (China). The reducibility of the metal (H₂-TPR), CO₂ temperature-programmed desorption (CO₂-TPD) and acidity of the composite catalyst (NH₃-TPD) were analyzed using a Micromeritics AutoChem II 2920 analyzer. The structural characteristics were examined by X-ray power diffraction (XRD) using a Shimadzu XRD-6100 diffractometer (Shimadzu, Japan). The chemical properties of the In_aZr_bO_x sample surface were analyzed by X-ray photoelectron spectroscopy (XPS) with a Thermo

Scientific K-Alpha spectrometer. The morphology of the metal oxide and molecular sieve components was analyzed with an Apreos field emission scanning electron microscope (FEI, USA). The lattice structure and distribution of the metal oxides were analyzed by transmission electron microscopy (TEM) with the Tecnai G2 F20 field emission electron microscope (FEI, USA).

1.4 Catalytic performance tests

The CO_x hydrogenation experiments were performed in the fixed-bed reactor shown in Figure 1. Both the quartz sand and the catalyst were sieved to 40–60 mesh. Two grams of catalyst were positioned at the center of the reactor tube, with quartz sand packed at both ends. The catalyst and quartz sand were densely packed to ensure effective and uniform heating of the catalyst. The reactor tube was subsequently placed into the furnace, and the airtightness of the entire system was checked. After the airtightness test was completed and the system was confirmed to be leak-free, the system was put into operation for subsequent reproducibility reaction tests. After setting the reaction temperature and pressure, the flow rates of H₂, CO and CO₂ were adjusted, and the reactant gases were introduced into the reactor. Once the reaction system reached steady state, the products were separated into gas and liquid phases using a cold trap for offline analysis. The gas-phase products were detected with a Micro GC 490 gas chromatograph, which was equipped with MS5A and PPU chromatographic columns. The liquid-phase products, collected in the cold trap, were examined with a gas chromatography-mass spectrometry (GC-MS) system from Agilent Technologies, equipped with a DB-1701 capillary column (60 m × 0.25 mm × 0.25 μm) from the 5977B/8890 series. The CO_x conversion rate (Conv._{CO_x}) and hydrocarbon selectivity (Sel._{C_nH_m}) were calculated using the following formulas:

$$\text{Conv.}_{\text{CO}_x} = (F_{\text{CO}_x,\text{in}} - F_{\text{CO}_x,\text{out}}) / (F_{\text{CO}_x,\text{in}}) \times 100\% \quad (1)$$

$$\text{Sel.}_{\text{C}_n\text{H}_m} = (nC_n\text{H}_{m,\text{out}}) / \left(\sum_n nC_n\text{H}_{m,\text{out}} \right) \times 100\% \quad (2)$$

where $F_{\text{CO}_x,\text{in}}$ is the molar concentration of CO_x at the inlet, and $F_{\text{CO}_x,\text{out}}$ and $C_n\text{H}_{m,\text{out}}$ are the corresponding values for the outlet flow of the reactor. The carbon balance correction method was used, and the consistency between the total carbon content in the products and the carbon content in the feed was analyzed to verify the accuracy of the conversion rate and selectivity calculations. The carbon balance (CB) of the reactor is defined and calculated as shown in Equation (3):

$$\text{CB} = (F_{\text{C},\text{in}} / F_{\text{C},\text{out}}) \times 100\% \quad (3)$$

where $F_{\text{C},\text{in}}$ and $F_{\text{C},\text{out}}$ represent the total carbon flow rates entering and exiting the reactor, respectively.

The CB closure rate in all experiments was greater than 94%.

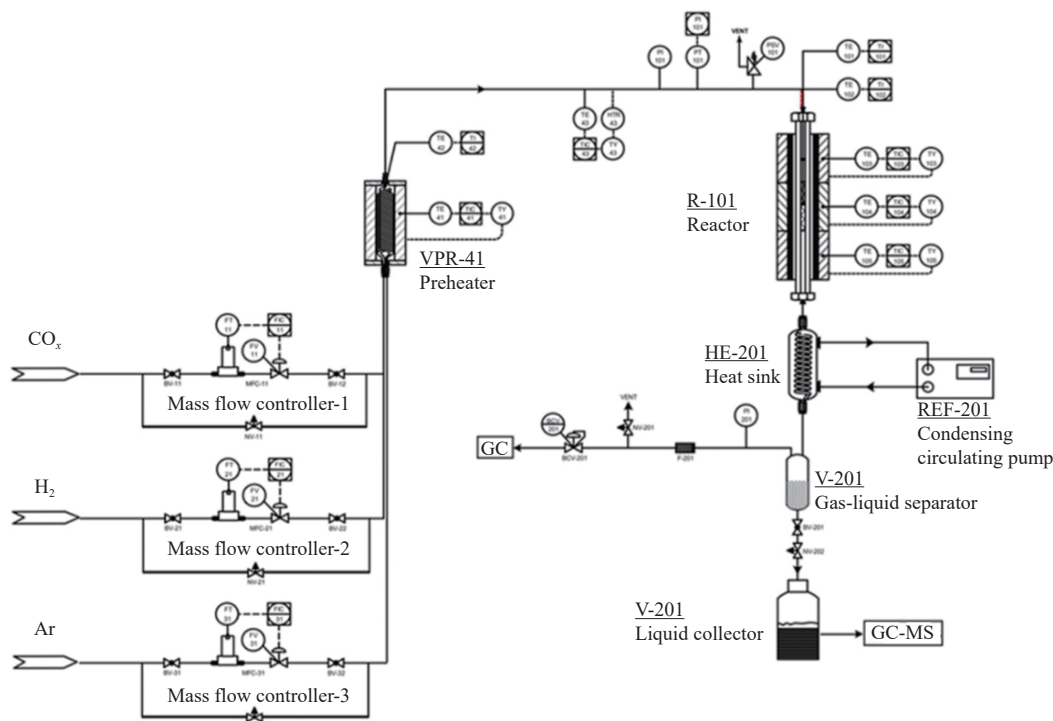


Fig. 1 Fixed-bed microreactor

2 Results and discussion

2.1 Catalyst characterization

2.1.1 XRD and textural properties

The XRD patterns of $\text{In}_a\text{Zr}_b\text{O}_x$ and SAPO-11 with different In/Zr ratios are shown in Figure 2. All the synthesized InZrO_x samples in Figure 2(a) exhibit diffraction peaks corresponding to In_2O_3 and ZrO_2 . Compared to $\text{In}_5\text{Zr}_1\text{O}_x$ and $\text{In}_4\text{Zr}_1\text{O}_x$, the diffraction peaks of $t\text{-ZrO}_2$ in $\text{In}_3\text{Zr}_1\text{O}_x$, $\text{In}_2\text{Zr}_1\text{O}_x$ and $\text{In}_1\text{Zr}_1\text{O}_x$ are significantly weakened or even difficult to be discerned. In contrast, the characteristic peaks of $m\text{-ZrO}_2$ become more prominent, indicating that the incorporation of In^{3+} leads to lattice distortion and thus stabilizes the $t\text{-ZrO}_2$ phase. As the In content decreases, this stabilizing effect diminishes, making ZrO_2 more prone to exist in the $m\text{-ZrO}_2$ form^[26]. As the In/Zr ratio increases, the characteristic peaks of In_2O_3 ($2\theta = 21.448^\circ$, 35.379° , 50.899°) gradually increased and became sharper, indicating an increase in grain size and the improved crystallinity. For $\text{In}_3\text{Zr}_1\text{O}_x$ and at lower In/Zr ratios, significant peak broadening was observed, which is consistent with the presence of smaller, more highly dispersed In_2O_3 crystallites. At lower In/Zr ratios, monoclinic $m\text{-ZrO}_2$ is observed in $\text{In}_2\text{O}_3\text{-ZrO}_2$, but when the In/Zr ratio exceeds 4, ZrO_2 gradually transforms from a two-phase coexistence to a tetragonal phase. This transition can be attributed to the lattice distortion induced by In^{3+} doping, making ZrO_2 more stable in the tetragonal phase structure^[27]. Interestingly, the main diffraction peaks of ZrO_2 in all samples shift to lower angles (left shift) in

Figure 2. According to Bragg's law ($n\lambda = 2d\sin\theta$), this phenomenon indicates that the interplanar spacing d of the samples generally increases. The possible mechanism is that the ionic radius of In^{3+} (0.81 Å) is larger than that of Zr^{4+} (0.72 Å), and when In^{3+} partially substitutes the ZrO_2 lattice sites, it causes lattice expansion and local distortion. At the same time, the charge imbalance caused by the heterovalent substitution promotes the formation of additional oxygen vacancies^[26]. Therefore, the overall left shift of the peaks can be considered as the direct evidence of In^{3+} doping into the ZrO_2 lattice, accompanied by oxygen vacancy formation, providing a structural basis for subsequent CO_2 adsorption and activation. Figure 2(b) shows strong diffraction peaks at 2θ values of 8.1° , 9.6° , 13.1° , 15.9° , 20.2° , 21.2° and $22.2^\circ\text{--}23.2^\circ$, indicating the formation of an AEL (JCPDS#47-0613) topology. Additionally, no extra peaks were observed, and the patterns well match the standard diffraction spectrum, confirming the samples are highly crystalline and nearly free of impurities.

The N_2 adsorption-desorption isotherms of $\text{In}_a\text{Zr}_b\text{O}_x$ with different In/Zr ratios and SAPO-11 are shown in Figure 3. All samples exhibit typical type IV isotherms accompanied by pronounced H3 type hysteresis loops in the relative pressure range of $p/p_0 = 0.6\text{--}1.0$. This indicates the occurrence of capillary condensation of gas molecules within mesopores, which confirms that the typical mesoporous structures of the synthesized oxides^[28]. Notably, when the In/Zr ratio exceeds 3, the H3 type hysteresis loops gradually become narrower with increasing In content, which may be likely due to the packing of irregular particles within the pores, resulting in the reduced pore sizes and a narrowed pore size distribution^[29]. The corresponding textural properties, including specific surface

area, pore volume and pore size are presented in Table 1. The results show that with increasing Zr content, the pore volume of the oxides gradually decreases, whereas the specific surface area exhibits an increasing trend. Among all samples, the oxide with a Zr/In ratio of 1:4 exhibits the highest specific surface area (76.7 m²/g) and pore volume (0.427 cm³/g). As illustrated in Figure 3(b), the SAPO-11 molecular sieve exhibits type IV isotherms with an IUPAC-classified H3 hysteresis loop observed in the relative high pressure range ($p/p_0 = 0.4-0.9$), suggesting the coexistence of microporous and mesoporous structures. In such materials, slit-like mesoporous structures typically result from the stacking of plate-like SAPO-11 crystals, aligning

with the plate-like structure seen in the scanning electron microscopy (SEM) images. At relative low pressures ($p/p_0 < 0.1$), a sharp increase in adsorption is observed, suggesting that nitrogen rapidly fills the 10-membered ring micropores of SAPO-11. From the pore size distribution, the pores are mainly concentrated around 3.91, 12.03 and 20.37 nm with an average pore size of 10.825 nm (Table 1). Therefore, SAPO-11 possesses a hierarchical pore structure with both micropores and mesopores. The micropores ensure excellent shape-selective catalytic ability, while the mesopores effectively enhance molecular diffusion, resulting in better intermediate conversion performance^[30].

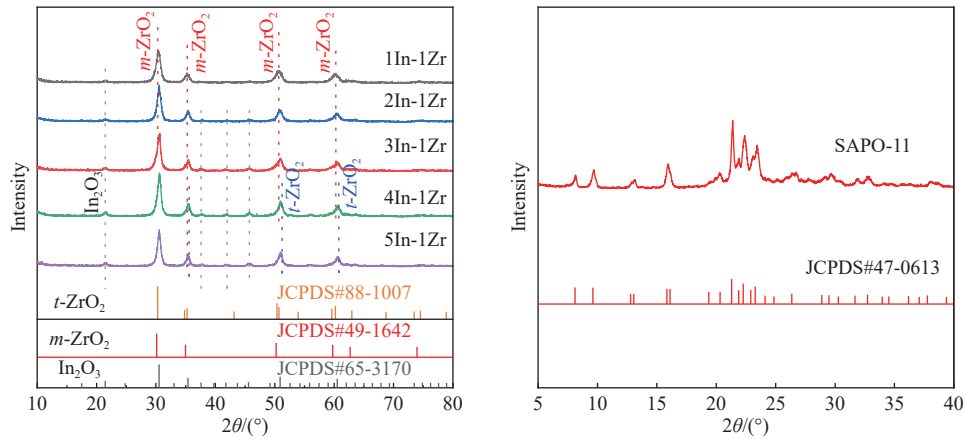


Fig. 2 XRD patterns of In_xZr_bO_x and SAPO-11

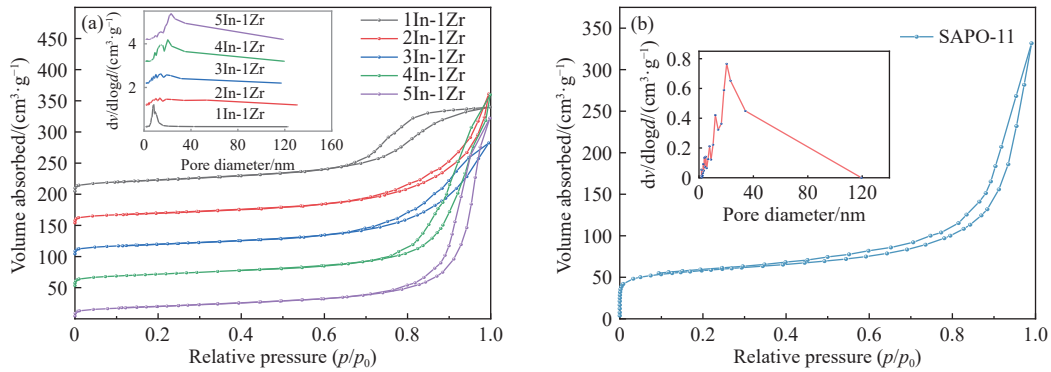


Fig. 3 N₂ adsorption-desorption isotherms and pore size distribution of In_xZr_bO_x (a) and SAPO-11(b)

Table 1 Specific surface area and pore structure parameters of In_xZr_bO_x and SAPO-11

Sample	SSA ^a /(m ² ·g ⁻¹)	S _{mi} ^b /(m ² ·g ⁻¹)	SA _e ^b /(m ² ·g ⁻¹)	v _{tp} ^c /(cm ³ ·g ⁻¹)	v _{mi} ^b /(cm ³ ·g ⁻¹)	v _{me} ^d /(cm ³ ·g ⁻¹)	Average pore size ^a /nm
1In-1Zr	82.5	1.5	81.0	0.215	0.0004	0.214	10.404
2In-1Zr	70.9	1.8	69.1	0.296	0.0006	0.296	16.709
3In-1Zr	70.6	1.2	69.5	0.274	0.0003	0.273	15.487
4In-1Zr	76.7	4.7	72.0	0.427	0.0021	0.425	22.299
5In-1Zr	70.1	3.5	66.6	0.473	0.0016	0.472	27.016
SAPO-11	189.1	103.7	85.4	0.512	0.0528	0.459	10.825

^a: SSA and average pore size obtained via the Brunauer-Emmett-Teller (BET) method; ^b: S_{mi}, SA_e and v_{mi} obtained via the t-plot method; ^c: Single point desorption v_{tp} of pores at $p/p_0 = 0.99$; ^d: v_{me} obtained via the BJH method.

2.1.2 H₂-TPR analysis

As shown in Figure 4, H₂-TPR characterization was conducted on In_aZr_bO_x with different In/Zr ratios to investigate its reduction performance. As expected, the pure In₂O₃ catalyst exhibits a lower reduction peak temperature in the H₂-TPR curve, indicating that In₂O₃ is more readily reduced. In contrast, ZrO₂ shows no reduction under the TPR conditions, suggesting it would also remain stable at the reaction temperatures employed in this study. Overall, as the In/Zr ratio increases, the reduction peaks shift progressively to higher temperatures. This is likely attributed to the introduction of ZrO₂, which modifies the electronic environment of In₂O₃, strengthens the interaction between the two oxides, and ultimately leads to an increased reduction temperature. This phenomenon suggests that ZrO₂ can effectively suppress the excessive reduction of In₂O₃, improving the structural stability of the catalyst and preventing the loss of active sites due to over-reduction of In₂O₃ under high-temperature conditions^[25,31–32]. However, when the In/Zr ratio exceeds 4, the suppressive effect of ZrO₂ on the reducibility of In₂O₃ gradually weakens. This trend implies that an optimal level of Zr doping is crucial to balance high reducibility with enhanced stability^[13,33]. Meanwhile, the reduction peak area also gradually increases, corresponding to a greater number of active sites exposed per unit mass. From the perspective of particle structure, smaller particles with higher dispersion tend to be more easily reduced, which is consistent with the increased specific surface area and reduced reduction temperature observed in the In/Zr ratio = 1 sample. It should be noted that ZrO₂ itself is difficult to be reduced, and its introduction not only enhances the overall structural stability but also, through strong interactions with In₂O₃, suppresses the excessive reduction of In₂O₃ to some extent. This may help preserve a high density of oxygen vacancies and stable active sites, both of which are crucial for an effective CO₂ hydrogenation process.

2.1.3 CO₂-TPD and NH₃-TPD analysis

CO₂-TPD analysis was performed to assess the CO₂ adsorption capacity, which is a critical factor influencing the catalytic activity in the formation of oxygenates. The results are presented in Figure 5. The CO₂-TPD curves display two prominent desorption peaks: a low-temperature peak around 100 °C and a high-temperature peak around 540 °C^[34–36]. Notably, as the In/Zr ratio decreases from 5:1 to 2:1, the CO₂ desorption peaks area gradually increases, suggesting an improved CO₂ adsorption capacity. This trend suggests that the introduction of ZrO₂ into In₂O₃ facilitates electronic transfer, leading to the generation of InZrO_x species and additional oxygen vacancies. The increase in oxygen vacancies can significantly enhance CO₂ adsorption performance^[32,37–39]. Interestingly, when the In/Zr ratio is 4, a distinct desorption peak appears in the range of 300–

350 °C, indicating that this catalyst exhibits a higher CO₂ adsorption capacity in the medium-temperature range relative to the other samples. This enhanced adsorption performance is likely due to a higher density of oxygen vacancies, and this hypothesis is strongly supported by XPS analysis of oxygen vacancy concentration.

NH₃-TPD characterizations of InZrO_x and SAPO-11 composite catalysts with different In/Zr ratios were performed and shown in Figure 6. All catalysts exhibit two prominent desorption peaks: a low-temperature peak around 150 °C and a high-temperature peak around 450 °C, corresponding to the weak and strong acid sites, respectively. The weak acid sites primarily originate from the weak Brønsted acid sites on SAPO-11 molecular sieve, while the partially reduced sites (such as In³⁺ and Zr⁴⁺) on the In-Zr metal oxide surface may also contribute to these sites. The strong acid sites are likely attributed to the Lewis acid sites introduced by the In-Zr metal oxides, along with the inherent Brønsted acid sites within the SAPO-11 framework^[5]. Notably, as the In/Zr ratio increases, the positions of both desorption peaks gradually shift towards higher temperatures. This phenomenon may be related to the higher In content, which introduces more low-strength Lewis acid sites, while the involvement of ZrO₂ enhances the binding strength between the Brønsted acid sites and NH₃ molecules. When the In/Zr ratio exceeds 3, the peaks gradually decrease^[5].

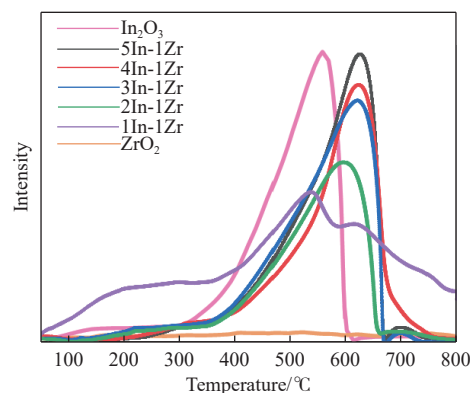


Fig. 4 H₂-TPR profiles of In_aZr_bO_x catalysts

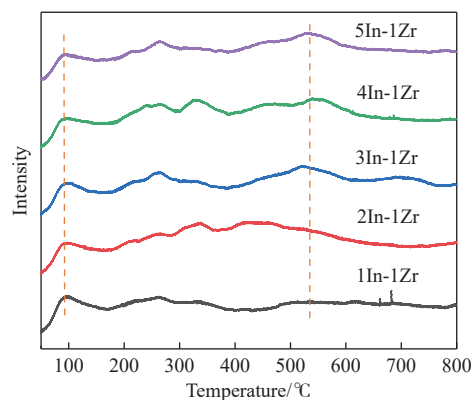


Fig. 5 CO₂-TPD profiles of In_aZr_bO_x catalysts

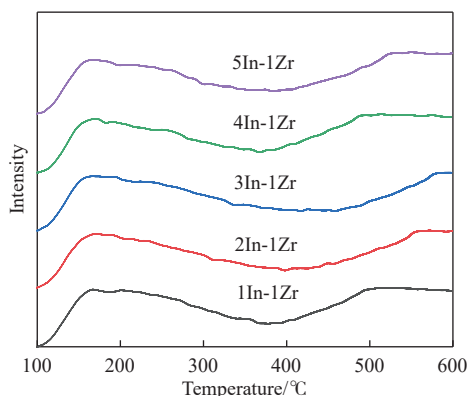


Fig. 6 NH₃-TPD profiles of In_aZr_bO_x catalysts

Additionally, when the In/Zr ratio exceeds 3, the areas of the desorption peaks also increase with the ratio, indicating that both the catalyst's adsorption capacity and reactant activation efficiency are improved. Although higher acid density helps enhance catalytic activity, excessive acidity may lead to undesired side reactions and even catalyst deactivation^[23]. Therefore, the distribution of acid sites and their relative strength must be rationally optimized to achieve a balance between high catalytic performance and the avoidance of detrimental side effects.

2.1.4 SEM and TEM analysis

Figure 7 presents the SEM and TEM images of the In₂Zr₁O_x and SAPO-11 samples, the In₂O₃-ZrO₂ sample exhibits a densely packed particulate morphology, in which the particles are closely interconnected, with an average particle diameter of approximately 20 nm, and the overall structure is composed of irregularly stacked nanoparticles (Figures 7(a) and (b)). In contrast, SAPO-11 displays a spherical morphology with particle sizes of about 3 μm. At a resolution of 2 μm, the surface morphology is clearly revealed as compact, plate-like structures.

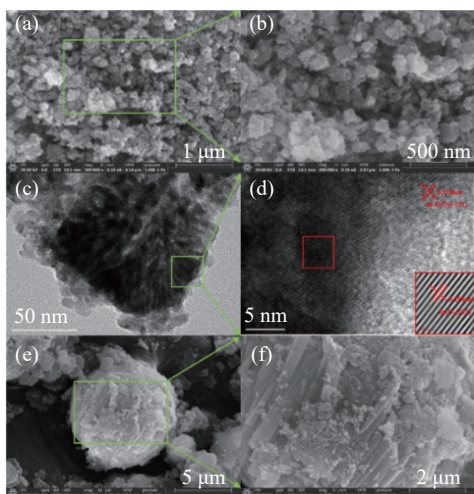


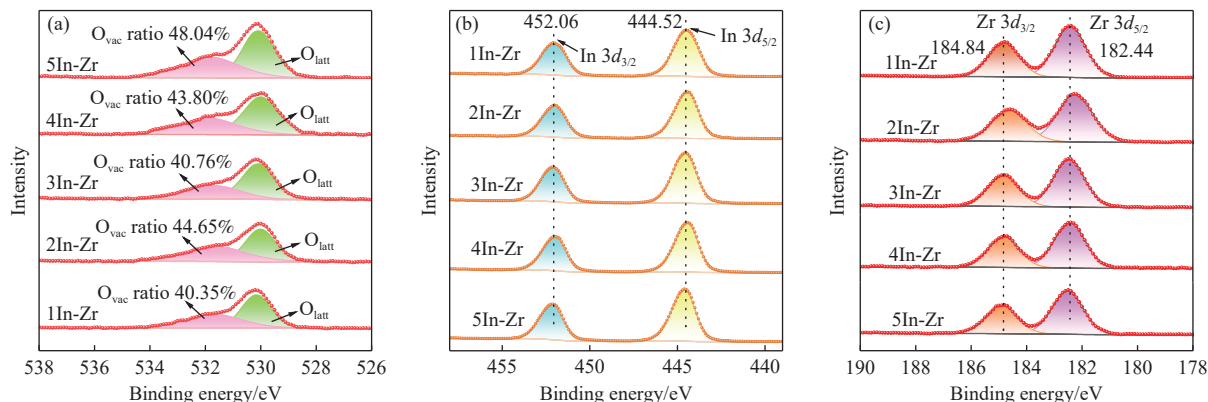
Fig. 7 SEM ((a) & (b)) and TEM ((c) & (d)) images of In₂Zr₁O_x catalyst and SEM((e) & (f)) images of SAPO-11

To gain further insight into the microstructural features, the In₂O₃-ZrO₂ sample was characterized by TEM. Low-magnification TEM images reveal a clustered aggregate morphology, while at a higher resolution of 10 nm, clear lattice fringes corresponding to the cubic-phase In₂O₃(222) crystal planes and the monoclinic *m*-ZrO₂(-111) crystal planes can be distinctly observed. These observations are consistent with the XRD data (Figure 3), confirming the presence of In₂O₃ and monoclinic *m*-ZrO₂ phases in the sample.

In addition, TEM images reveal a uniform particle size distribution and a well-developed porous structure, further confirming the previous N₂ adsorption-desorption results.

2.1.5 XPS analysis

Since the oxygen vacancies on the In_aZr_bO_x surface act as active sites for CO₂ activation, increasing the surface oxygen vacancy content by tuning the oxide's electronic structure is crucial for boosting its catalytic activity^[40]. As shown in Figure 8, valuable information regarding the electronic structure and elemental makeup of In_aZr_bO_x is provided by the XPS analysis. The O 1s spectrum (Figure 8 (a)) reveals peaks for lattice oxygen (O_{latt}) and oxygen vacancies (O_{vac}), which have distinct binding energies^[41–42]. Figure 8(a) shows that as the In/Zr molar ratio increases, the proportion of oxygen vacancies increases. This may result from the creation of a partial solid solution, in which In³⁺ ions substitute Zr⁴⁺ ions in the ZrO₂ lattice. This substitution enhances the dispersion of In within the lattice and fosters the development of more stable oxygen vacancies. The oxygen vacancy concentration for the In/Zr ratio = 5 sample is higher than that for the In/Zr ratio = 2 sample (In/Zr ratio = 5 (48.04%), In/Zr ratio = 2 (44.65%)). However, a comprehensive performance analysis shows that both excessive and insufficient oxygen vacancies hinder methanol production. DFT calculations by Cao et al.^[32] demonstrated that an insufficient number of surface oxygen vacancies leads to overly strong oxygen-catalyst bonding, raising the energy barrier for HCOO* hydrogenation. Conversely, an excessive number of vacancies weakens the surface binding with oxygen species, which is also detrimental to CO₂ activation and hydrogenation. Therefore, an appropriate and balanced oxygen vacancy concentration is crucial for efficient methanol formation on In₂O₃/ZrO₂ catalysts. The In 3d XPS spectrum in Figure 8(b) and the Zr 3d XPS spectrum in Figure 8(c) show that as the In/Zr ratio decreases, In shifts toward higher binding energy, while Zr shifts toward lower binding energy. This transition results from the strong electronic interaction between In and Zr within the InZrO_x framework. Within the partial solid solution, the In–Zr bonding induces a migration of outermost electrons from In to Zr, thereby increasing the electron cloud density on Zr and reducing its electron binding energy. These findings strongly suggest that part of the Zr in the In₂O₃-ZrO₂ matrix may be replaced by In, forming an InZrO_x solid solution.


 Fig. 8 O 1s (a), In 3d (b) and Zr 3d (c) XPS spectra of In_xZr_bO_x samples

2.2 Catalytic activity

2.2.1 Effect of catalyst type

The catalytic performances of In₂O₃, ZrO₂, In₂O₃-ZrO₂, In₂O₃/SAPO-11, ZrO₂/SAPO-11 and In₂O₃-ZrO₂/SAPO-11 were compiled in Figure 9. The results show that, relative to single metal oxide components and other OX/SAPO-11 catalysts, In₂O₃-ZrO₂/SAPO-11 exhibited enhanced CO_x conversion and C₅₊ selectivity, while simultaneously and notably suppressed the formation of CO and CH₄. The separate In₂O₃-ZrO₂ catalyst achieves a CO_x conversion of only 21.3%, with methanol as the primary product. In contrast, the catalytic performance of In₂O₃-ZrO₂/SAPO-11 is significantly improved. This improvement stems from a synergistic effect that facilitates the conversion of mixed gas into methanol, followed by its highly selective transformation to C₅₊ hydrocarbons *via* the methanol-to-gasoline (MTG) reaction. Furthermore, the synergistic interaction between the active sites of In₂O₃-ZrO₂ and SAPO-11 significantly affects the dissociative adsorption behavior of H₂ on the In₂O₃-ZrO₂ surface. ZrO₂ enhances the CO₂ adsorption capacity, while In₂O₃ sites promote H₂ dissociation under close contact with ZrO₂^[43], significantly enhancing CO₂ conversion. These results align well with the results of the H₂-TPR (Figure 4) and CO₂-TPD (Figure 5) characterization. Under the same reaction conditions, the overall catalytic performance of In₂O₃-ZrO₂/SAPO-11 outperforms all other OX/SAPO-11 catalysts, with a CO_x conversion of 24% and C₅₊ selectivity of 68%, while ZrO₂/SAPO-11 shows the poorest performance with CO_x conversion of 23.8% and C₅₊ selectivity of only 52%. Compared to In₂O₃/SAPO-11 and ZrO₂/SAPO-11, In₂O₃-ZrO₂/SAPO-11 shows higher selectivity for C₅₊ products. This improvement is primarily due to the introduction of ZrO₂, which enhances the stability of the In₂O₃ component and improves the utilization efficiency of H₂ and CO₂ at its active sites. Additionally, the shape-selective control

exerted by the SAPO-11 pore structure results in a proportion of *iso*-alkanes of 32.6% and an iso-to-normal ratio of 12.3 (Table 2 and Figure 10), significantly enhancing the quality and combustion performance of the gasoline fraction.

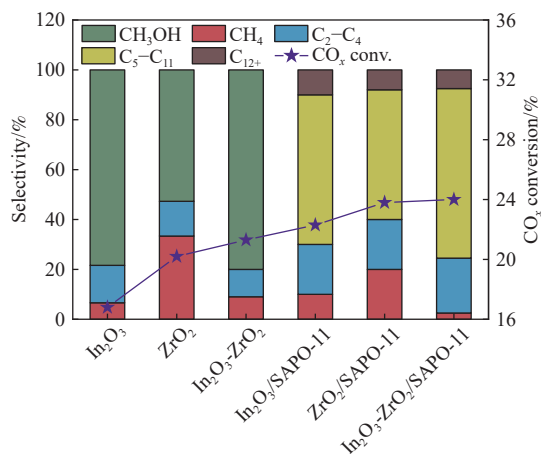
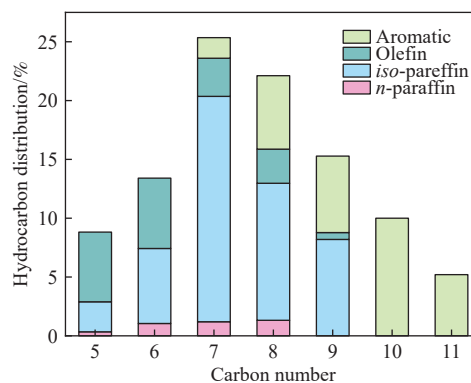

 Fig. 9 Effect of catalyst type (Reaction condition of 380 °C, 3 MPa, H₂/CO_x = 3 and GHSV = 2400 mL/(min·g))

 Fig. 10 Distribution of CO_x hydrogenation products on the In₂Zr₁O_x/SAPO-11 composite catalyst

 Table 2 Distribution of hydrocarbon substances in the In₂Zr₁O_x/SAPO-11 composite catalyst

Sample	CH ₄ /%	C ₂ -C ₄ /%	C ₅ -C ₁₁ (68%)				C ₁₂₊ /%	C _{iso} /C _n
			<i>iso</i> -paraffins	<i>n</i> -paraffins	olefins	aromatics		
In ₂ Zr ₁ O _x /SAPO-11	2.5	22.0	32.6	2.7	12.6	20.0	7.5	12.3

Based on its optimal performance among the synthesized OX/SAPO-11 catalysts, In₂O₃-ZrO₂/SAPO-11 was therefore selected for subsequent study.

2.2.2 Effect of In/Zr ratio

Furthermore, the catalytic performance is significantly affected by the ZrO₂ content in the oxide. The effect of different In/Zr molar ratios on CO_x conversion and product selectivity is shown in Figure 11. It can be observed that as the In/Zr ratio increases, the CO_x conversion gradually rises. When the In/Zr ratio is 2 or 3, the CO_x hydrogenation conversion is increased from 21% for the In/Zr ratio = 1 catalyst to 24% and 23.5%, respectively. This increase in conversion results from the strong electronic interaction between the two oxides, which generates additional oxygen vacancies that enhance the CO₂ adsorption capacity, thus improving the CO_x conversion. It should be noted that compared to the composite metal oxides, the parent catalyst generates slightly more oxygenated intermediates during hydrogenation. This suggests that the weak acidic sites (Lewis acid sites) provided by ZrO₂ in the composite metal oxide can promote and activate the “dual-cycle” mechanism, thereby accelerating the conversion of oxygenated intermediates into lower-carbon hydrocarbons^[5]. Additionally, as the In/Zr ratio increases, the proportion of C₅₊ hydrocarbons also rises. This further indicates that the introduction of ZrO₂ provides more accessible active sites than pure In₂O₃. However, when the Zr/In ratio becomes overly high, the CH₄ content significantly increases, which is primarily due to the fact that under a hydrogen atmosphere, the generated oxygenates are more likely to undergo dissociation reactions, leading to methane formation.

2.2.3 Effect of CO/CO_x ratio

To investigate how CO concentration influences CO₂ hydrogenation performance, a comparative analysis was performed at different CO/CO_x ratios. As shown in Figure 12, the CO₂/CO_x ratios in the feed significantly affect the product distribution during the catalytic conversion process on the In₂O₃-ZrO₂ catalyst. When pure CO or CO₂ was used as feed, the methane yield was 5.6% and 3.9%, respectively. However, when the CO to CO₂ concentration ratio was 1:1, the methane yield decreased to 2.5%, and the selectivity for gasoline hydrocarbons reached its maximum. This phenomenon can be attributed to the dual regulatory effect of CO co-feeding on the reaction mechanism. The addition of CO reduces the driving force for the CO₂ → CO reaction, thus partially inhibiting the RWGS reaction and preventing hydrogen consumption in ineffective side reactions^[44]. Additionally, CO molecules can also directly participate in WGS and the formation of methanol intermediates, with both processes occurring synergistically at the oxide-molecular sieve interface, facilitating the subsequent C-C coupling reaction^[18].

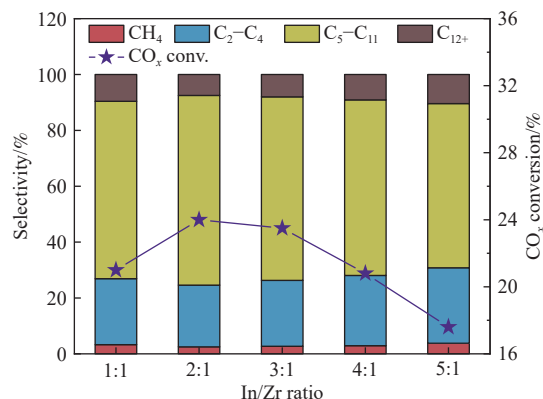


Fig. 11 Effect of In/Zr ratio (Reaction condition of 380 °C, 3 MPa, H₂/CO_x = 3 and GHSV = 2400 mL/(min·g))

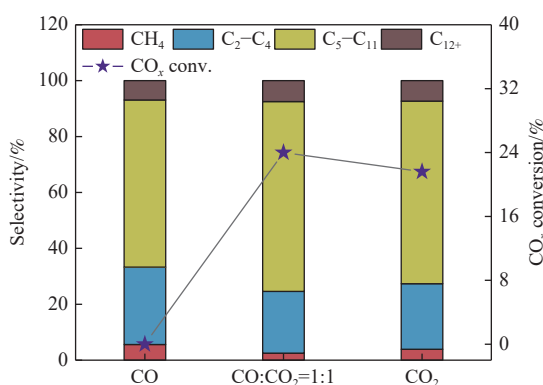


Fig. 12 Effect of CO/CO_x ratio (Reaction condition of 380 °C, 3 MPa and GHSV = 2400 mL/(min·g))

When pure CO is fed, In₂O₃ is easily over-reduced to a metallic indium phase at high temperatures. Despite its high reducibility, this metallic phase fails to promote the hydrogenation of CO₂ to generate methanol and other oxygenates, resulting in a marked decline in the reaction rate^[28]. Excessive CO₂ content can cause the catalyst surface to be oxidized, thereby reducing the activity at the metal-oxide interface and also exacerbating the occurrence of the RWGS reaction^[42]. These results further confirm that the appropriate introduction of CO can partially suppress the RWGS reaction and thermodynamically favor methanol production. Therefore, a CO/CO_x ratio of 0.5 was selected as optimal for the initial stage over the In₂O₃-ZrO₂. This ratio strikes the optimal balance between CO_x conversion and gasoline hydrocarbon selectivity. Mechanistically, this result reflects the complementary role of CO and CO₂ within the interfacial synergistic catalysis.

2.2.4 Effect of temperature

The time-dependent trends of CO_x conversion and product selectivity at five different reaction temperatures are shown in Figure 13. The results indicate that within the temperature range of 375 to 400 °C, as the temperature increases, the CO_x conversion gradually rises, and the selectivity for C₅₊ products also improves.

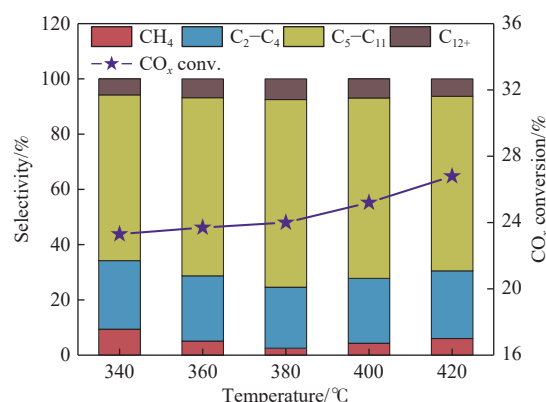


Fig. 13 Effect of temperature (Reaction condition of H₂/CO_x = 3, 3.0 MPa and GHSV = 2400 mL/(min·g))

This phenomenon results from the generation of numerous oxygen vacancies on the In₂O₃-ZrO₂ surface under the H₂ and CO_x atmosphere, with the conversion of methanol/dimethyl ether in the second stage also promoted by the increase in temperature. However, when the temperature is further increased, the selectivity for C₅+ starts to decline. This is because high temperatures favor the hydrogenation of CO₂ to form CO, and under a CO and H₂ mixed atmosphere, In₂O₃ is more easily reduced to metallic indium. The metallic indium phase tends to promote the RWGS reaction, resulting in an increase in the side product CO rather than methanol^[10]. Additionally, the decrease in C₅+ selectivity could be attributed to either a higher activation energy of the chain termination reaction relative to the chain growth reaction, or to enhanced thermal cracking of heavier hydrocarbons under high-temperature conditions^[45].

Based on the comprehensive comparative analysis, 380 °C was selected as the optimal reaction temperature for the In₂O₃-ZrO₂/SAPO-11 catalyst in the CO_x hydrogenation-to-gasoline hydrocarbon reaction.

2.2.5 Effect of pressure

The variation trends of CO_x conversion and product selectivity at different reaction pressures (1 to 5 MPa) are shown in Figure 14. With an increase from 1 to 3 MPa, the CO_x conversion increases by 3.1%, and the selectivity for C₅+ products increases by 9.9%. This result indicates that moderately increasing the pressure enhances the hydrogen activation and hydrogenation ability on the metal oxide surface. This promotes the conversion of syngas to oxygenates (e.g., methanol) and subsequently promotes the generation of hydrocarbon products, especially gasoline hydrocarbons. The increase in CO_x conversion is primarily attributed to the enhanced adsorption and activation of CO molecules on the In₂O₃-ZrO₂ surface. High pressure can increase the surface coverage of reactants, thereby accelerating the formation and conversion of key intermediates (such as formyl and methoxy groups), driving the subsequent pathways for olefin and gasoline

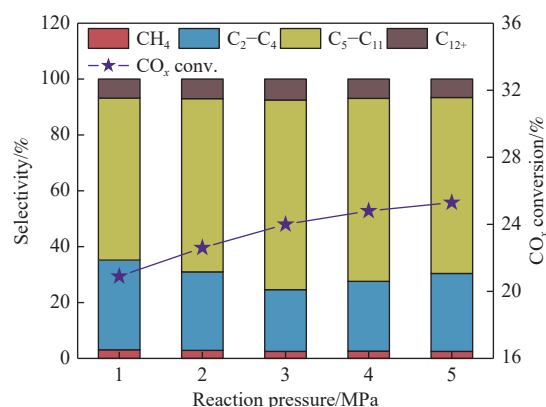


Fig. 14 Effect of pressure (Reaction condition of H₂/CO_x = 3, 380 °C and GHSV = 2400 mL/(min·g))

hydrocarbon formation^[46].

However, when the reaction pressure is further increased to above 4 MPa, the proportion of *iso*-alkanes in C₅+ starts to decrease. This trend may be attributed to two factors: on one hand, at high pressure conditions, the steric hindrance effect of C-C coupling and chain growth reactions increases, inhibiting the growth of longer chains^[47], secondly, the increased hydrogen partial pressure cause the C₁₂+ hydrocarbons to undergo hydrogen cracking, resulting in the production of more C₂-C₄ light hydrocarbons. The combination of these two effects results in a relative reduction in heavy hydrocarbons and a higher proportion of light hydrocarbons. Overall, moderate reaction pressure can achieve a better balance between CO_x conversion and C₅+ product selectivity, and thus, 3 MPa was selected as the optimal pressure condition in this study.

2.2.6 Catalysis stability tests

The stability of the In₂O₃-ZrO₂/SAPO-11 catalyst for the synthesis of C₅-C₁₁ gasoline hydrocarbons is shown in Figure 15. After 100 h of continuous CO_x hydrogenation reactions, the catalyst was still able to maintain around 24% CO_x conversion and approximately 63% gasoline hydrocarbon selectivity, demonstrating excellent activity and stability. During the first 40 h of the reaction, due to the strong CO₂ adsorption capability of the metal oxides, both the CO_x conversion and gasoline hydrocarbon selectivity showed an increasing trend. As the reaction progressed, the catalyst surface was gradually covered by carbon deposition, and the conversion and selectivity slowly declined, eventually reaching a “pseudo-stable” state. The excellent stability of In₂O₃-ZrO₂/SAPO-11 is primarily attributed to the synergistic effect: the unique non-crossing elliptical 10-membered ring pore structure of SAPO-11, along with its strong acidic sites, not only effectively increases the diffusion rate and shortens the residence time of molecules in the pores but also rapidly converts intermediates like methanol into hydrocarbon products.

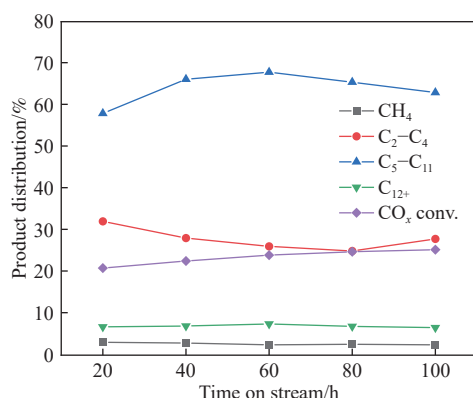


Fig. 15 Stability test plot of In₂O₃/SAPO-11 catalyst (Reaction condition of H₂/CO_x = 3, 380 °C, 3 MPa and GHSV = 2400 mL/(min·g))

2.3 Reaction mechanism of the bifunctional catalyst

The successful development and application of novel In₂O₃-based bifunctional catalyst largely depend on a deep understanding of its active sites and potential reaction mechanisms. This need has become a central consensus in the field of CO₂ hydrogenation to hydrocarbons, particularly for the methanol-mediated pathway using In₂O₃-zeolite bifunctional systems^[43,48–51]. Numerous studies have shown that the oxygen vacancies on the surface of In₂O₃ play a central role in CH₃OH synthesis^[37,52–55]. Sun et al.^[54] systematically studied the adsorption and activation processes of CO₂ on the In₂O₃ surface using DFT calculations. The results confirmed that In₂O₃ effectively activates CO₂ molecules while suppresses the RWGS reaction. In the catalytic process, the methanol generation supplements the surface oxygen vacancies, while H₂ facilitates their regeneration. This interaction establishes a dynamic cycle between the perfect surface and the defective surface state, thereby sustaining continuous methanol formation^[56]. Additionally, the introduction of ZrO₂ components significantly enhances the adsorption capacity of key intermediates, promotes the activation of adsorbed CO₂* and stabilizes intermediates such as HCOO*, H₂COO*, and H₃CO*^[57–61]. Methanol subsequently migrates to the acidic sites of the molecular sieve, where it is catalytically transformed into olefins^[62]. These olefins undergo a series of reactions including oligomerization, cyclization and aromatization, ultimately leading to aromatic hydrocarbons. On the molecular sieve, methanol conversion follows the “dual-cycle mechanism,” which includes competing olefin and aromatic cycles. In the MTG reaction, the chain growth of olefins is mainly catalyzed by weak acids, while aromatization requires strong acids. SAPO-11, with its abundant moderate strength acid sites and minimal strong acid sites, generates only a small amount of aromatic hydrocarbons during methanol conversion, with the olefin pathway being the main reaction route^[63].

Based on the findings above, the reaction mechanism for the In₂O₃-ZrO₂/SAPO-11 bifunctional catalyst is illustrated

in Figure 16. CO₂ first undergoes hydrogenation at the oxygen vacancies on the In₂O₃-ZrO₂ surface, generating CH₃O species. These intermediates then migrate to the SAPO-11 molecular sieve and are further converted into gasoline hydrocarbons. This process includes both olefin and aromatic cycles^[30]. Notably, introducing co-fed CO into the CO₂/H₂ acts dually as an oxygen vacancy generator and a promotor for CO₂ hydrogenation. The mechanism involves two key aspects: increasing the oxygen vacancy density without losing surface area, and suppressing the RWGS reaction by reaching thermodynamic equilibrium, thereby favoring the hydrogenation of CO₂ to the critical methoxy species (H₃CO*), for methanol formation^[64–65]. Therefore, the In₂O₃-ZrO₂/SAPO-11 catalytic system exhibits significantly enhanced activity for gasoline hydrocarbon production.

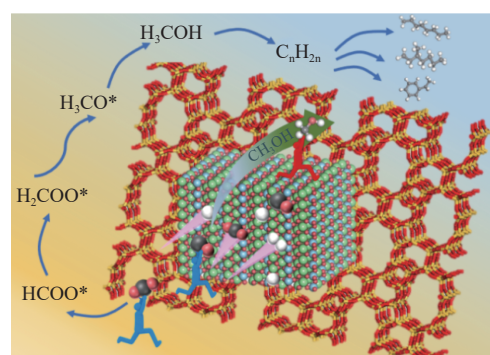


Fig. 16 Possible reaction mechanisms for CO_x conversion over In₂O₃-ZrO₂/SAPO-11 bifunctional catalysts

3 Conclusion

Herein, this study primarily investigated the enhancement of methanol production from CO₂-rich syngas hydrogenation by doping In₂O₃ with varying amounts of Zr. By strategically leveraging the synergistic effect with SAPO-11, we achieved a product distribution that significantly exceeds the maximum gasoline hydrocarbon selectivity predicted by the ASF model. Detailed characterizations indicate that In₂O₃-ZrO₂/SAPO-11 functions as a bifunctional catalyst: In₂O₃-ZrO₂ is responsible for CO_x hydrogenation to produce CH₃OH, while SAPO-11 (particularly its acidic sites) facilitates the subsequent conversion of CH₃OH into gasoline hydrocarbons. The influence of reaction conditions (including catalyst type, In/Zr ratio, CO/CO_x ratio, temperature, and pressure) was conducted and the results show that at 380 °C, 3 MPa and 2400 mL/(min·g), the In₂O₃-ZrO₂/SAPO-11 tandem catalyst with an In/Zr ratio of 2 achieved a CO_x conversion rate of 24% and C₅-C₁₁ selectivity of 68%. After 100 h of stability testing, with the catalyst remained a CO_x conversion of 24% and a C₅-C₁₁ selectivity of 65%, demonstrating stable performance. Additionally, the proportion of *iso*-alkanes in the gasoline fraction reached 32.6%, and the *iso*-to-normal ratio was as

high as 12.3, indicating that the catalyst significantly promoted alkane isomerization due to the shape-selective effect exerted by SAPO-11 pores, thereby improving the octane number and combustion performance of the gasoline and thus demonstrating outstanding application potential.

Declaration of Competing Interest

The authors declare no conflict of interest.

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In₂O₃-ZrO₂/SAPO-11 催化富含 CO₂ 合成气转化高品质汽油烃的研究

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摘 要: 利用二氧化碳制备汽油烃, 是应对交通运输业深度脱碳的可持续途径。然而, 传统的费托合成(FTS)工艺产物分布宽泛, 使汽油烃(C₅-C₁₁)的最高选择性受限于 45%。本研究采用由 In₂O₃/ZrO₂ 金属氧化物与 SAPO-11 分子筛构成的双功能催化剂, 实现 CO₂/CO 混合物直接转化为 C₅-C₁₁ 汽油烃。通过共沉淀法制备不同 In/Zr 物质的量比的催化剂, 并引入 CO_x(CO/CO₂)共进料策略(CO/CO_x=0.5), 显著抑制了副产物 CO 的生成, 汽油烃选择性突破了 Anderson-Schulz-Flory (ASF)分布的理论限制。在相同的反应参数下, 与 In₂O₃/SAPO-11 和 ZrO₂/SAPO-11 催化剂相比, In₂Zr₁O_x/SAPO-11 催化剂的 CO_x 转化率分别提高了 1.7% 和 0.2%, C₅-C₁₁ 选择性分别提高了 8.0% 和 16.0%。此外, In₂Zr₁O_x/SAPO-11 催化剂在 380 °C、3 MPa、空速(GHSV)2400 mL/(min·g) 条件下, 实现了 24% 的 CO_x 单程转化率和 68% 的 C₅-C₁₁ 选择性, 其中, 异构烷烃占总组分的 32.6%, 异构烷烃/正构烷烃比为 12.3。经过 150 h 稳定性测试, CO_x 单程转化率仍保持在 23%, C₅-C₁₁ 选择性维持在 65% 左右, 显示出优异的活性与工业化应用潜力。

关键词: 富 CO₂ 合成气; 双功能催化剂; In₂O₃-ZrO₂/SAPO-11; 汽油烃

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