

Regulation strategies of atom economy for iron-based catalysts in syngas catalytic conversion

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Abstract

As a key evaluation metric for direct catalytic syngas conversion, hydrogen atom economy or carbon atom economy can accurately quantify the different atom flows during the main and side reactions, which would provide new insight for the rational design. This work reviewed the active phase types, structural evolution patterns, and regulatory mechanisms for syngas conversion on iron-based catalysts. On this basis, it elaborated the optimization paths of carbon and hydrogen atom economies and analyzed the coupling and trade-offs. It was pointed out that the balance of hydrogen atom economy and carbon atom economy was the goal for improving the atomic utilization efficiency in iron-based catalytic syngas conversion. Moreover, the appropriate application of interdisciplinary strategies could open up new perspectives for the efficient regulation of atom economy and provide novel insights for developing high-performance catalytic systems.

Keywords: syngas, atom economy, iron-based catalyst

Main:

Since the syngas conversion reaction was discovered by German chemists Franz Fischer and Hans Tropsch in 1925, it always played a central role in producing liquid fuels and basic chemicals, without relying on petroleum resources. For long times, the feedstock of syngas is mainly relied on coal and natural gas. Now, it is finding new applications with the burst development of biomass gasification and the conversion of CO₂ from air or factories, assisted by green H₂ from renewable electricity (Figure 1). It provided diverse clean choices for producing sustainable chemicals and fuels, gradually independently of fossil fuels^[1]. In this case, direct catalytic conversion of syngas is becoming again the central topic in the energy and chemical industry, although Fischer-Tropsch (F-T) synthesis has been developed for more than 100 years. Recent intensively investigated catalytic routes include reverse water gas shift (RWGS) of CO₂, dry reforming of CH₄, syngas to hydrocarbons (olefins, aromatics) and various power-to-X routes (sustainable aviation fuel, methanol and synthetic natural gas, etc.). Atom economy is a key issue to distinguish the atomic loss difference between the main reaction and side reactions, such as water-gas shift (WGS), over-hydrogenation, and coke deposition, and can also provide a quantitative basis for catalyst design, reaction-process optimization, and mechanistic elucidation. With a new mission to enhance the application of expensive green H₂, hydrogen atom economy (HAE) is becoming a critical economical issue. Meanwhile, control carbon emission also called for a high carbon atom economy (CAE), in order to reduce the cycled carbon elements. Considering these issues are scarcely concerned in the past R&D for long times, it is necessary to address it specially from most of the F-T synthesis.

In this review, iron-based catalysts are emphasized mainly considering their dynamic features (various FeO_x/FeC_x phase evolution, intrinsic WGS activity and adjustable carburization behavior) and wide operating windows for temperature, pressure, space velocity and gas partial pressures. These all resulted in different CAE and HAE trends, as well as numberless modification methods. Systematically analyzing the atom economy of syngas conversion over iron-based catalysts, achieving targeted optimization of the atom economy of the reaction system are new research hotspots and critical scientific issues for industrial scale-up and sustainable development.

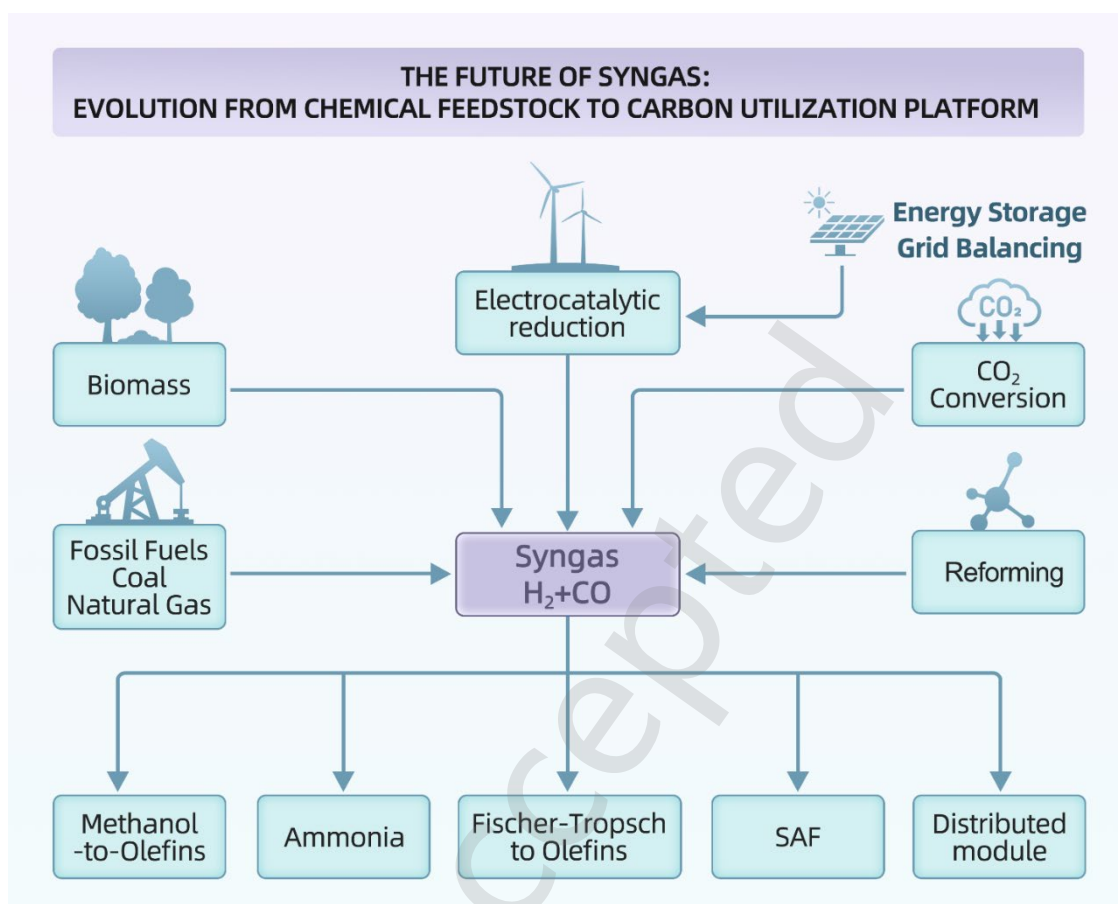


Figure 1. Applications of syngas conversion.

1. Active phase of iron-based catalyst

Conventional iron-based catalysts often employ iron oxide microcrystals as the main precursor phase, which are subsequently reduced and activated under H_2 , CO , or a syngas atmosphere. By inserting carbon atoms into the iron lattice vacancies, these microcrystals are gradually converted into the active iron carbide phases. Extensive studies were made on the catalytic functions, intrinsic activities and mechanisms of different iron-based phases. In general, there are three main types of active iron species in iron-based catalysts for syngas conversion^[2], for elemental iron (α -Fe), oxide (including α - Fe_2O_3 , γ - Fe_2O_3 , Fe_3O_4 , FeO , etc.), and iron carbides, such as χ - Fe_5C_2 (Hägg carbide), ϵ' - $Fe_{2.2}C$ (pseudo-hexagonal iron carbide), ϵ - Fe_3C (hexagonal iron carbide), θ - Fe_3C (cementite), and Fe_7C_3 (Eckstrom-Adcock iron carbide) as list in Figure 2. Definitely, the dynamic evolution process of the iron phase in the syngas atmosphere can lead to dynamic changes in catalytic activity and selectivity, such as the transformation from the carbonized state to the oxidized state or between different iron carbide structures, which in turn trigger changes in the ineffective or effective consumption pathway of atoms. For instance, α - Fe_2O_3 was preferentially converted into a shell-type γ - Fe_2O_3 structure in H_2 condition. However, it is successively transformed through the intermediate phases of γ - Fe_2O_3 and Fe_3O_4 , and finally into a dense iron carbide surface layer on the surface of the particles in CO atmosphere. In addition, the reducing phase transition pathway of the iron oxide precursor in syngas atmosphere, was consistent with those in CO atmosphere, but a discrete iron carbide particle layer was generated on the surface^[3]. Structurally, iron carbides are intermetallic compounds composed of iron and carbon, the most representative phase of which is cementite (θ - Fe_3C), as widely reported in steel industry. In the syngas atmosphere,

the aforementioned iron carbides mostly coexist as mixed phases, the phase transition of iron carbide is controlled by the chemical potential (μ_C) in F-T reaction. Factors influencing μ_C include gas composition, temperature, pressure, and water vapor produced during the reaction. Water vapor regulates the concentrations of H_2 and CO via the WGS reaction, therefore affecting the stability of μ_C . At higher μ_C , the ϵ - Fe_2C and χ - Fe_5C_2 phases are readily formed, while low μ_C promotes the formation of the more stable θ - Fe_3C phase. Among them, ϵ - Fe_2C was widely regarded as one of the most promising active phase due to its excellent catalytic activity^[4]. Under low-temperature conditions, the catalytic activity of ϵ - Fe_2C was found to be higher than that of χ - Fe_5C_2 ^[5]. For instance, Huo et al.^[6] reported that the energy barrier of CO hydrogenation on the ϵ - $Fe_2C(011)$ crystal plane was lower than those on χ - $Fe_5C_2(010)$ and θ - $Fe_3C(001)$ crystal planes. Xu et al.^[7] found that the catalytic activity of ϵ - Fe_2C was higher than that of χ - Fe_5C_2 in the F-T reaction at $200^\circ C$, and the catalyst activity was positively correlated with the ϵ - Fe_2C content^[8]. However, ϵ - Fe_2C became unstable under high-temperature conditions, limiting its industrial application. χ - Fe_5C_2 is a common activated iron carbide phase with strong activity for CO dissociation and C-C bond coupling. Using density functional theory (DFT) calculations, Pham et al.^[9, 10] found that (510) crystal plane of χ - Fe_5C_2 was of the highest proportion and was the most stable. Direct dissociation activation of CO occurred on this crystal plane, and the reaction on the (510) crystal plane could inhibit CH_4 formation while favoring C_{2+} formation. Work of Yang et al.^[11] supported the similar high catalytic activity of χ - Fe_5C_2/SiO_2 for the formation of long-chain hydrocarbons. In the Fe-Mn catalyst system, the additive Mn could affect the electronic state of surface carbon species and promote the formation of θ - Fe_3C . With the increase of θ - Fe_3C content in the catalyst, the selectivity and olefin molar ratio of light olefins also increased^[12]. Using DFT calculations, Wang et al.^[13] found that (031) crystal planes of θ - Fe_3C was the dominant planes and was the most stable. CH_4 selectivity generated on this crystal plane was low, while the selectivity of C_{2+} was high. For the Fe/ SiO_2 catalyst, Chang et al.^[14] proposed that Fe_7C_3 exhibited higher intrinsic activity than χ - Fe_5C_2 and ϵ - Fe_2C .

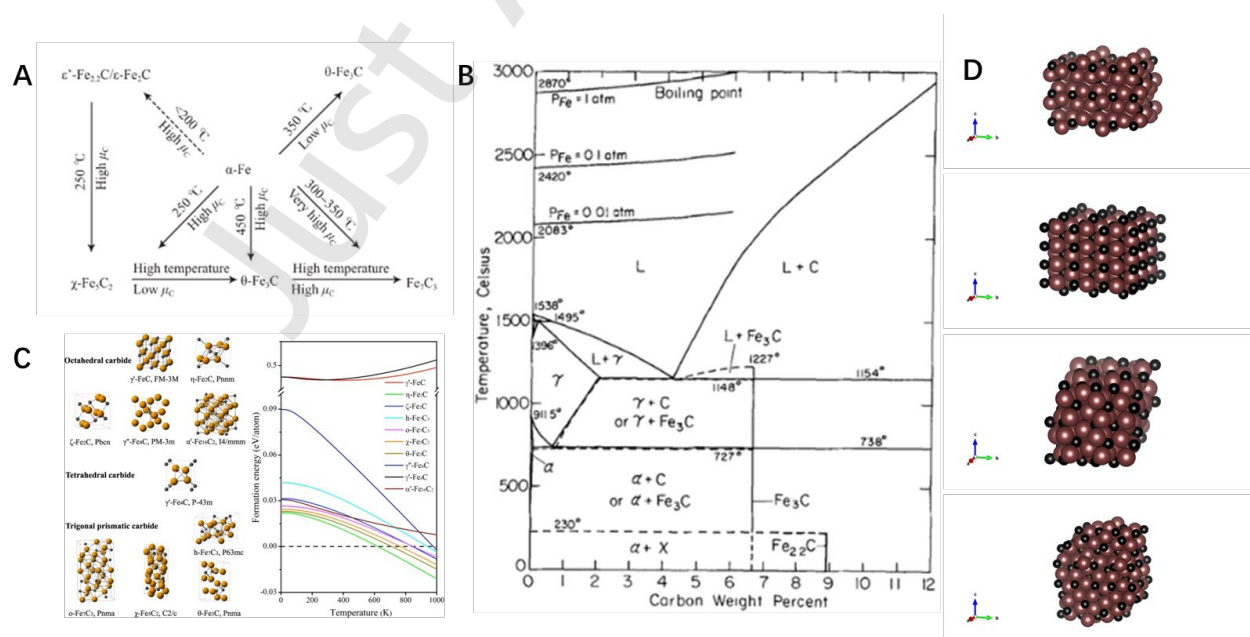


Figure 2. (A) The structure of iron carbide and its mutual conversion pathway obtained by the calculation of atomic thermodynamics^[15]. Reprinted with permission from Ref. [15]. Copyright © 2010 American Chemical Society. (B) Fe-C

phase diagram. Reprinted with permission^[16]. Reproduced with permission from Ref. [16], Springer Nature. Copyright © 1972 Springer Nature. (C) The crystal structure of iron carbide classified by octahedron, tetrahedron, and triangular prismatic carbides, as well as the generation energy that varies with temperature^[17]. Reprinted with permission from Ref. [17]. Published under CC-BY 4.0. (D) Schematic diagram of the molecular model of FeC_x.

As to the crystal plane sensitivity of iron carbides, χ -Fe₅C₂ with (202) and (112) crystal planes were prepared as shells by reconstruction of Fe₃O₄ nanocubes and octahedrons^[18], respectively. In F-T synthesis, activity and stability are highly sensitive to the exposed crystal plane, while crystal surface sensitivity is not significant in terms of chain growth. Notably, in-situ characterization and phase observation of iron-based catalysts are challenging in real reaction (high-pressure). Co-existence of amorphous iron carbides was observed during the reaction process^[15]. Basically, iron carbide is the core active phase of C-C coupling to form hydrocarbons in syngas conversion, and its crystal orientation, and particle size directly determine CO activation efficiency and carbon chain growth selectivity, which in turn affects CAE. Iron oxides, Fe₃O₄ for example, are mainly involved in H₂O activation. Their oxygen vacancy concentration, crystal defects and interface interactions^[19] regulate the transfer efficiency and utilization pathway of hydrogen atoms, which is related to HAE.

2. The atom economy regulatory mechanisms

Through analysis of CAE and HAE, it is possible to guide the modification design of iron-based catalysts, to help overcome the thermodynamic limitations of Anderson-Schulz-Flory (ASF) product distribution among syngas conversion, and to alleviate the trade-off between catalytic activity and product selectivity, of which essence can be attributed to the flow distribution of carbon and hydrogen atoms in the reaction system.

Notedly, CAE refers to the efficiency of the flow of converted carbon elements towards effective products, while HAE refers to the efficiency of the flow of converted hydrogen elements towards effective products. Their definitions are independent of the conversion rate and limited solely to the reaction itself, without considering the industrial utility burden.

2.1 Optimization strategy of CAE

The shunt and dissipation of non-target carbon species constitute the central focus of CAE research. In the actual reaction, suppression of by-products must be achieved according to the desired product. Systems with heavy hydrocarbons and light olefins as the main products focus on suppressing the generation of CO₂, and systems with C₂₊ hydrocarbons as the target product prioritize reducing methane selectivity.

For iron-based catalysts, oxide-rich or water-rich microenvironments tend to promote CO₂. Considering that the main source of CO₂ is the WGS side reaction, and that water is a necessary reactant for the WGS reaction, several strategies can be employed to inhibit the generation of H₂O in reaction systems. These include hydrophobic modification of the catalyst surface to reduce water adsorption and retention, thereby effectively inhibiting the WGS reaction, introducing trace amounts of adsorbed species to change the chemical properties of the catalyst surface and block the WGS reaction pathway, or developing pure-phase iron carbide catalysts lacking active WGS sites, as list in Figure 3.

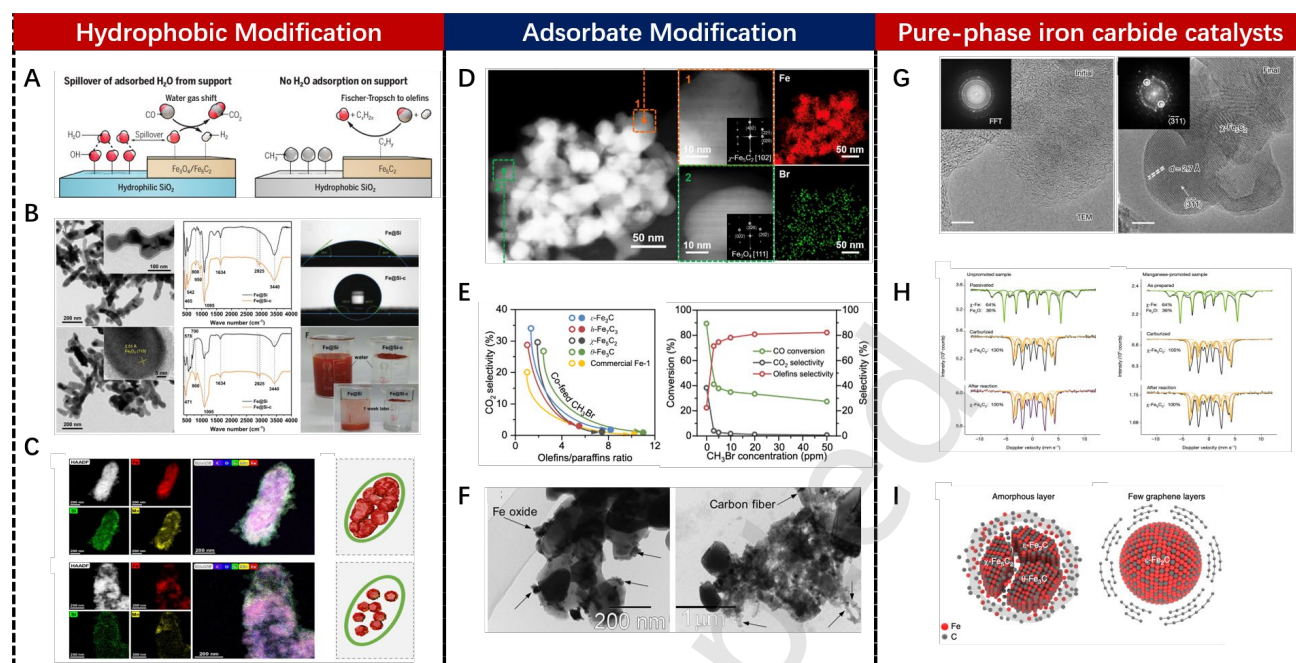


Figure 3. Iron-based strategies for improving CAE in syngas conversion. (A) Hydrophobic-support concept for limiting water adsorption and suppressing the water-gas shift reaction, thereby improving Fischer-Tropsch olefin production [20]. Reprinted with permission from Ref. [20]. Copyright © 2021 The American Association for the Advancement of Science. (B) Structural characterization of the Fe@Si and Fe@Si-c catalysts, including TEM images, FTIR spectra of fresh and spent catalysts, water-droplet contact angle tests, and photographs of catalysts dispersed in water initially and after 1 week [21]. Reprinted with permission from Ref. [21]. Copyright © 2021 The American Association for the Advancement of Science. (C) TEM images, EDS elemental mapping, and structural models of the spent Fe@Mn@0.2Si catalyst and the spent Fe@Mn@0.2Si-c catalyst [22]. Reproduced with permission from Ref. [22], Springer Nature. Copyright © 2024 Springer Nature. (D) HAADF-STEM image and corresponding EDS mapping of Fe and Br distributions in χ -Fe₅C₂-Br-spent catalyst [23]. (E) CO conversion, CO₂ and olefin selectivity versus cofeed CH₃Br concentration, and olefin/paraffin ratio and CO₂ selectivity over four iron carbides and commercial Fe-1. [23]. Reprinted with permission from Ref. [23]. Copyright © 2025 The American Association for the Advancement of Science. (F) Spent Fe/ α -Al₂O₃ catalyst images [24]. Reprinted with permission from Ref. [24]. Copyright © 2012 AAAS. (G) Environmental HRTEM images of the transformation from the initial state of Raney iron, through carburization to the final state. [25]. Reprinted with permission from Ref. [25]. Published under CC-BY 4.0. (H) In situ Mössbauer spectra tracking the transformation of unpromoted and Mn-promoted Raney iron during carburization and FTLAO reaction [25]. Reprinted with permission from Ref. [25]. Published under CC-BY 4.0. (I) Conventional catalysts with unconfined iron carbide (Fe_xC) particles as the active phase and graphene layer-confined ϵ -Fe₂C [26]. Reprinted with permission from Ref. [26]. Published under CC-BY 4.0.

At present, one of the core strategies for hydrophobic modification is to construct a core-shell structure featuring a hydrophobic shell and an active center. The hydrophobic shell serves as a barrier to block the contact between water and the active sites. Xu et al. [21] confirmed that the hydrophobic SiO₂ shell could reduce the microenvironmental water pressure on the surface of the catalyst, block water-induced side reactions by accelerating the desorption and diffusion of water molecules, efficiently inhibit WGS reactions generation, and optimize the overall hydrocarbon product distribution in syngas conversion. Related studies [22] also found that the appropriate shell thickness was crucial to stabilize the active phase of iron carbide and achieve excellent catalytic performance. In addition, other studies [27, 28] have also achieved a high

reduction in CO₂ selectivity using similar methods, further verifying the effectiveness of hydrophobic modification strategies. In addition to inorganic hydrophobic materials, carbon-based materials were also used due to their excellent hydrophobicity and structural tunability. Zhang et al. [29] prepared a core-shell catalyst with graphene tightly wrapping χ -Fe₅C₂ via pyrolysis. The hydrophobicity of the graphene layer effectively inhibited the occurrence of WGS reaction, reducing CO₂ selectivity to 5%~6%, a value significantly lower than that of the catalyst without a graphene coating. Lyu et al. [26] also prepared a ϵ -iron carbide catalyst coated with a graphene layer, which acted as a stable active phase, prevented it from being oxidized by H₂O and CO₂, and exploited its inherent hydrophobicity to inhibit secondary adsorption of H₂O on the surface. Besides, some researchers have used hydrophobic polymer materials. Feng et al. [30] mixed and ground KFeMnMg catalyst with hydrophobic polydivinylbenzene (PDVB) [31]. The experimental results showed that the hydrophobicity of PDVB molecule reduced the contact between water and the surface of the catalyst, thereby mitigating the oxidation effect of water on the active iron carbide phase.

In the method of surface modification, scholars have proposed a sulfur modification strategy [24], which used iron-based nanoparticle catalysts co-modified with sodium to be uniformly dispersed on weakly interacting α -alumina or carbon nanofiber supports, which could achieve a high olefin selectivity. In addition, halogen modification and regulation strategies have been explored. By introducing trace amounts of halogen-containing compounds [23], such as bromomethane, into the feed gas together with syngas, iron-based catalysts could achieve significant improvements in CAE and in synthetic optimization of catalytic performance. The results indicated that bromine could selectively act on the iron active site, inhibiting the dissociation of H₂O and the conversion or migration of oxygen species into CO₂. This strategy effectively improved the selectivity of olefins relative to paraffins. The core mechanism was that the surface-bound halogen species could precisely regulate the surface microstructure of the catalyst and selectively block the side reaction pathways between CO₂ generation and olefin hydrogenation.

The controllable synthesis and precise construction of pure-phase iron carbide have become an important research direction for high CAE. The key design principle is to modulate the synthesis atmosphere, heat treatment temperature, precursor type, reduction carbonization process, etc., to achieve the synthesis of the target iron carbide. For the first time, Wang et al. [32] prepared single-phase iron carbides (Fe₃C, Fe₇C₃ and Fe₅C₂) with high purity of the output phase by the liquid-phase synthesis method. They obtained the correlation between the surface phase and reactivity using transient characterization technology and clarified the intrinsic activity of the different iron carbides for C-C coupling. All three types of iron carbides had the catalytic activity of the F-T reaction, of which Fe₅C₂ was the active phase with the best activity. Besides, scholars [26] have successfully confined pure ϵ -Fe₂C nanocrystals to a graphene layer and stabilizing them for at least 400 hours under high-temperature conditions. The highly stable ϵ -Fe₂C was successfully synthesized via pyrolysis of Prussian blue analogues (PBAs) through a nitrogen induction strategy. The excellent performance of ϵ -Fe₂C-xMn catalysts, particularly in suppressing CO₂ generation, was largely attributed to the interface between dispersed MnO clusters and ϵ -Fe₂C, which critically limited the conversion of CO to CO₂ [33]. Using the original pure-phase χ -Fe₅C₂, researchers could improve carbon utilization efficiency [25]. After customization and optimization for the F-T to linear α -olefin process, this catalyst could operate efficiently and stably for 200 hours. Under industrially relevant conditions, the selectivity of non-target CO₂ was 9% based on carbon. These diversified preparation strategies realized the directional

synthesis of typical iron carbide phases, and also provided an experimental basis for revealing the phase evolution of iron carbides, associated catalytic properties, and atom economy through precise regulation of phase composition and structure.

2.2 Optimization strategy of HAE

The low HAE utilization represents another core bottleneck that restricts the yield of target products in the iron-based system, for the mismatch between the H/C ratio of the target product and that of the syngas feed, and the incompatibility between the rate of hydrogen dissociation or migration and the rate of carbon chain growth. Among these, the hydrogenation of oxygen atoms to generate water constitutes the most important pathway for the ineffective consumption of hydrogen atoms.

The influence of water-involved side reactions on HAE is highly dependent on the feed composition and reaction pathway. For example, in the CO methanation system, the theoretical HAE calculated from the stoichiometric equation $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ is 66.67%. Because the water formed during methanation can participate in the WGS reaction, a survey of the literature indicated that the experimentally reported HAE values were often higher than the theoretical value (Supplementary Table S1). This implied that appropriately promoting the WGS reaction could raise the effective H utilization in CO methanation. By contrast, in CO_2 hydrogenation to methanol, the theoretical HAE from the stoichiometric equation $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$ is also 66.67%. However, the presence of the RWGS reaction ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$) generates additional water while consuming H_2 , and the HAE values reported in the literature were consequently lower than the theoretical value (Supplementary Table S2). Therefore, suppressing the RWGS reaction was essential to avoid HAE penalties in CO_2 -to-methanol processes. These contrasting cases indicated that WGS-related pathways should not be treated simply as unfavorable side reactions. Instead, they need to be either promoted or suppressed according to the specific reaction network.

Using the WGS reaction to drive the main reaction equilibrium is an attractive new strategy. Gao et al. [34] designed a sodium-modified $\text{FeC}_x@\text{Fe}_3\text{O}_4$ core-shell catalyst, and innovatively adopted a micro-interface coupling strategy that integrates the WGS reaction with the syngas-to-olefin (STO) reaction (Figure 4). This method could significantly increase system HAE to 66%~86%, far surpassing the traditional process range of <50%. Traditional routes have drawbacks such as low hydrogen utilization and strong dependence on high H_2/CO ratios, accompanied by large amounts of wastewater and CO_2 emissions. Relying on the core-shell catalytic structure, the catalyst combined high carbon monoxide conversion efficiency with excellent olefin selectivity. The system precisely coupled the WGS and STO reaction interface, converting process wastewater into recyclable active hydrogen sources, fundamentally breaking the reliance of traditional processes on feedstock hydrogen while improving wastewater discharge models. This technology provided a valuable solution for efficient conversion of low-hydrogen syngas and precise regulation of hydrogen atom utilization in one-step olefin production.

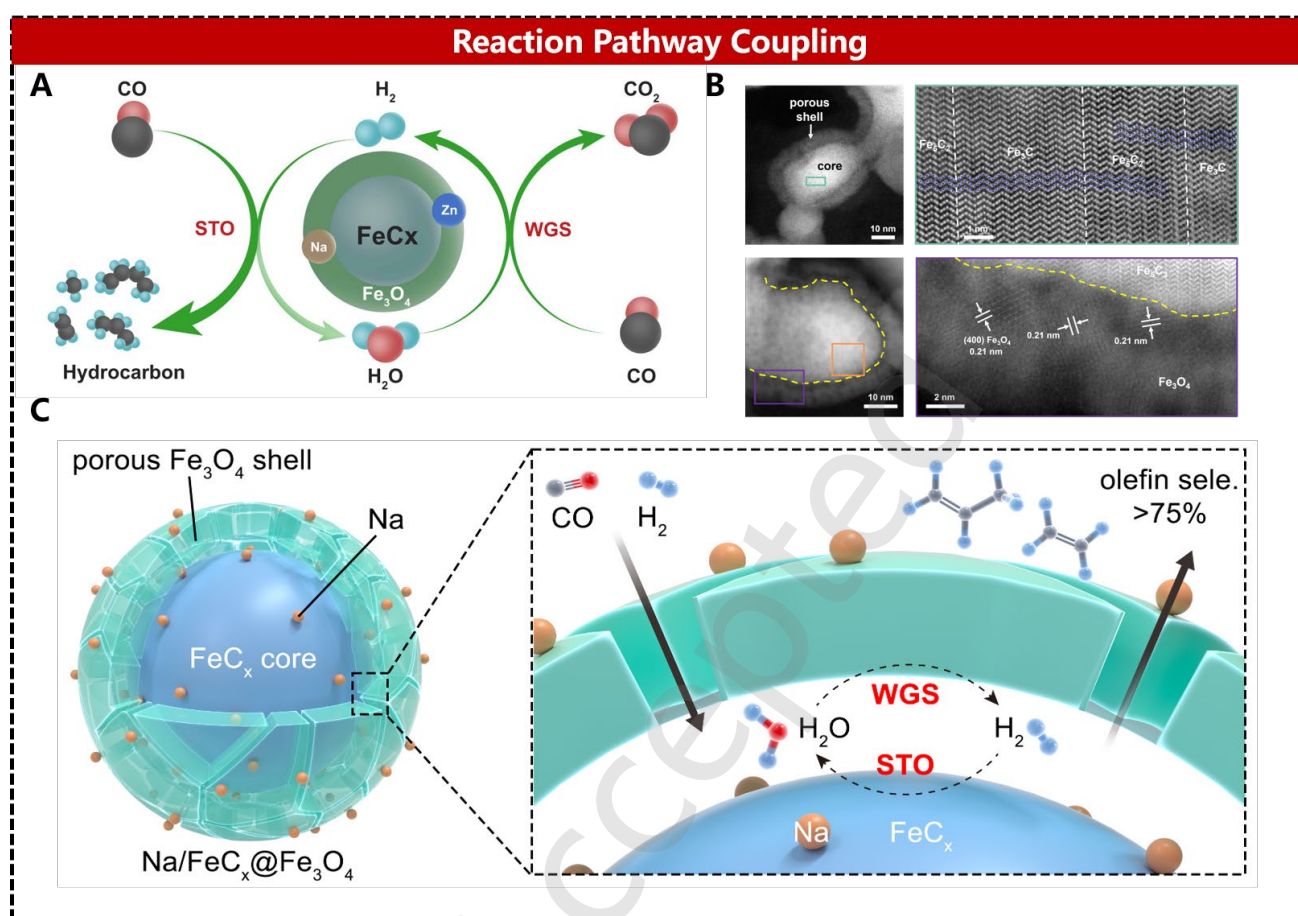


Figure 4. HAE regulation centered on iron-based syngas conversion and supplemented by cross-catalyst mechanistic references. (A) Improvement of HAE and olefin yield under the WGS-STO coupling effect^[34]. (B) ADF-STEM image of sodium-modified $\text{FeCx}@Fe_3O_4$ core-shell catalyst particles^[34]. (C) Coupled WGS-STO reaction scheme^[34]. Reprinted with permission from Ref. [34]. Copyright © 2025 The American Association for the Advancement of Science.

3. Synergistic balance of CAE and HAE

The removal of oxygen atoms from CO, which have two main destinations as entering into water flow or CO_2 flow, is the key to determining atom economy in F-T synthesis if not considering the minor amount of oxygenates. Competition between these two pathways directly determines the HAE and CAE of the system. Lower HAE is always due to the producing useless wastewater when oxygen atoms react with hydrogen. Conversely, when the WGS reaction contributes significantly, part of the hydrogen can be regenerated, thereby increasing the ratio of hydrogen atoms into target hydrocarbons. In fact, from the perspective of raw material costs, the preparation or modulation process of hydrogen (water electrolysis, natural gas steam reforming, and the WGS reaction, etc.) consumes a lot of energy, making hydrogen the most expensive feedstock in this reaction system. The generation of H_2O is not only a waste of hydrogen resources, but also the main source of system energy consumption and product separation complexity. Moreover, upon discharge or recycling, these as-produced wastewater needed the costly purification, considering they always contain organic residues, dust particles, and other impurities from the industrial loop.

In recent years, outstanding progress has been made in improving the conversion efficiency of carbon atoms. However, pursuing CAE conflicts with the intrinsic properties of iron-based catalysts, particularly their naturally strong WGS activity.

Several studies aiming to extremely low CO₂ selectivity have shown that stronger suppression of CO₂ formation is accompanied by a lower overall CO conversion rate. This implies that reducing CO₂ emissions simultaneously decreases the absolute yield of desired products. To maximize target product yield, the optimization of carbon and hydrogen atom economies must be balanced, which requires guiding the flow of carbon and hydrogen atoms towards the target product, through catalyst structure design, reaction parameter optimization, and reconstruction of reaction paths, and simultaneously inhibiting the invalid dissipation paths of these atoms. Therefore, it is necessary to identify and quantify the sources of the improved conversion and distinguish between effective and inefficient conversion of carbon and hydrogen resources. Meanwhile, it is worth avoiding false activity enhancement driven by side reactions via scientific design and achieving efficient utilization of carbon and hydrogen resources.

Table 1. Turnkey equations for CAE and HAE calculations.

Product	Basic reaction	Turnkey equation	Carbon Atom Economics (CAE)	Hydrogen Atom Economics (HAE)
Aromatics (CH₁)	CO+1.5H ₂ =CH ₁ +H ₂ O CO+H ₂ O=CO ₂ +H ₂	(1+α)CO+(1.5-α)H ₂ =CH ₁ +αCO ₂ +(1-α)H ₂ O	CAE=1/(1+α)	HAE=1/(3-2α)
Olefins (CH₂)	CO+2H ₂ =CH ₂ +H ₂ O CO+H ₂ O=CO ₂ +H ₂	(1+α)CO+(2-α)H ₂ =CH ₂ +αCO ₂ +(1-α)H ₂ O	CAE=1/(1+α)	HAE=1/(2-α)
Alkanes (CH₃)	CO+2.5H ₂ =CH ₃ +H ₂ O CO+H ₂ O=CO ₂ +H ₂	(1+α)CO+(2.5-α)H ₂ =CH ₃ +αCO ₂ +(1-α)H ₂ O	CAE=1/(1+α)	HAE=3/(5-2α)
Methane (CH₄)	CO+3H ₂ =CH ₄ +H ₂ O CO+H ₂ O=CO ₂ +H ₂	(1+α)CO+(3-α)H ₂ =CH ₄ +αCO ₂ +(1-α)H ₂ O	CAE=1/(1+α)	HAE=2/(3-α)

In the iron-based catalyst syngas conversion system, the correlation between CAE and HAE for different hydrocarbon products can be quantified. The intrinsic relationship between product composition and atomic utilization efficiency was also visualized (Table 1). Taking the reaction parameter α ($0 \leq \alpha \leq 1$) as an independent variable, a two-dimensional coordinate system was constructed with HAE and CAE (Figure 5A), presenting the atom economy of methane (CH₄), the primary syngas conversion unit (CH₂), aromatics (CH₁), and alkanes (CH₃). From the perspective of the reaction mechanism and the data features, for HAE, methane (H/C=4) exhibited the highest value, followed by alkanes (CH₃) with a higher HAE than the primary syngas conversion unit (CH₂), and aromatics (CH₁) showing the lowest. This gradient distribution directly correlated with the hydrogenation behavior of each product. Methane, as a deep hydrogenation product, implied high HAE modulation potential. In the CAE dimension, all products exhibited a reverse trend with the increase of reaction parameter α , which was mainly due to the generation of CO₂ in the system. This chart realized the quantitative distinction among different products, and also established the correspondence between side reaction types and atomic loss. Thus, it highlighted the core role of the balance between CAE and HAE in the iron-based syngas catalytic system.

For the chemical reaction of syngas to produce hydrocarbons (Table 2), if the product composition (CH_x) is described using the general package chemical formula, we can obtain:



Notably, this equation serves as a schematic equation for the reacting species and does not represent the actual stoichiometric ratio. If the molar flow rate of feed CO is m , the conversion rate of CO is p , the carbon-based selectivity of CO₂ in the product is q ($0 \leq q \leq 0.5$), and x is the average H content of hydrocarbon products (weighted average of the mixed product's mole fraction), the following equation can be obtained.

Table 2. Schematic equations for calculating HAE and CAE using element conservation.

	CO	H ₂	=	CH _x	CO ₂	H ₂ O
Feeding	m	$0.5mp[x(1-q)+2(1-2q)]$		0	0	0
Elements	C, O	H		C, H	C, O	H, O
Conversion of molar flow	mp	$0.5mp[x(1-q)+2(1-2q)]$		$mp(1-q)$	mpq	$mp(1-2q)$
Element C	$m(1-p)$	/		$mp(1-q)$	mpq	0
Element O	$m(1-p)$	/			$2mpq$	$mp(1-2q)$
Element H		$mp[x(1-q)+2(1-2q)]$		$xmp(1-q)$		$2mp(1-2q)$

Therefore, if x , p , q are mastered, the corresponding CAE and HAE can be obtained for the hydrocarbon reaction of CO, as detailed by the following formula:

$$CAE = \frac{C \text{ in } CH_x}{\text{total converted } C} = \frac{mp(1-q)}{mp} = 1-q$$

$$HAE = \frac{H \text{ in } CH_x}{\text{total converted } H} = \frac{xmp(1-q)}{mp[x(1-q) + 2(1-2q)]} = \frac{x(1-q)}{x(1-q) + 2(1-2q)}$$

It can be found that HAE and CAE are related, namely

$$HAE = \frac{x * CAE}{x * CAE + 2(1-2q)}$$

The relationship between q and a can be deduced as

$$\frac{a}{1+a} = q \text{ or } \frac{q}{1-q} = a$$

Specifically, for specified products (such as CH₄), when x is an integer value, typical HAE, CAE, and their relationships with these variables can also be obtained (Supplementary Tables S3 and S4).

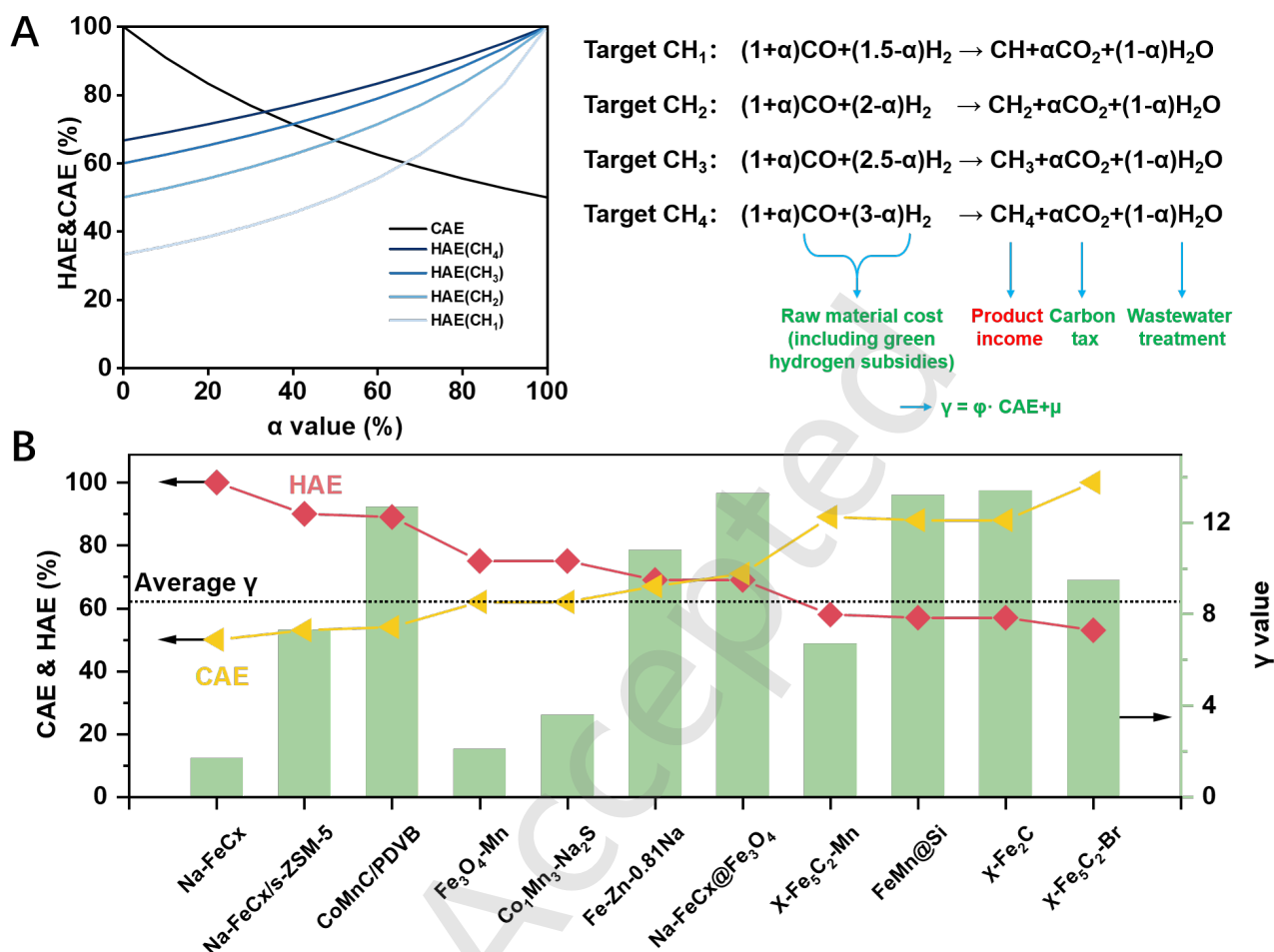


Figure 5. The connection between atomic economy and the technological economy in actual production processes. (A) The impact of α on the targeted generation of CAE and HAE of different products, as well as the economic analysis of raw materials, products, carbon taxes, and wastewater treatment. (B) The economic index γ , CAE and HAE under different advanced catalysts^[12, 21, 34-41].

Atom economy defines the directed conversion of feed atoms into target products and determines the extent of side reactions, the quantity of by-products, and the theoretical upper limit of resource utilization. As theoretical indexes for evaluating catalytic reactions and green chemical processes, these indicators ultimately translate into the atomic-utilization efficiency at the industrial scale. Accordingly, we proposed the average H/C atomic ratio x ($x = 1-4$) of the target product as a core index for atom economy evaluation. We then developed an effective and simple stoichiometry-based tool to assess the economics of syngas-to-hydrocarbon products. The model omitted non-process costs (e.g., equipment and labor) and focused on four core metrics, such as feedstock cost, product revenue, carbon-emission cost, and wastewater treatment cost, to enable rapid comparison. Taking the contribution of the WGS reaction (α) as a key parameter, we defined the CAE and derived expressions for the HAE for different products, confirming that CAE was negatively correlated with HAE. Based on the material balances, we constructed an economic index $\gamma = \text{revenue} - (\text{feedstock cost} + \text{CO}_2 \text{ treatment cost} + \text{wastewater treatment cost})$, derived a general expression with α and CAE as independent variables (Supplementary Table S5 to S9), and obtained a linear relationship $\gamma = \varphi \times \text{CAE} + \mu$ that quantitatively characterized reaction economics. We

parameterized the model by CO conversion rate, CO₂ selectivity, average H/C ratio x of products, and market prices, and benchmarked it across advanced olefin catalysts (Figure 5B). Under syngas-based valuation, γ was positive and aligned with industrial reality. This method could quickly quantify the economic differences among different catalysts and processes, and provide a direct basis for route selection and condition optimization, especially for iron-based routes (Supplementary Table S10). The α and q values for the best-performing Na-FeCx@Fe₃O₄ catalyst were calculated as 0.42 and 29%, demonstrating the feasibility and universality of the CAE and HAE calculation methods. The methodology is feasible to the product system containing only hydrocarbon, carbon oxides and water. Some typical reaction systems exhibit both high HAE and CAE, such as the preparation of heavy hydrocarbons from CO and H₂O and the preparation of HCOOH from CO₂ and H₂, where the research method demonstrated in this work may provide a reference for the development of these reaction systems or new routes. As extending the product system to contain oxygenates, CAE and HAE and oxygen atom economy (OAE) will be changed, which, however, is the next step effort.

4. Interdisciplinary strategies for regulating atom economy

With the rapid development of interdisciplinary sciences and technologies, atomic economy scope from traditional chemical engineering research have been enriched and expanded as the supplement of valuable deep insights.

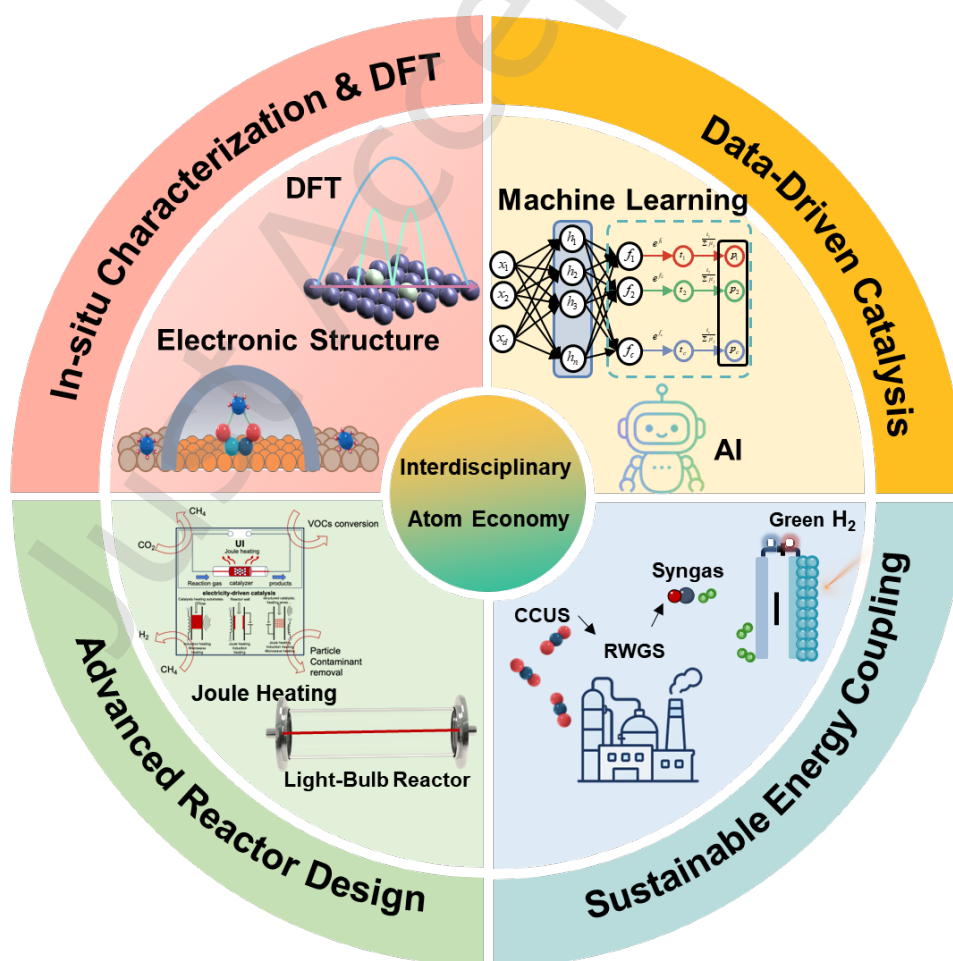


Figure 6. Interdisciplinary strategies for atomic economic regulation of iron-based syngas conversion.

(1) The in-situ characterization and theoretical calculations have proven essential for analyzing the core mechanism of the syngas reaction, especially in clarifying the role of additives, carriers, and key species such as water molecules. For instance, spatially resolved MRI has characterized industrial-scale FTS reactors, confirming the coexistence of hydrocarbons and a water-rich liquid at the pore surface^[42]. In addition, scanning tunneling microscopy and synchrotron radiation techniques^[43] visualize solid catalysts in space and time to reveal their structure and function, which are promising experimental protocol. For example, Boller et al.^[44] observed model catalysts at the atomic scale under near-industrial conditions, finding a significant linear positive correlation with step density, which identified that the step-edge sites is active site of F-T synthesis. Besides, various physical or chemical means was proposed to modify the surface and reaction microenvironment of catalysts, so as to suppress the negative effects of water. However, it remained challenges to tap the positive regulation of water molecules in the system and realize the functional utilization of water iron-based catalysts, considering their high intrinsic water-gas conversion activity.

(2) Machine learning (ML) and automation laboratory is effective to build high-quality catalytic databases and accurate catalyst screening. It is currently impossible to exploring all configurations in conventional DFT and microkinetic modeling, is due to the high computational cost and exponential growth of possible structures with size. However, ML potential energy neural networks have been trained on DFT data, which can replace DFT calculation with near-DFT accuracy while accelerating predictions by several orders of magnitude. For example, an Fe-C-H-O machine learning potential have been developed to screen more phases of FeC_x, further proving that CO activation can occur at the carbon vacancies on the surface^[45]. Additionally, ML descriptors can extract low-dimensional variables, providing clear directions for catalyst design. For instance, experimental data and macroscopic catalyst properties can be used as descriptors in random-forest models to optimize the yield of heavy olefins^[46]. Large language model can extract catalyst information including composition, reaction conditions, and others from published papers, which reduce the labor cost for database. The combination of embodied intelligence and laboratory can obtain real experimental data under test conditions^[47]. Even laboratories with limited resources can build platforms with simplified modular devices to accumulate structured data, which can significantly advance catalytic research of iron-based syngas^[48].

(3) Innovative technologies such as 3D printing, intelligent synthesis, and flash Joule heating are helpful to broaden the preparation and reaction design approaches of iron-based catalysts^[49]. Transformative technologies like 3D printing, have garnered significant attention. For example, metal-printed products can serve as both chemical reactors and catalysts (autocatalytic reactors) to directly convert C₁ molecules into high-value chemicals. Iron-based autocatalytic reactors (Fe-SCRs) have successfully catalyzed the synthesis of liquid fuels^[50]. Separately soft carbon-assisted flash Joule heating (FJH) enables the conversion of low-grade iron minerals and soft carbon into electron-rich nano-Fe⁰/FeS heterostructures embedded graphene layers^[51]. In addition, filament-catalyst reactor, inspired by the luminous mechanism of incandescent bulbs, break the trade-off between activity and selectivity through radial temperature gradient between the filament and the reactor wall. This design has been applied to methane activation at >1000°C and ethylene and BTX generation at ~300°C^[52].

(4) Multi-level challenges in technology, economy and environment call for interdisciplinary research to facilitate the green and low-carbon transformation of the energy. Facing the forthcoming era of carbon-neutrality, there still exists a bottleneck of highly costive supply of green hydrogen by water electrolysis. And the technological upgrade path from gray hydrogen to blue hydrogen is also subject to the shortcomings and application constraints of CCS technology. When

powered by green electricity, an alternative route is direct catalytic decomposition of diesel to produce “Jadeite hydrogen” and carbon nanomaterials^[53]. Additionally, multi-stage floating catalyst chemical vapor deposition reactors (FCCVD) can convert methane into hydrogen and carbon nanotube aerogels, eliminating the need for exogenous hydrogen by circulating carrier gases, thus achieving a net output of 85% hydrogen^[54]. Further, Choisez et al.^[55] proposed that iron-base catalysts can be used from reduced Fe₂O₃ to complete energy storage by green hydrogen or green ammonia, and then release heat energy and H₂ through oxidation reaction. This perspective extends iron-based materials from heterogeneous catalysis into energy carriers for storage and transportation. Apparently, it calls for interdisciplinary theories and methodology to tackle the integrated systems.

As combining the above multidimensional research approaches, it is expected that an interdisciplinary research system integrating theoretical mechanism analysis, intelligent catalysis development, reaction equipment innovation, and low-carbon engineering implementation will be established. It provides systematic solutions for achieving high atom economy transformation of iron-based catalytic systems.

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Data availability

Not applicable.

Author contributions

C.G. and Zhili L. drafted the full text. Y.L., Z.H., and M.M. screened references. Z.Y., H.Y., Y.Z., N.W., H.S., L.Y., Zhe L., R.Z., X.L., and H.L. participated in the content discussion. C.C. and W.Q. revised manuscripts and supervised the entire work. All authors read and approved the final manuscript.

Competing interests

The authors declare no competing interests that are relevant to this article.

Use of AI statement

None.

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