Trace-level halogen blocks CO_2 emission in Fischer-Tropsch synthesis for olefins production

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Abstract

Sustainable production of fuels and olefins from syngas (carbon monoxide/hydrogen) through the Fischer-Tropsch synthesis process requires catalysts that deliver high selectivity, industrial productivity, and minimal CO_2 emissions. Current industrial iron catalysts form substantial CO_2 by-product that limits carbon efficiency. We report that introducing trace amounts (ppm-level) of halogen-containing compounds into the feed gas can suppress CO_2 formation using Fe-based catalysts and boost olefin selectivity over paraffins and olefin productivity. Co-feeding 20 ppm CH_3Br over an iron carbide catalyst decreased CO_2 selectivity to <1% and increased olefin selectivity to ~85% among all carbon-containing products. Surface-bound halogens modulated the catalyst surface structure and selectively inhibited pathways responsible for CO_2 generation and olefin hydrogenation. This strategy provides a simple, scalable, and broadly applicable route for carbon-efficient syngas conversion.

Developing efficient catalytic systems for direct α-olefin production from syngas (CO/H_2) via Fischer-Tropsch synthesis (FTS) is essential to address the growing global demand for olefins and is of importance for regions with limited petroleum resources (*1-3*). A key challenge is the design of low-cost, non-noble-metal catalysts that operate under moderate conditions that also minimize CO_2 emissions to ensure sustainable carbon utilization (*4-8*). Among current approaches, iron-based Fischer-Tropsch to olefins (FTO) catalysts (*9-11*) and oxide-zeolite (OX-ZEO) tandem systems (*2, 12, 13*) have emerged as leading candidates. However, iron-based catalysts often yield only moderate olefin selectivity, whereas OX-ZEO systems suffer from high CO_2 selectivity (32 to 45%) and limited olefin space-time yields (*12*). These limitations constrain overall carbon efficiency and hinder their large-scale industrial implementation. Thus, there is an urgent need for new catalytic systems that combine ultra-low CO_2 selectivity, high α-olefin space-time yields, and robust long-term stability.

Iron-based catalysts are particularly attractive for FTS because of their low cost, natural abundance, tunable product distribution, and high space-time yields of the products. Currently, more than two-thirds of the global FTS capacity (15.70 million tons/year) relies on iron catalysts. However, one drawback is their intrinsic promotion of the water-gas shift (WGS) and Boudouard reactions, resulting in excessive CO_2 formation that reduces carbon utilization efficiency (*14, 15*). The formation of CO_2 not only contributes to greenhouse gas emissions, but also depletes valuable carbon feedstocks.

Suppressing CO_2 formation in Fe-based FTS remains a major challenge. Previous strategies to inhibit the WGS reaction have focused on limiting water re-adsorption by shielding iron catalysts with hydrophobic silica coatings (*11*) or graphene layers (*8*), which effectively reduces CO_2 selectivity to below 13%. More recently, modified pure-phase iron carbide catalysts have achieved CO_2 selectivity as low as ~10% (*10, 16*), but only under conditions of low CO conversion and limited olefin productivity (~0.6 $g \cdot g_{cat}^{-1} \cdot h^{-1}$) (*10*). Therefore, the development of catalytic systems that concurrently minimize CO_2 formation and maximize α-olefin productivity under practical conditions remains a critical and unmet challenge.

We demonstrate that the introduction of parts-per-million (ppm) concentrations of

halomethanes into the syngas feed fundamentally transforms the catalytic behavior of Fe-based FTS systems. Specifically, co-feeding 20 ppm of CH_3Br effectively suppressed CO_2 formation, reducing CO_2 selectivity to < 1% and dramatically enhancing the olefin/paraffin (o/p) ratio from 1.3 (on unpromoted χ-Fe_5C_2) to as high as 13. Under optimized conditions, this strategy achieved an olefins space-time yield of 1.08 $g \cdot g_{cat}^{-1} \cdot h^{-1}$ with an unprecedented olefin selectivity of 85.2%, calculated relative to all carbon-containing products. Importantly, this simple and easily implementable halomethane-promotion strategy is compatible with a broad range of Fe-based FTS catalysts, including commercial formulations. Mechanistic insights from transient kinetic analyses and density functional theory (DFT) calculations reveal that surface-bound halogens modulate the properties of the catalyst and selectively inhibit key side reactions—specifically, the Boudouard reaction and WGS reaction—thereby suppressing CO_2 generation. We introduce a simple, yet robust and broadly applicable strategy to achieve sustainable and highly efficient olefin/liquid fuels production with exceptional carbon efficiency.

The impact of halogen over Fe-based FTS process

A series of iron carbide catalysts (ε-Fe_2C, θ-Fe_3C, h-Fe_7C_3, χ-Fe_5C_2) were synthesized following established protocols (*17, 18*). The unpromoted χ-Fe_5C_2 catalyst, one of the most active phases for FTS, exhibited a CO_2 selectivity of 31.4% at a CO conversion of 93.3% (Fig. 1A) (*19*). The primary products were C_{2+} olefins and paraffins with an o/p ratio of 1.3 under typical FTS conditions (H_2/CO = 2, 300 °C, 20 bar, 12,000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$). The native iron carbide catalysts favored CO_2 formation and exhibited similar selectivity toward olefins and paraffins.

We then introduced 20 ppm of halomethanes (CH_3X, X = F, Cl, Br, and I) into the syngas during FTS. CH_3F reduced CO_2 selectivity to 27.8%, accompanied by a slight increase in olefin content. A progressive trend was observed from CH_3F to CH_3Cl, CH_3Br, and CH_3I, with CO_2 selectivity continuously decreasing (Fig. 1A and Table S1). Notably, cofeeding CH_3Br or CH_3I suppressed CO_2 formation, yielding near-zero CO_2 selectivity (~1%). Concurrently, olefin selectivity was substantially enhanced, with the o/p ratio rising to ~7 in the case of CH_3Cl.

These results demonstrate that co-feeding trace amounts of halomethane effectively suppressed CO_2 production while promoting olefin selectivity in Fe-based FTS catalysts.

We next investigated the effect of CH_3Br concentration in the syngas on performance of FTS. Even a low co-feed concentration of 3 ppm CH_3Br markedly suppressed CO_2 formation, reducing its selectivity to 4.2%, decreasing CO conversion from 89.4% to 41.1%, and increasing the o/p ratio from 1.0 to 6.1 (Fig. 1B, Figs. S1, S2 and Table S2). Chain propagation remained unaffected, and the olefin selectivity was much higher than that obtained with the unmodified χ-Fe_5C_2 catalyst (81% *vs.* 23%; Fig. 1B, Figs. S3, S4 and Table S2). The decrease in CO conversion mainly came from the inhibition of the WGS reaction (Figs. S2), which accounted for >70% of the reduction in CO conversion, in case of 3 ppm CH_3Br co-feeding (Table S3). Although previous studies reported that co-feeding HCl or HBr can reduce CO_2 selectivity (*20*), they also observed a pronounced decline in FTS activity and limited CO_2 suppression (Fig. S5). In contrast, CH_3Br co-feeding in this work enables near-zero CO_2 formation with minimal loss in FTS activity (Fig. S5 and Table S3). As the concentration of co-fed CH_3Br increased, CO_2 selectivity progressively decreased—dropping to < 1% at 50 ppm—whereas olefin selectivity showed a slight increase (Fig. 1B).

This halogen modulation strategy was further extended to other iron carbide phases, including ε-Fe_2C, θ-Fe_3C and h-Fe_7C_3 (Fig. S6) (*17, 18*). In all cases, ppm concentrations of CH_3Br co-feeding suppressed CO_2 selectivity to < 5% and enhanced o/p ratios by factors of 3 to 4 (Fig. 1C), underscoring the broad applicability and robustness of the approach. Importantly, when we applied this strategy to a commercial iron catalyst (Commercial Fe-1), CO_2 selectivity could be suppressed to <1% (Fig. 1C).

To benchmark this halogen co-feeding method, we performed comparative analyses with state-of-the-art olefin synthesis catalysts, that is, Fe-, Co- based FTO catalysts and OX-ZEO systems (*8-11, 13, 16, 21*) (Fig. 1D, Figs. S7 to S11 and Tables S4 to S8). Notably, the χ-Fe_5C_2 catalyst with Br co-feeding (denoted χ-Fe_5C_2-Br) exhibited superior olefin yield (~48% of total carbon-containing products) while maintaining ultralow CO_2 selectivity (<3%). In contrast,

previously reported Fe-, Co- based, and OX-ZEO catalysts typically exhibited CO_2 selectivity exceeding 10% or had a relatively low olefin yield (Fig. S12 and S13).

Our strategy overcame the traditional trade-off between high olefin yield and low CO_2 selectivity, demonstrating unprecedented performance in the syngas to olefins reaction. A plot of ratio of olefin-to-CO_2 selectivity ($S_{olefins}/S_{CO2}$) versus olefin space-time yield ($STY_{olefins}$) shows the overall catalytic performance (Fig. 1E). Although OX-ZEO catalysts offer good olefin selectivity among hydrocarbons, their low $STY_{olefins}$ and high CO_2 emissions constrain their practical utility (*13*). Similarly, Ru- and Co-based systems suffer from low $STY_{olefins}$ under conventional FTS conditions (*21, 22*). In contrast, χ-Fe_5C_2-Br (Cl) catalysts delivered both high $STY_{olefins}$ and favorable olefin-to-CO_2 ratios. These results establish halogen co-feeding as an effective solution that enables high olefin space-time yield and high olefin yield with low CO_2 emissions in FTS. Importantly, if C_{5+} olefins are used as liquid fuels, this strategy could also benefit conventional Fe-based FTS by blocking CO_2 emissions in standard FTS processes.

We also tracked the fate of CH_3Br in the product stream. Of the 20 ppm CH_3Br introduced, approximately 70% (14.2 ppm) was recovered as unreacted CH_3Br in the outlet gas, with less than 6 ppm detected in the aqueous phase. Only trace amounts of Br (<1 ppm) were found in the oil-phase products, indicating negligible incorporation into the hydrocarbon products (Fig. S14 and Tables S9 to S11). Notably, although only a small amount of Br remained on the surface of the iron catalyst (Fig. S15 and Table S12), it exerted a pronounced effect on the overall catalytic performance.

Structure of χ-Fe_5C_2 Catalyst with CH_3Br co-feed

Co-feeding halomethanes induced a dramatic shift in the reaction behavior of Fe-based FTS and largely suppressed CO_2 emissions (Fig. S16). We hypothesized that halogen species played a critical role in modulating the structure of the working iron catalyst. To probe the structural consequences of halogen exposure, we characterized the χ-Fe_5C_2 catalyst after CH_3Br-co-feeding reaction (termed as χ-Fe_5C_2-Br-spent). The catalysts with or without co-

feeding halogen had similar morphologies and particle sizes (Fig. S17). X-ray diffraction (XRD) analysis revealed that, in addition to the dominant χ-Fe_5C_2 phase, χ-Fe_5C_2-Br-spent exhibited new diffraction peaks associated with Fe_3O_4. In contrast, the control sample (χ-Fe_5C_2-spent, without CH_3Br) retained dominantly the carbide phase (Fig. 2A).

These results were corroborated by Mössbauer spectroscopy, electron microscopy, and extended X-ray absorption fine structure (EXAFS) fitting (Figs. S18 to S24 and Tables S13 to S16). X-ray photoelectron spectroscopy (XPS) further confirmed the presence of surface FeO_x, with detectable iron oxide species on both spent samples (Fig. 2B). The presence of FeO_x is commonly associated with the WGS reaction and therefore the CO_2 production in Fe-based FTS (*23, 24*). Thus, the role of halogen was not to suppress the formation of iron oxides during the reaction.

Notably, elemental analysis, Br *K*-edge X-ray absorption near-edge structure (XANES), and Br 3*d* XPS revealed residual bromine species on χ-Fe_5C_2-Br-spent (Fig. 2C and Fig. S25). The Br *K*-edge XANES spectra exhibited fingerprinting features similar to those of iron bromide, indicating strong Fe-Br interactions like that in iron bromide. High-angle annular dark-field scanning transmission electron microscopy (HADDF-STEM) imaging coupled with energy-dispersive X-ray spectroscopy (EDS) mapping showed homogeneous Br distribution across both Fe_3O_4 and χ-Fe_5C_2 domains (Fig. 2D and Figs. S26 and S27), demonstrating homogeneous co-localization of Br and Fe species.

It remained uncertain whether Br was incorporated into the bulk lattice or was distributed on the surface. XRD showed no evidence of a new bromine-containing iron phase, suggesting a surface-bound Br species was more likely (Fig. 2A and Fig. S6). To confirm this hypothesis, we performed variable-energy XPS, which revealed substantial Br surface enrichment on the χ-Fe_5C_2-Br-spent catalyst (Fig. S28). High-sensitivity low-energy ion scattering spectroscopy (HS-LEIS) is a surface-sensitive technique (*25*). From the HS-LEIS depth profile of the catalyst, we observed that Br was primarily enriched on the surface of the catalyst (Fig. 2E). Collectively, these findings strongly suggest that surface-bound Br modulates the chemical environment of

active sites of Fe catalysts (both the iron carbide and oxide domains), suppressing CO_2 formation and enhancing olefin selectivity.

Inhibition mechanism of Br on CO_2 and paraffin formation

The reaction networks of FTS process depicted in Fig. 3A were used to understand the mechanistic origin of this inhibition effect. Aside from the main reactions leading to the production of olefin/paraffin, there are two major side reactions that produce CO_2: WGS (highlighted in red) over iron oxide and Boudouard reaction ($2CO \rightarrow C + CO_2$, highlighted in blue) over iron carbide *(14, 26)*. Although the primary products of Fe-based FTS were olefins, undesirable hydrogenation of olefins could lead to the production of less valuable paraffins ($C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$, highlighted in purple) and a low o/p ratio (*27*).

On χ-Fe_5C_2 catalysts, both the Boudouard reaction and WGS routes contributed appreciably across typical reaction temperatures, with WGS reaction becoming more pronounced at high conversions (Fig. S29) (*15, 24, 26, 28*). The dramatic suppression of CO_2 formation observed in halogen-modified FTS suggested a fundamental alteration of reaction pathways by the Br on the surface of iron catalysts (Fig. S30). To elucidate the underlying mechanism, we investigated both experimental reactivity by using transient kinetic analyses, surface-sensitive characterizations, as well as computational modeling of reaction energetics, focusing on these two dominant CO_2-producing reactions in Fe-based FTS.

Both iron oxides (e.g., Fe_3O_4 and FeO_x clusters) and iron carbides may contribute to the observed WGS activity (*23, 26, 29-31*). In this study, Fe_3O_4 was selected as the model WGS catalyst under our conditions, while acknowledging that iron carbides can also play a role depending on temperature and surface state. We found that CH_3Br co-feeding could suppress WGS activity by over two orders of magnitude (Fig. 3B and Fig. S31). Given the established WGS mechanism wherein H_2O dissociates to generate surface hydroxyl (OH*), which then reacts with CO to form CO_2 (Figs. S32 and S33), we first checked the adsorption and activation behavior of H_2O on catalysts. Water temperature-programmed desorption (H_2O-TPD) experiments revealed that both Fe_3O_4 and Br-pretreated Fe_3O_4 (termed Fe_3O_4-Br) showed

similar H_2O adsorption abilities (desorbed at ~120 °C). However, H_2 formation, an indicator for H_2O dissociation, was active on Fe_3O_4 but completely absent on Fe_3O_4-Br (Fig. 3C). In-situ XPS further confirmed this suppression effect, showing minimal OH* production on Fe_3O_4-Br compared to Fe_3O_4 (Fig. 3D; Figs. S34 and S35; Tables S17 and S18). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and transient kinetic analysis (TKA) experiments corroborated this inhibition effect (Figs. S33 and S36). These results established that Br disrupted the key step of H_2O dissociation in WGS reaction, then effectively blocking CO_2 generation through this pathway.

These experimental findings were supported by DFT calculations on Fe_3O_4 (111). In the absence of Br, H_2O can readily dissociate ($H_2O \rightarrow OH^* + H^*$) with the activation barrier (E_{a2}) of 0.73 eV. However, increasing Br coverage from $\theta_{Br} = 1/5$ to 1/3 raised this barrier to $E_{a2} >$ 1.2 eV. At a higher coverage of $\theta_{Br} = 2/5$, H_2O dissociation was completely inhibited (Fig. S37). These findings aligned with TPD and XPS results, suggesting that surface-bound Br passivates reactive Fe sites and disrupts WGS reaction.

We then considered the Boudouard reaction. We performed CO pulse experiments on χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts. Both catalysts exhibited similar CO adsorption properties (Figs. S38 and S39). However, CO_2 formation was observed on χ-Fe_5C_2, which was nearly completely suppressed on the χ-Fe_5C_2-Br in CO-pulse, indicating that the Boudouard reaction was largely inhibited (Fig. 3E). Moreover, Ar → $C^{18}O$ TKA experiments also showed no production of $C^{16}O^{18}O$ and $C^{18}O_2$ on χ-Fe_5C_2-Br but formation of $C^{16}O$ after introduction of $C^{18}O$, which may result from the recombination of dissociatively adsorbed CO (Fig. 3F). Notably, introduction of ^{13}CO to ^{18}O-precovered surface yielded $^{13}C^{18}O$ on χ-Fe_5C_2-Br (Fig. S40), confirming that CO dissociation remained active. Temperature-programed surface reaction (TPSR) experiments using a mixture of $C^{18}O$/He/Ar as feed further substantiated this selective blocking effect (Fig. S41). These results suggest that Br selectively inhibits CO*-O* recombination step while preserving CO dissociation activity, which were in good agreement with DFT calculations (Fig. S42).

From the results presented above, we conclude that surface Br species suppressed both WGS and Boudouard reactions. Another question is how Br modulated the o/p ratio in the

reaction. Although promoters like alkali metals or Mn for Fe-based catalysts are typically required to achieve a high olefin selectivity (*16, 27, 32, 33*), we added no alkali metal or Mn in the current high-olefin-selectivity χ-Fe_5C_2-Br catalysts. To understand the origin of the ability of χ-Fe_5C_2-Br to achieve high o/p ratio, we used propene hydrogenation as a probe to study the olefin hydrogenation process. Propene pulse experiments in H_2 showed a dramatic reduction in propene hydrogenation activity on χ-Fe_5C_2-Br as compared to χ-Fe_5C_2 (Fig. 3G), which indicated that surface Br species suppressed the olefin hydrogenation reaction.

Weakened H_2 activation ability on the Br-modified surface could be one reason for high olefin selectivity, but this explanation appeared unlikely, because hydrocarbon formation was still observed. Another possibility is that the olefin hydrogenation step is suppressed. To further substantiate this point, we conducted temperature-programmed surface reaction (TPSR) experiments using a $C_3H_6/H_2/D_2/Ar$ = 1/82/10/7 mixture feed. HD formation through H-D exchange was used as a probe to monitor H_2 activation. On χ-Fe_5C_2, both H-D exchange and C_3H_6 hydrogenation increased with temperature, reaching near-complete C_3H_6 conversion at around 180 °C. In contrast, on χ-Fe_5C_2-Br, although activation of H_2 was slightly suppressed at low temperatures and became very active above 200 °C, and no detectable hydrogenation of C_3H_6 was observed even at temperatures up to 300 °C (Fig. 3H). These results demonstrated that the high olefin selectivity came from inhibition of olefin hydrogenation ability by Br.

DFT simulations confirmed that Br altered hydrogenation energetics. On clean χ-Fe_5C_2 (100), the two-step hydrogenation of C_3H_6 proceeds with low barriers (0.22 and 0.26 eV), facilitating paraffin formation (Fig. 4A). With θ_{Br} = 1/3, the barrier of first step (C_3H_6* + H* → C_3H_7*) increased to 0.66 eV, surpassing C_3H_6 desorption energy, making desorption more favorable than hydrogenation. Detailed electronic analyses (Figs. S43 to S45) and optimized transition state geometries (Figs. S46 and S47) revealed that surface-bound Br species not only electronically modified Fe active sites but also introduced substantial steric hindrance. This steric effect obstructed the H* approach and altered the Fe-C_3H_6 binding geometry. As a result, secondary hydrogenation was selectively suppressed under Br-modified conditions.

Finally, we examined the catalytic stability of the χ-Fe_5C_2 catalyst with 20 ppm CH_3Br co-feeding, a critical measurement for practical applications. As shown in Fig. 4B, the catalyst

exhibited excellent stability for > 450 hours. At a steady CO conversion of ~ 35%, the system maintained a remarkably high C_{2+} olefin selectivity of > 80%. Notably, the formation of undesired by-products such as methane and CO_2 remained minimal throughout the test, with CO_2 selectivity consistently < 1.5%. Such sustained performance—combining high olefin selectivity and near-zero CO_2 emissions has not been previously reported in the century-long development of Fe-based FTS. These findings underscore the transformative potential of halogen co-feeding for enabling low-emission, high-efficiency olefin production at scale.

Conclusion

We demonstrated a simple yet powerful strategy to enhance FTS to olefins performance by co-feeding ppm-level of CH_3Br into Fe-based catalytic systems. Surface-bound Br species electronically interacted with Fe active sites, selectively inhibiting H_2O dissociation, CO*-O* recombination, and olefin hydrogenation, while largely preserving CO and H_2 adsorption/activation. The strategy reported in this work enables a near-zero-CO_2 pathway for highly selective olefin (or liquid fuels) production in Fe-based FTS processes that achieved high α-olefin selectivity and maintained industrially competitive activity, surpassing other reported low-CO_2 systems (Table S8).

Although halogen-containing co-feed could pose challenges in scaled-up industrial reactors, similar strategies have been adopted in commercialized processes, such as chlorine co-feed silver-catalyzed ethylene epoxidation process (*34, 35*). Coupled with CO_2-free gasification reaction (e.g., $CH_4 + 3CO_2 = 4CO + 2H_2O$) and green hydrogen from water electrolysis (*36*), the process developed in this work could offer a viable pathway toward carbon-neutral coal-to-liquid/olefins or gas-to-liquid/olefins processes.

Figure 1. Impact of halogen co-feeding on catalytic performance in FTS. (A) Effect of co-feeding halomethanes (CH_3F, CH_3Cl, CH_3Br, and CH_3I, 20 ppm) on CO conversion and product selectivity in FTS reaction over χ-Fe_5C_2 catalyst. Reaction conditions: 300 °C, 20 bar, 12000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$, $H_2/CO = 2$. (B) Dependence of CO conversion, selectivity of CO_2 and olefin on the concentration of co-feeding CH_3Br (0-50 ppm). Reaction conditions: 300 °C, 10 bar, 12000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$, $H_2/CO = 2$. (C) Influence of olefin/paraffin ratio and CO_2 selectivity for different iron carbide catalysts (ε-Fe_2C, h-Fe_7C_3, χ-Fe_5C_2, and θ-Fe_3C) and commercial Fe-1 under 20 ppm CH_3Br co-feeding. Reaction conditions: 300 °C, 10 bar, $H_2/CO = 2$, CO conversion controlled at ~30% for all data points. (D) Comparison of catalytic selectivity and olefin yield of χ-Fe_5C_2 catalyst with CH_3Br co-feed against representative literature-reported catalysts. The χ-Fe_5C_2-Br catalyst demonstrates simultaneous ultra-low CO_2 selectivity and higher olefin yield compared to state-of-art catalytic systems. (E) Plot of olefin-to-CO_2 selectivity ratio ($S_{olefins}/S_{CO2}$) against olefin space-time yield ($STY_{olefins}$) on χ-Fe_5C_2-Br (this work) and various catalytic systems from literature: OX-ZEO *(12-13, 37-41)* (blue triangles), Fe-based *(8-11, 16, 20, 27, 32, 42-45)* (yellow circles), Co-based *(21, 46-47)* (purple circles), and Ru-based *(22)* (green squares), and this work (red circles). Note that the selectivity of olefins is based on all carbon-containing products. The shaded region highlights the exceptional catalytic performance of the χ-Fe_5C_2-Br catalyst.

Figure 2. Structure of χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts. Synchrotron XRD patterns (A) and Fe 2*p* XPS spectra (B) of pristine and spent χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts. (C) Br *K*-edge XANES spectra of χ-Fe_5C_2-Br-spent catalyst compared with reference bromide compounds. (D) HAADF-STEM image and corresponding EDS mapping of Fe and Br distributions in χ-Fe_5C_2-Br-spent catalyst. (E) HS-LEIS depth profile of χ-Fe_5C_2-Br-spent catalyst. Reaction conditions: 100 mg catalyst, 300 °C, 10 bar, SV = 12000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$, $H_2/CO = 2$. χ-Fe_5C_2, syngas; χ-Fe_5C_2-Br, syngas with co-feeding 20 ppm CH_3Br. Catalysts were pretreated at 280 °C and 1 bar for 6 h, SV = 12000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$, $H_2/CO = 2$ (χ-Fe_5C_2, syngas; χ-Fe_5C_2-Br, syngas with co-feeding 20 ppm CH_3Br).

Figure 3. Mechanism of Br in regulating the catalytic behavior. (A) The reaction pathways in FTS network. (B) Inhibition effect of CH_3Br co-feeding on CO_2 formation in water-gas shift reaction over Fe_3O_4 catalyst. Reaction conditions: 50 mg catalyst, 300 °C, 1 bar, 10 mL/min $CO/H_2O/Ar$ = 2/2/96 switched to $CO/H_2O/Ar$ = 2/2/96 with co-feeding 300 ppm CH_3Br. (C) Temperature-programed desorption of H_2O over Fe_3O_4 and Fe_3O_4-Br catalysts. Reaction conditions: 100 mg catalyst, 1 bar, pretreated in 20 mL/min H_2O/Ar = 2.5/97.5 at 50 °C; then switched to 20 mL/min Ar, purging for 20 min, followed by temperature ramping from 50 °C to 300 °C at 10 °C/min. (D) Near ambient pressure XPS results of Fe_3O_4 and Fe_3O_4-Br catalysts at different temperatures in 1 mbar H_2O. Conditions: catalysts were pretreated at 400 °C in Ar for 1 h, cooled to room temperature, introduced to 1 mbar H_2O and treated at different temperatures. (E) CO pulse experiment over χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts. Reaction conditions: 100 mg catalyst, 300 °C, 1 bar, 5 mL/min Ar, 250 μL sampling loop, pulse gas: CO/He = 0.5/99.5. (F) Transient kinetic analysis of Ar → $C^{18}O$/He/Ar = 5/15/80 over χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts. Reaction conditions: 50 mg catalyst, 300 °C, 1 bar, 10 mL/min Ar switched to $C^{18}O$/He/Ar = 5/15/80. (G) Pulse experiment of C_3H_6 in H_2 for χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts. Reaction conditions: 50 mg catalyst, 300 °C, 1 bar, 20 mL/min H_2, 250 μL sampling loop, pulse gas: C_3H_6/Ar/He = 3/3/94. (H) Temperature-programed experiment of C_3H_6 hydrogenation for χ-Fe_5C_2 and χ-Fe_5C_2-Br catalysts with co-feeding D_2. Reaction conditions: 50 mg catalyst, 1 bar, 10 mL/min $C_3H_6/H_2/D_2/Ar$ = 1/82/10/7, temperature ramping from 50 °C to 300 °C at 10 °C/min.

Figure 4. Theoretical investigation of olefin hydrogenation inhibition mechanism and catalytic stability of χ-Fe_5C_2 catalyst with CH_3Br co-feed in FTS process. (A) DFT calculated reaction energy profiles for propene hydrogenation on clean and Br-covered (θ_{Br} = 1/3) χ-Fe_5C_2 (100) surfaces. Reaction intermediates and transition states illustrate two hydrogenation pathways, through $CH_3CH_2CH_2$ (solid line) and CH_3CHCH_3 (dashed line), highlighting increased hydrogenation barriers upon Br modification. (B) Catalytic stability and product selectivity of the χ-Fe_5C_2-Br catalyst. Reaction conditions: 100 mg catalyst, 300 °C, 5 bar, H_2/CO = 2, co-feeding 20 ppm CH_3Br. The catalyst exhibited stable CO conversion and sustained high selectivity toward C_{2+} olefins with minimal CH_4 and CO_2 byproduct formation over 450 hours at two different space velocities (12000 and 6000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$).

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List of Supplementary Materials

Materials and Methods

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