Enhancing Gasoline Production from CO_2 Hydrogenation through optimizing ZnO-ZrO_2 Catalysts in tandem with HZSM-5 zeolite

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Highlights

- Gasoline yield was boosted by tuning ZnO-ZrO_2 catalyst.
- High conversion was achieved, and it was stable for more than 16 h.
- Highly isoparaffinic gasoline was obtained, with predominant C_5 and C_6 hydrocarbons.

1. Introduction

The increasing levels of CO_2 emissions and the threat of global warming have motivated carbon dioxide capture and utilization (CCU) technologies into the spotlight of environmental solutions. Among the diverse array of CO_2 valorization processes, the catalytic conversion of CO_2 holds particular importance, with a special emphasis on the generation of hydrocarbons. The direct synthesis of hydrocarbons from CO_2/CO hydrogenation involves two distinct stages: firstly, the synthesis of oxygenates (methanol/DME) from CO_2 and/or CO; and secondly, the subsequent *in situ* conversion of these oxygenates into hydrocarbons. This process is carried out with OX/ZEO tandem catalysts, combining a metal oxide and a zeolite [1]. Integrating these catalysts into a single phase confers a significant advantage by shifting the equilibrium of the oxygenates synthesis and boosting the conversion of CO_2 and CO [2]. Among the metallic catalysts utilized (OX), some stand out, such as In_2O_3, In_2O_3-ZrO_2, and ZnO-ZrO_2 [3,4] However, these catalysts are not yet optimized and still require refinement. In the context of hydrocarbon synthesis within the gasoline range, the predominant zeolite is HZSM-5 (ZEO) [5].

In this context, this work focuses on the improvement of the process by optimizing the OX catalyst. A mixture of CO_2 and CO (CO_x) was fed and a tandem catalyst consisting of ZnO-ZrO_2 (OX) and a nano-sized HZSM-5 (ZEO) was employed. The ratio between Zn and Zr was adjusted for enhanced efficiency. The four catalysts with different Zn/(Zn+Zr) relation (0.07, 0.15, 0.3 and 0.45) were thoroughly characterized, and their performance in gasoline synthesis was analyzed. Furthermore, the quality of the obtained gasoline was studied to provide a comprehensive understanding of the overall process.

2. Methods

Four different ZnO-ZrO_2 catalysts with different Zn/(Zn+Zr) relations were prepared using a co-precipitation method, denoted as 7ZZ, 15ZZ, 30ZZ, and 45ZZ, corresponding to Zn/(Zn+Zr) ratios of 0.07, 0.15, 0.3, and 0.45, respectively. For the second stage, a nano-sized HZSM-5 with a SiO_2/Al_2O_3 molar ratio of 371 was used (nH371). Characterization included X-ray diffraction (XRD) for structure analysis, X-ray fluorescence (XRF) for composition, temperature-programmed desorption with ammonia (TPD-NH_3) for acidity assessment, and N_2 adsorption-desorption for physical property evaluation. Reaction conditions were set at 420 ºC, 50 bar, space time of 10 $g_{cat}\cdot h/mol_C$, H_2/CO_x ratio of 3 and CO_2/ CO_x ratio of 0.5.

3. Results and discussion

The results from XRD characterization indicate that the metallic catalyst is primarily composed of a mixed oxide of Zn and Zr. As the amount of Zn increases, additional ZnO begins to appear in the structure, alongside the mixed oxide [6]. Furthermore, all physical properties (BET surface area, pore volume, and particle diameter) increase with the Zn fraction, influencing catalytic performance. In

Figure 1a, a maximum in C_{5+} hydrocarbon yield (20%) is observed at a Zn/(Zn+Zr) ratio of 0.3, correlating with the optimal combination of the mixed structure and pure ZnO. Additionally, methane yield is negligible across all catalysts.

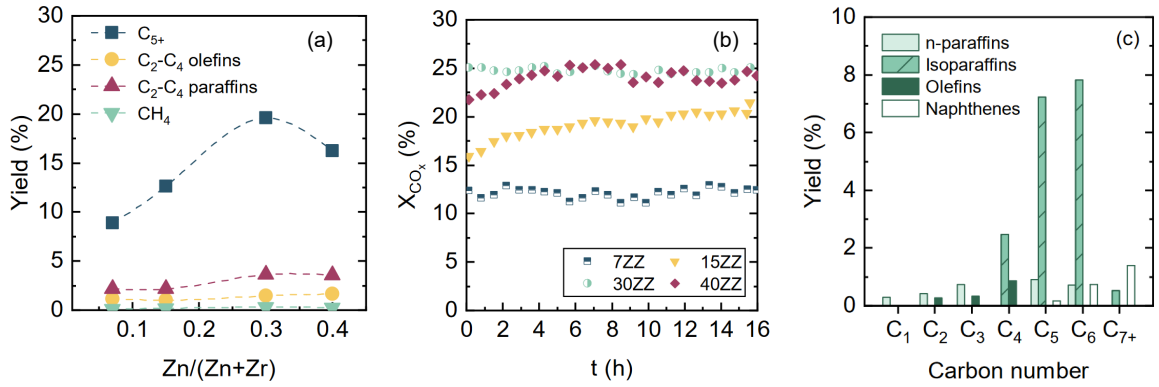

Figure 1. (a) Influence of the Zn/(Zn+Zr) ratio on the yield of the products, (b) stability of CO_x conversion with TOS, (c) product distribution by carbon number with the 30ZZ/nH371 catalyst.

Regarding stability, all catalysts exhibit sustained CO_x (CO_2+CO) conversion without apparent deactivation over 16 hours of TOS (Figure 1b). However, 15ZZ and 40ZZ display an initial activation period during the first 2 hours. Nevertheless, the optimal catalyst 30ZZ/nH371 demonstrates remarkable stability. Analyzing the product distribution by carbon number with the 30ZZ/nH371 catalyst (Figure 1c), it is notable that C_5-C_6 hydrocarbons, especially isoparaffins, are predominant. There is a negligible presence of linear paraffins, olefins, or aromatics, making this product highly suitable for blending into the gasoline pool.

4. Conclusions

The Zn/(Zn+Zr) ratio significantly influenced structural composition and catalytic performance, with the 30ZZ catalyst exhibiting superior stability and yielding a predominant distribution of C_5-C_6 hydrocarbons, particularly isoparaffins. Incorporating a nano-sized HZSM-5 zeolite further enhanced the desirable product profile. These findings highlight the importance of catalyst composition for optimal performance, showcasing promising implications for environmentally friendly hydrocarbon synthesis processes.

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Keywords
CO_2 valorization, Gasoline synthesis, ZnO-ZrO_2 catalyst, HZSM-5 zeolite