Bifunctional Core-interlayer-shell Catalyst of Cu-Fe_2O_3/3TP-MFI for Direct Conversion of CO_2 to BTX

3P Research Scheme –Top Tier Research

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Abstract

One promising CO_2 utilization pathway is its conversion into value-added aromatic hydrocarbons, particularly benzene, toluene, and xylene (BTX), which are conventionally produced through petroleum catalytic reforming. This study develops bifunctional Cu-modified iron oxide–zeolite catalysts for BTX production via CO_2 hydrogenation. Particularly, the effect of catalyst configuration, composition, and reaction conditions on the reaction pathway and performance are carefully investigated.

Keyword: CO_2 conversion, BTX, Fe-based, zeolite.

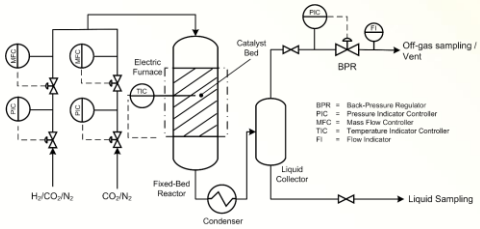
Introduction

Conversion of CO_2 into aromatic hydrocarbons, particularly benzene, toluene, and xylene (BTX), through direct hydrogenation using bifunctional Fe-zeolite catalysts has attracted considerable interest. This process involves the initial conversion of CO_2 into short-chain hydrocarbons through Fischer–Tropsch synthesis over Fe-based active sites, followed by the transformation of these intermediates into aromatic compounds over zeolite acid sites. Despite its potential, achieving high aromatic production remains challenging due to the complexity of the reaction pathways. In particular, excessive hydrocarbon chain growth over Fe sites and insufficient control of subsequent reactions over zeolite acid sites can disrupt the balance between the two catalytic functions. Several approaches have been investigated to improve catalytic performance. Metal promoters, including alkali and transition metals, have been introduced to facilitate CO_2 adsorption and activation, thereby increasing conversion.

In parallel, modifications to zeolite properties, such as morphological engineering, external surface modification, and the development of hybrid catalytic systems, have been explored to enhance light aromatic formation. Our previous work highlighted the importance of multi system of pore in zeolite architectures in promoting BTX production. Nevertheless, the influence of catalyst composition, reactor configuration, and operating conditions on product distribution, particularly C_6–C_8 aromatic formation, requires further investigation. Accordingly, this study examines the effects of catalyst configuration and reaction parameters on direct CO_2 hydrogenation, emphasizing the formation of C_6–C_8 light aromatics.

Research Method

The Cu-modified Fe-based catalyst was synthesized from nitrate salt precursors using a co-precipitation method, whereas the 3TP-MFI zeolite was prepared via a solvent-free synthesis route. The two catalyst components were subsequently arranged in two configurations, namely metal-on-top/zeolite-on-bottom (M–Z) and zeolite-on-top/metal-on-bottom (Z–M), as illustrated in Scheme 1.



Scheme 1. Reactor set-up for CO_2 to BTX

Both configurations were evaluated for CO_2 hydrogenation using the reactor setup shown in Scheme 1. The catalytic reactions were conducted using 2 g catalyst with ratio metal to zeolite 2:1, 1:1, and 1:2 at temperatures of 300–320 °C, a pressure of 3 MPa, and a gas hourly space velocity (GHSV) of 3000 h^{-1}.

Discussion & Result

Fig.1 summarizes the structural characteristics of the bifunctional catalyst. HZSM-5 exhibited characteristic MFI diffraction peaks at 2θ = 22–25°. The fresh CuFeOx showed only hematite reflections, with no detectable CuO peaks, suggesting high Cu dispersion. After CO reduction, Fe_5C_2 became the dominant phase, indicating iron oxide transformation. As illustrated in Fig.1c, Fe_2O_3 theoretically undergoes sequential reduction to Fe_3O_4, FeO, and metallic Fe before forming iron carbide upon interaction with CO. TEM revealed spherical CuFeOx nanoparticles with an average size of approximately 100 nm based on DLS analysis.

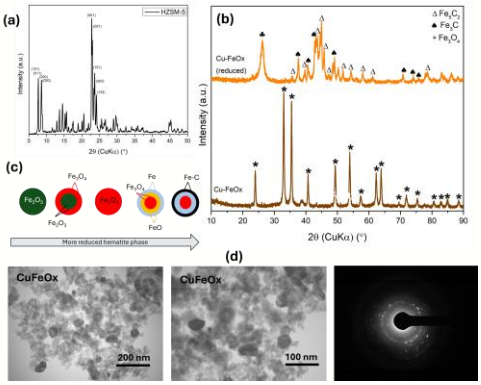


Fig. 1. XRD Pattern of (a) HZSM-5, (b) fresh and reduced Cu-FeOx (c) Phase transformation of Fe-based during reduction (d) TEM images of CuFeOx

The effect of catalyst configuration on CO_2 hydrogenation is presented in Fig. 2-d. The Z–M arrangement achieved approximately 20% higher CO_2 conversion than M–Z; however, it favored CH_4 formation over higher hydrocarbon production, resulting in lower C_5+ selectivity. Notably, aromatic compounds were exclusively detected in the M–Z configuration. This behavior highlights the importance of catalyst sequencing in the tandem reaction system. In the Z–M arrangement, the gas stream encounters the zeolite before the Fe-based catalyst, potentially limiting the conversion of Fe-derived hydrocarbon intermediates over zeolite acid sites.

Furthermore, excessive hydrogenation and limited availability of suitable olefinic intermediates may account for the predominant formation of lighter hydrocarbons rather than aromatics.

Catalyst composition significantly influenced CO_2 conversion and product distribution (Fig. 2e-g). Reducing the metal-to-zeolite ratio from 2:1 to 1:1 nearly doubled CO_2 conversion and lowered CO selectivity. Although the 2:1 ratio exhibited higher aromatic selectivity, the 1:1 composition achieved greater aromatic yield and BTX content, suggesting a more favorable balance between hydrocarbon formation and subsequent aromatization.

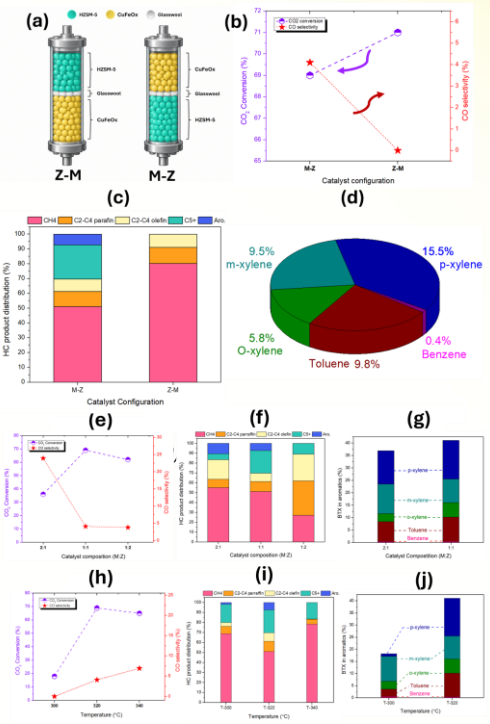


Fig. 2. (a) Catalyst configuration and its effect on catalytic performance (b,c,d). (e-g) the effect of catalyst composition and (h-j) temperature on the catalytic performances

Conversely, a higher zeolite proportion (1:2) suppressed aromatic formation, with C_2–C_4 paraffins becoming the dominant products. Reaction temperature also played a critical role (Fig. 2h-j). Increasing the temperature from 300 to 320 °C enhanced C_5+ and BTX formation while reducing CH_4 selectivity. However, further heating to 340 °C favored methane production and completely suppressed aromatic formation, indicating that excessive hydrogenation and limited hydrocarbon chain growth may hinder aromatization. Overall, 320 °C provided the most favorable conditions for BTX production, with para-xylene as the predominant product.

Conclusion

The catalyst arrangement and metal-to-zeolite ratio play essential roles in directing the reaction toward aromatic formation or light hydrocarbon production. In addition, reaction temperature strongly influences CO_2 conversion and the balance between competing reaction pathways.