

# **ZnFe<sub>2</sub>O<sub>4</sub> Produced from Fe/Zn Catalysts at Different Ratios for Catalyzing CO Hydrogenation**

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## **Abstract**

The effect of different Fe/Zn ratios in catalysts on Fischer-Tropsch synthesis was investigated. The Fischer-Tropsch behavior of the catalyst exhibited optimal performance at a Fe/Zn ratio of 2:1. In contrast, the Fe catalyst without Zn addition showed significant agglomeration, and a substantial amount of  $\alpha$ -Fe remained after the reaction. Characterization results indicate that the Fe/Zn catalyst prepared via the coprecipitation method can form a ZnFe<sub>2</sub>O<sub>4</sub> spinel structure after calcination. This structure significantly increases the catalyst's specific surface area and promotes the formation of Hägg iron carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>). ZnFe<sub>2</sub>O<sub>4</sub> separates into ZnO and Fe during the subsequent reduction stage. At this point, ZnO acts as a barrier, mitigating the agglomeration effect of Fe. N<sub>2</sub> adsorption-desorption results indicate a significant increase in the catalyst's specific surface area. XRD confirmed the formation and subsequent decomposition of ZnFe<sub>2</sub>O<sub>4</sub>. Mössbauer spectroscopy and XRD results indicated a significant reduction in catalyst particle size and a substantial improvement in dispersion. TEM analysis indicates reduced particle size and increased dispersion.

**Keywords:** Fe/Zn Catalysts; Fischer-Tropsch Synthesis; ZnFe<sub>2</sub>O<sub>4</sub> Spinel Structure; Catalyst Agglomeration; Mössbauer Spectroscopy

## 1. Introduction

Fischer-Tropsch synthesis refers to the process of converting synthesis gas ( $\text{CO} + \text{H}_2$ ) into high-value-added hydrocarbons through a series of chemical reactions. As global energy challenges become increasingly prominent, Fischer-Tropsch synthesis has garnered widespread attention as an effective countermeasure. For Fischer-Tropsch synthesis, appropriate catalysts can regulate the reaction rate and effectively enhance the selectivity of specific products. Metal catalysts are commonly employed as reactive agents, with Fe, Co, and Ru being typical examples. Among these, iron-based catalysts have garnered significant attention due to their low cost and high operational flexibility. [1–3]

Although iron-based catalysts exhibit lower activity than cobalt-based catalysts[4], they demonstrate higher water-gas shift (WGS) activity. This makes the catalyst suitable for converting syngas with a  $\text{H}_2/\text{CO}$  ratio below 2 produced from coal or biomass[5]. Fe-based catalysts are sensitive to promoter. Therefore, alkali metals (K, Na, Cs, Rb), inorganic oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ), and transition metals (Cu, Ru, Zn, Mn)[6] are typically incorporated into catalyst formulations to simultaneously enhance deactivation resistance and the selectivity for long-chain hydrocarbons[5].

Iron-based catalysts are prone to phase transitions during the reaction process, such as oxidation deactivation of the active phase or carbon deposition, which adversely affects catalytic performance and stability. [3, 7] Many researchers have sought to obtain catalysts with stable performance by adding structural aids/carriers. Structural promoter (such as  $\text{ZnO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) [8, 9] have a significant impact on the formation of iron carbide phases and the Fischer-Tropsch synthesis catalytic performance of iron-based catalysts. [10]

Iron carbides (particularly  $\chi\text{-Fe}_5\text{C}_2$ ) formed in the synthesis gas environment are considered the active phase responsible for activating CO and C-C bonding[11, 12]. To enhance carbon chain growth and durability in iron-based catalysts, researchers attempted to modify the catalyst by doping transition metals such as zinc (Zn), copper (Cu), manganese (Mn), and cobalt (Co) [13]. Numerous studies have demonstrated

that adding Zn as a promoter to iron-based catalysts exhibits unique advantages[14], ZnO is the most extensively studied metal oxide promoter[14], acting as a structural promoter to aid in the dispersion of iron species and thereby enhance the conversion of carbon monoxide. Zn and Fe can form a spinel structure of  $\text{ZnFe}_2\text{O}_4$ [15]. Within the resulting spinel lattice structure, the strong interaction between zinc and iron enhances surface alkalinity, thereby increasing the adsorption capacity for carbon monoxide (CO) and preventing iron sintering[16].

Studies indicate that Zn addition enhances the formation of iron carbides essential for promoting  $\text{C}_{5+}$  formation. [16] Zn also acts as a structural promoter, altering the size of iron species. [11]

In this study, by regulating different Fe/Zn ratios and evaluating Fischer-Tropsch reaction behavior, it was found that a Fe/Zn ratio of 2:1 generates a large amount of  $\text{ZnFe}_2\text{O}_4$  spinel structure<sup>16</sup>, significantly increasing the catalyst's specific surface area. During subsequent processing stages, it is reduced to Fe and ZnO[17]. At this point, ZnO acts as a barrier to inhibit agglomeration of the active components, generating a large amount of iron carbide. This reduces particle size, enhances dispersion, and thereby increases the proportion of  $\chi\text{-Fe}_5\text{C}_2$  formed. This achieves the dual functions of accelerating reaction rates and adjusting product distribution.

## 2. Experimental

### 2.1 Materials and Manufacturers

The materials used in the experiment included iron(III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), zinc(II) nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), all purchased from Aladdin Company. All reagents were of analytical grade, procured directly from commercial suppliers without additional purification.

### 2.2 Catalyst Preparation

The catalyst was prepared using the co-precipitation method[18]. Specifically, place a measured amount of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  into a beaker. Next, add 300 mL of deionized water to dissolve the solids. Place the beaker in a water bath and heat while stirring until the solution reaches 60°C. Titrate with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  to adjust the pH. During titration, a distinct red precipitate will form. Stop adding  $\text{NH}_3 \cdot \text{H}_2\text{O}$  when the pH reaches 9. After standing for 2 hours, a distinct red solid precipitate settles at the bottom of the beaker, with the upper layer remaining clear. Rinse repeatedly with deionized water until neutrality is achieved. Subsequently, calcine the mixture in a muffle furnace at 400°C under an air atmosphere for 4 hours to obtain the x-1-Fe-Zn catalyst (where x-1 represents the molar ratio of Fe to Zn).

### 2.3 Catalyst Characterization

The phase composition of the catalyst was characterized by using X-ray diffraction (XRD) to determine the crystal structure. XRD patterns were recorded using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the 10–80° range at scanning rates of 4°/min and 2°/min for both of produced catalysts after calcination 、 fresh and used catalysts, employing a Dandong Haoyuan Instrument Limited DX-27 mini X-ray diffractometer.

The particle size, dispersion, morphology, and elemental composition of the catalysts were analyzed by using high-resolution transmission electron microscopy (HRTEM, JEM-2100F) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. The sample preparation procedure is as follows: Take an appropriate amount

of catalyst and disperse it in anhydrous ethanol. Sonicate for 30 minutes. Using a needle, apply a small droplet of the suspension onto the surface of the support mesh. Allow it to dry at room temperature for later use.

The textural properties of the fresh catalysts were determined by using a Gemini VII 2390t physical adsorption instrument (Mack). Nitrogen (N<sub>2</sub>) was used as the adsorbate. The specific surface area, pore size, and pore volume were determined by using nitrogen adsorption–desorption iso-therms. The BET method was used to calculate the surface area, and the BJH method was used to analyze the pore size distribution. In the testing process, the foam tray was first weighed, and the sample tube and stopper were recorded. After the addition of 0.15–0.2 g of sample, degassing was performed at 200 °C under a vacuum of 1.33 Pa (10 μmHg) for 2 h before cooling. After being degassed, the sample tube and sample were weighed to ensure the mass change met the required standards. The sample tube was then mounted on the instrument, and nitrogen was introduced before the adsorption test.

The metal content of the catalyst was analyzed using an Agilent ICP-OES 720 inductively coupled plasma optical emission spectrometer. The sample preparation process involved: precisely weighing approximately 0.1 grams of sample into a 50-milliliter test tube, adding about 20 milliliters of aqua regia, and heating until the sample was completely dissolved. After the solution cooled to room temperature, it was transferred to a 100-milliliter volumetric flask and subsequently analyzed on the ICP-OES instrument.

The reduction characteristics of the active metal in the fresh catalyst were analyzed via hydrogen temperature-programmed reduction (H<sub>2</sub>–TPR). Approximately 50 mg of catalyst was placed in a quartz tube and heated from 80°C to 800°C at a rate of 10°C/min under a 5% H<sub>2</sub>/N<sub>2</sub> atmosphere (flow rate 50 mL/min), while hydrogen consumption was monitored.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo ESCALAB 250 instrument equipped with an Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The measurement voltage was set at 12 kV, and the measurement current at 20 mA. Prior to analysis, data calibration was performed using the C 1s standard binding

energy of 284.8 eV.

The Mössbauer spectra were measured at room temperature using a MR-351 conventional accelerator Mössbauer spectrometer (FAST, Germany). A triangular wave was employed as the reference signal to determine the phase state and content of iron compounds in the catalyst. The gas detector utilized a palladium matrix radioactive source containing 25 millicuries of  $^{57}\text{Co}$ . The Mössbauer spectra were processed using nonlinear least-squares fitting, modeling the spectra as single, double, and sextuple peaks with Lorentzian line shapes. Component identification was achieved through fitting parameters including isomer shift, quadrupole splitting, and hyperfine magnetic field  $H_{\text{hf}}$ . The hyperfine magnetic field was calibrated using the  $\alpha$ -Fe magnetic field at room temperature (330 kOe).

## 2.4 FTS Catalytic Reaction

The evaluation of fresh catalyst performance in Fischer-Tropsch synthesis was conducted in a fixed-bed reactor. This reactor employed a vertical stainless steel tubular structure with an inner diameter of 10 mm.

Place 0.5 grams of catalyst sample (strictly controlled to 40-60 mesh (1-2 mm)) into the reactor. To ensure axial centering of the catalyst bed and mitigate radial temperature gradients that could cause localized overheating, symmetrically pack graded quartz sand at both ends (including 10-20 mesh、20-40 mesh、40-60 mesh and 60-80 mesh), thereby establishing a thermally and hydrodynamically stable configuration.

Prior to the reaction, the catalyst is reduced in a hydrogen atmosphere at 400°C. The temperature is raised at a rate of 2°C/min until reaching 400°C, at which point reduction commences and continues for 6 hours. Following the reduction process, the temperature was allowed to drop below 100°C before introducing the synthesis gas mixture ( $\text{H}_2/\text{CO} = 2:1$ ). The temperature was raised from room temperature to 270°C at a rate of 1°C/min, and the reaction was initiated after temperature stabilization. The prepared  $\text{Fe}_{x-1}\text{-Fe-Zn}$  catalyst was evaluated under FTS conditions at 20 bar pressure and  $\text{WHSV} = 5400 \text{ mL}/(\text{g}\cdot\text{h})$ .

During the reaction process, the composition and concentration of the products were analyzed online using gas chromatography (GC). The gaseous products were analyzed using a gas chromatograph (Agilent 7890A) equipped with a 60/80-type Carboxen 1000 column. Wax, water, and oil products were collected in a hot trap (130 °C, 2 MPa) and a cold trap (10 °C, 2 MPa), respectively. Both the carbon balance and mass balance in the FTS process were maintained within the range of  $(100 \pm 5)\%$ , ensuring the accuracy and reliability of catalyst performance evaluation.

### 3.Results

#### 3.1 FTS Catalytic Performance

All newly prepared catalysts were reacted under isothermal conditions to simulate industrial operations. Prior to reaction, in-situ reduction was performed using hydrogen ( $H_2$ ) in a fixed-bed reactor. The primary objectives of this study were: to investigate the differences in Fischer-Tropsch behavior among Fe-Zn catalysts with varying ratios, and to examine the structural changes in the generated  $ZnFe_2O_4$  during the Fischer-Tropsch process.

Figure 1A–D shows the FTS performance of Fe-Zn catalysts with different ratios. FTS reaction test results indicate that CO conversion rates exhibit significant differences across Fe-Zn catalysts with varying Fe/Zn ratios. Comparison with Fe catalysts demonstrates that Zn addition substantially enhances CO conversion efficiency. Specifically, the 2-1-Fe-Zn catalyst exhibited the highest CO conversion rate, reaching 49%, while the Fe catalyst without Zn addition achieved only 30%. Moreover, the 2-1-Fe-Zn catalyst exhibited the lowest  $CH_4$  selectivity (13.61%) and the highest  $C_5^+$  selectivity (60.46%). This indicates that Zn addition promotes C-C bond formation, leading to increased production of long-chain hydrocarbons ( $C_{5+}$ ) while reducing the formation of smaller molecular products ( $C_{2-4}$ ). In summary, the addition of Zn significantly enhances the catalyst's activity, with the highest activity achieved at a Fe/Zn molar ratio of 2:1. Typically,  $CO_2$  generation is associated with the water-gas shift (WGS) reaction. As shown in Figure 2B, except for the 2-1-Fe-Zn

catalyst, the CO<sub>2</sub> selectivity of the remaining catalysts remained essentially identical (25%) after 192 hours. The global greenhouse effect issue is becoming increasingly prominent, making the optimization of the water-gas shift reaction and the adjustment of product distribution core research directions for the future. In summary, the addition of Zn<sup>2+</sup> not only enhances catalyst activity but also optimizes product distribution, thereby improving the yield of high-value products.

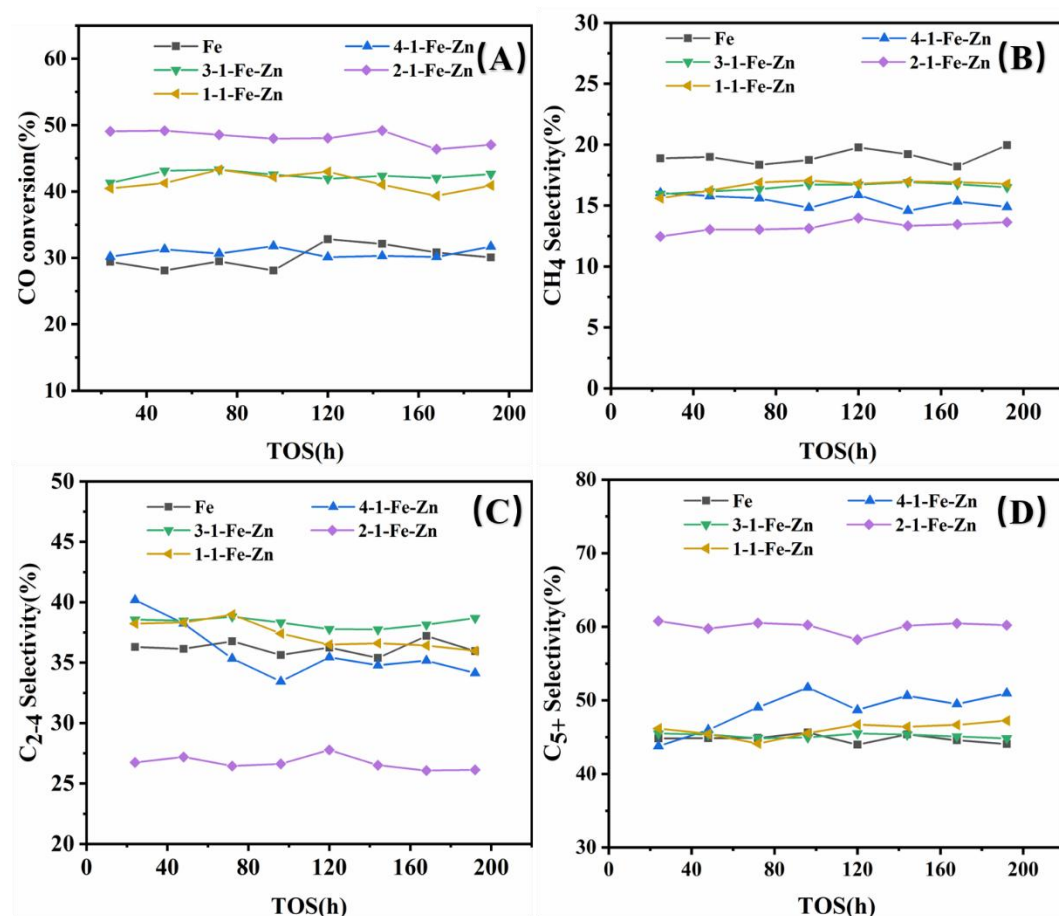


Figure 1. FTS catalytic performance of the produced catalysts: (A) CO conversion, (B) CH<sub>4</sub> selectivity, (C) C<sub>2</sub>–C<sub>4</sub> selectivity, and (D) C<sub>5+</sub> products selectivity.

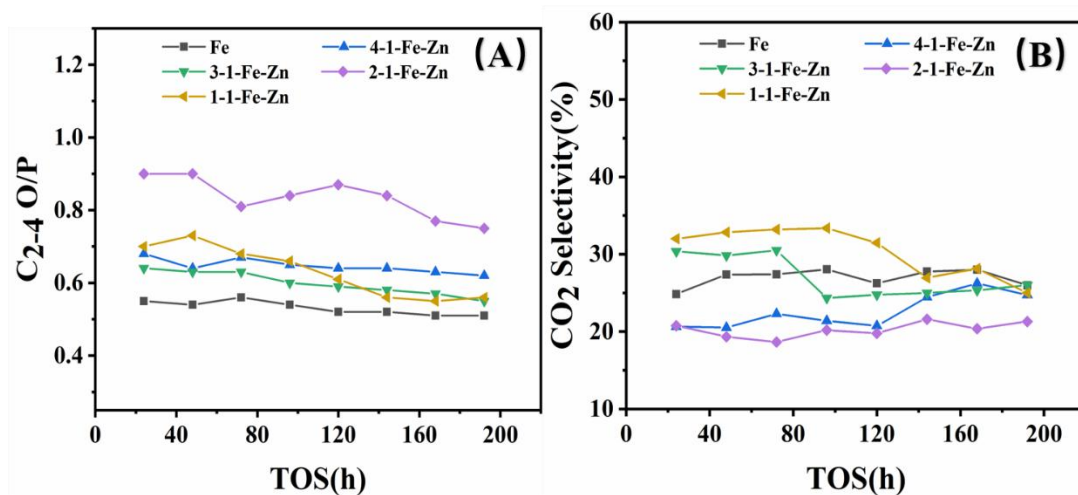


Figure 2. FTS catalytic performance of the produced catalysts: (A) C<sub>2-4</sub> O/P, (B) CO<sub>2</sub> Selectivity.

### 3.2 Characterization of the Catalysts

#### 3.2.1 Hole Structure Analysis

The textural properties of the catalyst were investigated by measuring N<sub>2</sub> adsorption-desorption isotherms. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was analyzed with the Barrett-Joyner-Halenda (BJH) method.

According to IUPAC classification, all samples exhibit Type IV isotherms. The hysteresis loops observed in all isotherms are primarily attributed to thermodynamic effects. The Fe catalyst formed an H<sub>1</sub>-type hysteresis loop, while the x-1-Fe-Zn catalyst formed an H<sub>2</sub>-type hysteresis loop. This phenomenon indicates that the addition of zinc alters the pore structure of the catalyst, reducing pore size, while also demonstrating that the catalyst exhibits a highly uniform pore size distribution. This uniformity promotes homogeneous diffusion of reactants within the catalyst, thereby enhancing reaction rate and selectivity.

The fabric properties of the catalyst were determined through physical adsorption and desorption of N<sub>2</sub>. The relevant results are summarized in Table 1. BET analysis indicates that catalysts with different Fe/Zn ratios exhibit variations in specific surface area and pore structure. The specific surface area and pore volume of a catalyst exert a significant influence on its catalytic performance.

It can be observed that the addition of Zn significantly increases the specific surface area of the catalyst, with 2-1-Fe-Zn exhibiting the largest specific surface area of  $149.64 \text{ m}^2\cdot\text{g}^{-1}$ , whereas the Fe catalyst only reaches  $47.36 \text{ m}^2\cdot\text{g}^{-1}$ . A larger specific surface area provides more active sites, increasing the contact between reactant molecules and the catalyst surface, thereby significantly enhancing reaction rates. Simultaneously, the magnitude of the specific surface area also influences the catalyst's selectivity. An appropriate specific surface area can both promote the target reaction pathway and suppress side reactions, thereby improving the purity and selectivity of the main product. For catalysts with mesoporous structures, the size of their specific surface area directly influences the number of reactant molecules that can access active sites. This may be one reason why the 2-1-Fe-Zn Fischer-Tropsch catalyst exhibits optimal performance. The increase in specific surface area can be attributed to the addition of Zn, which forms a spinel structure of  $\text{ZnFe}_2\text{O}_4$ . This structure enables more uniform dispersion of the active phase Fe. Following the subsequent reduction stage,  $\text{ZnFe}_2\text{O}_4$  undergoes phase separation to form Fe and ZnO, further preventing Fe agglomeration and enhancing Fe dispersion. In summary, BET analysis confirms that the catalyst exhibits the highest specific surface area and optimal pore size distribution at a Fe/Zn ratio of 2:1.

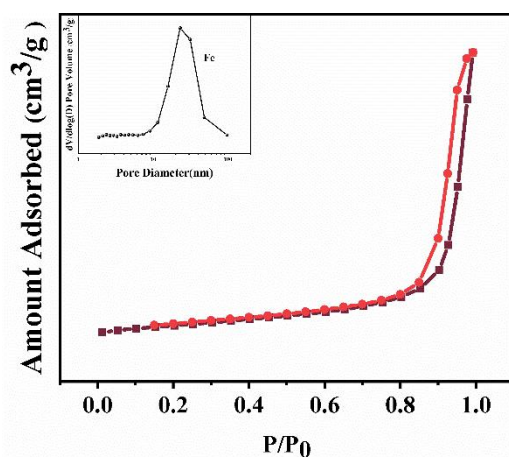


Figure 3.  $\text{N}_2$  adsorption-desorption and BJH pore size distribution curves of Fe catalysts.

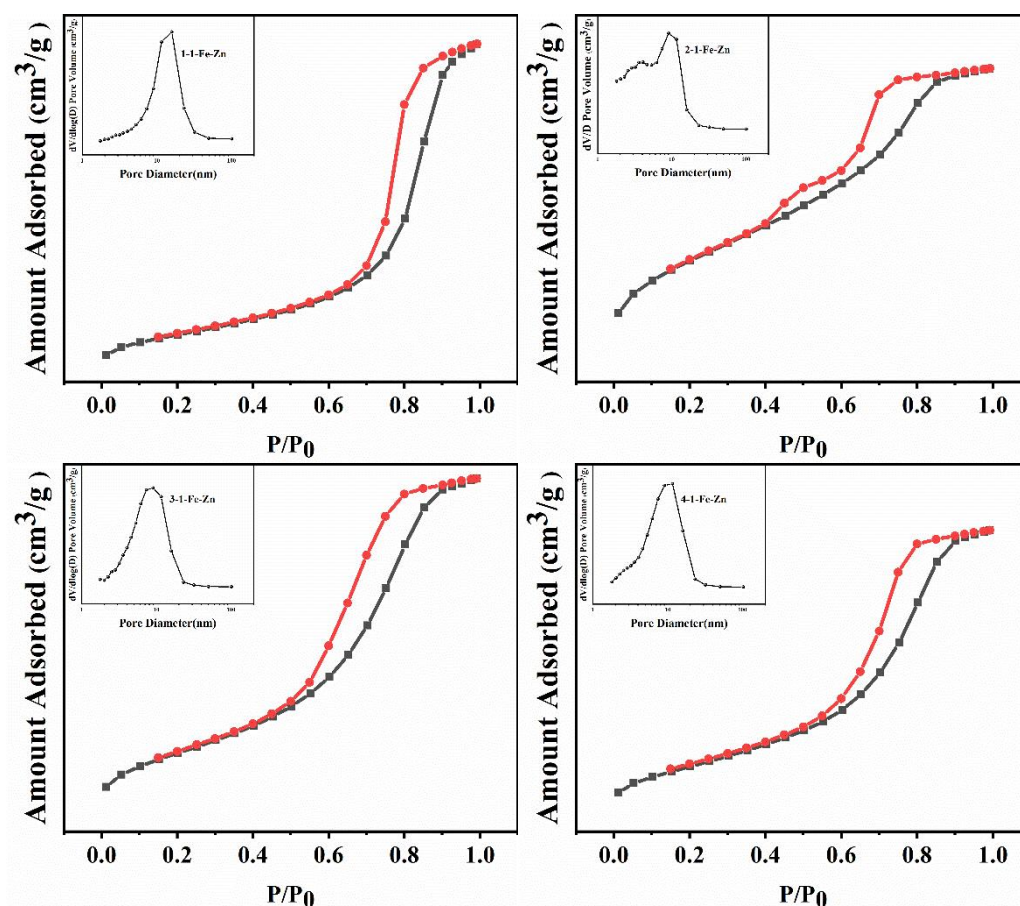


Figure 4. N<sub>2</sub> adsorption-desorption and BJH pore size distribution curves of x-1-Fe-Zn catalysts.

Table 1. The structural properties of various catalysts

| Catalysts | $S_{\text{BET}}(\text{m}^2 \cdot \text{g}^{-1})$ | $V_{\text{pore}} (\text{cm}^3 \cdot \text{g}^{-1})$ | $D_{\text{pore}} (\text{nm})$ |
|-----------|--------------------------------------------------|-----------------------------------------------------|-------------------------------|
| Fe        | 47.36                                            | 0.30                                                | 20.72                         |
| 4-1-Fe-Zn | 96.14                                            | 0.17                                                | 6.01                          |

|           |        |      |      |
|-----------|--------|------|------|
| 3-1-Fe-Zn | 97.53  | 0.18 | 6.43 |
| 2-1-Fe-Zn | 149.64 | 0.21 | 8.53 |
| 1-1-Fe-Zn | 69.87  | 0.14 | 5.43 |

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### 3.2.2 XRD

The crystal structures of the after calcination catalyst, fresh catalyst, and spent catalyst were analyzed using XRD . As shown in Figure 5A and 5B, the XRD results indicate that the addition of Zn formed a  $\text{ZnFe}_2\text{O}_4$  spinel structure (PDF#22-1012). The diffraction peak signal for  $\text{Fe}_2\text{O}_3$  (PDF#33-0664) was the weakest, suggesting the most uniform dispersion of  $\text{Fe}_2\text{O}_3$ . Simultaneously, the reduced fresh catalyst exhibits only two phases: Fe (PDF#06-0696) and ZnO (PDF#36-1451). This confirms that  $\text{ZnFe}_2\text{O}_4$  undergoes phase separation during the reduction stage (400°C, 4 h,  $\text{H}_2$  atmosphere), yielding Fe and ZnO. At this stage, ZnO acts as a barrier component, preventing excessive Fe aggregation. As shown in Figure 6, the XRD pattern of the spent catalyst reveals that a significant amount of Fe species remains after the reaction. This is attributed to the excessive aggregation of Fe species, which reduces the number of active sites participating in the reaction and results in the lowest CO conversion rate.

To gain a deeper understanding of specific iron phases and their content in both fresh and spent catalysts, Mössbauer spectroscopy analysis was conducted. The specific results will be presented in subsequent sections.

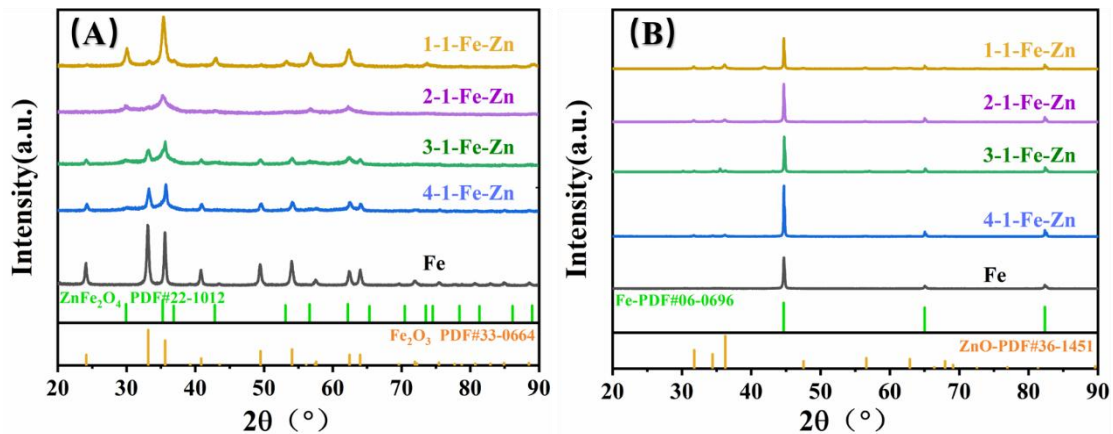


Figure 5. XRD patterns of (A) after calcination produced catalysts and (B) fresh produced catalysts.

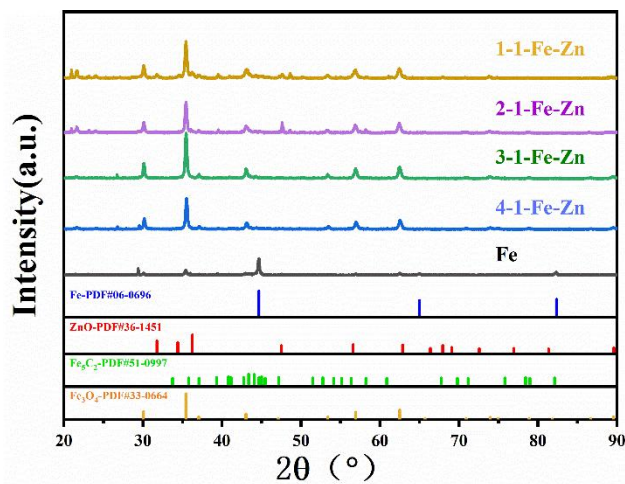


Figure 6. XRD patterns of spent catalysts.

### 3.2.3. Mössbauer spectra

The fitted curves are shown in Figures 7 and 8, with detailed data summarized in Tables 2 and 3. As shown in Table 2, the Fe-catalyzed superparamagnetic state without Zn addition exhibits an extremely low  $\text{Fe}^{3+}$  content of only 4.44%, consistent with the morphology observed in TEM, indicating severe Fe agglomeration. Moreover, in the x-1-Fe-Zn catalysts, both the 1-1-Fe-Zn and 2-1-Fe-Zn catalysts achieved 100% superparamagnetic  $\text{Fe}^{3+}$ , indicating that the particle sizes of these two catalysts were significantly smaller than those of other catalysts. This suggests that the addition of Zn contributes to enhancing the dispersion of iron compounds.

Figure 8 displays the Mössbauer spectra of the spent catalyst, with detailed data corresponding to Table 3. These spectra typically exhibit a central doublet peak

alongside multiple hexaples. Analysis revealed the presence of an iron carbide phase (specifically, Hägg iron carbide— $\chi$ -Fe<sub>5</sub>C<sub>2</sub>) within the catalyst, alongside Fe<sub>3</sub>O<sub>4</sub> and spm Fe<sup>3+</sup>. These results are consistent with the XRD findings. Notably, the Mössbauer spectroscopy of the spent Fe catalyst, along with the XRD results, simultaneously indicates that a significant amount of Fe phase remains after the reaction. This is likely due to severe agglomeration, which prevents a large portion of the Fe phase from participating in the reaction and hinders the formation of iron carbide. Meanwhile, Table 3 reveals that the  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> content of the spent 2-1-Fe-Zn catalyst reached 49.99%, consistent with its catalytic activity, exhibiting the highest C<sub>5</sub><sup>+</sup> selectivity and CO conversion capability. This further demonstrates that the formation of ZnFe<sub>2</sub>O<sub>4</sub> strongly promotes catalyst dispersion and the formation of iron carbide.

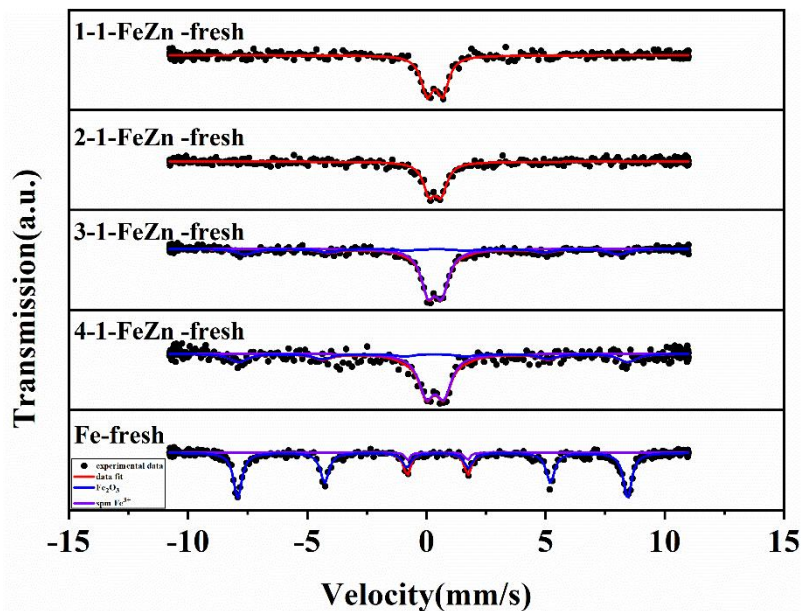


Figure 7. Mössbauer spectra of the fresh prepared catalysts .

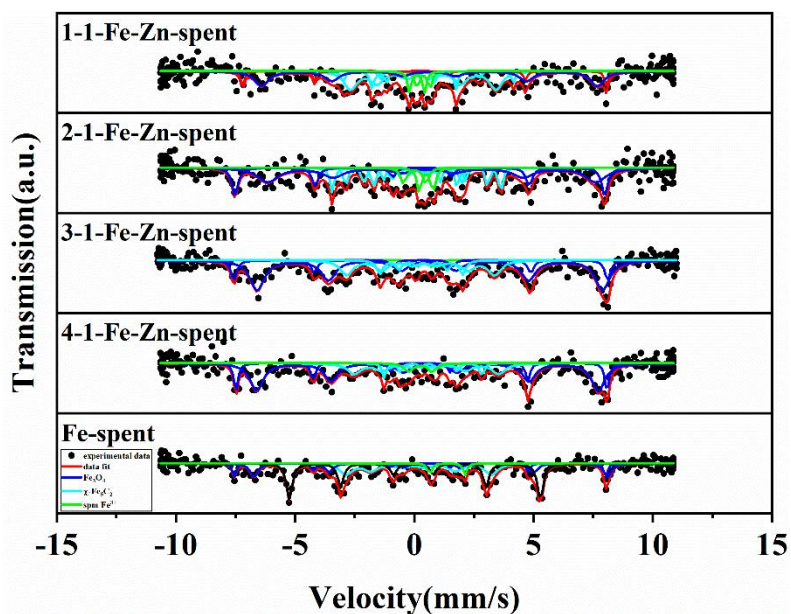


Figure 8. Mössbauer spectra of the spent prepared catalysts .

Table 3. Mössbauer analysis for iron phase compositions of the fresh catalysts

| Catalyst        | IS<br>(mms <sup>-1</sup> ) | QS<br>(mms <sup>-1</sup> ) | Hhf<br>(kOe) | Area<br>(%) | Phase                          | Composition<br>(%) |
|-----------------|----------------------------|----------------------------|--------------|-------------|--------------------------------|--------------------|
| Fe-fresh        | 0.37                       | -0.20                      | 508.3        | 95.56       | Fe <sub>2</sub> O <sub>3</sub> | 95.56              |
|                 | 0.46                       | 2.51                       |              | 4.44        | spm Fe <sup>3+</sup>           | 4.44               |
| 1-1-Fe-Zn-fresh | 0.35                       | 0.65                       | 486.6        | 100         | spm Fe <sup>3+</sup>           | 100                |
| 2-1-Fe-Zn-fresh | 0.36                       | 0.50                       |              | 100         | spm Fe <sup>3+</sup>           | 100                |
| 3-1-Fe-Zn-fresh | 0.31                       | -0.18                      | 507.3        | 27.9        | Fe <sub>2</sub> O <sub>3</sub> | 27.9               |
|                 | 0.35                       | 0.57                       |              | 72.1        | spm Fe <sup>3+</sup>           | 72.1               |
| 4-1-Fe-Zn-fresh | 0.33                       | -0.08                      | 507.3        | 34.5        | Fe <sub>2</sub> O <sub>3</sub> | 34.5               |
|                 | 0.36                       | 0.73                       |              | 65.5        | spm Fe <sup>3+</sup>           | 65.5               |

Table 4. Mössbauer analysis for iron phase compositions of the spent catalysts

| Catalyst        | IS<br>(mms <sup>-1</sup> ) | QS<br>(mms <sup>-1</sup> ) | Hhf<br>(kOe) | Area<br>(%) | Phase                                        | Composition<br>(%) |
|-----------------|----------------------------|----------------------------|--------------|-------------|----------------------------------------------|--------------------|
| Fe-spent        | 0.25                       | -0.03                      | 484.1        | 9.5         | Fe <sub>3</sub> O <sub>4</sub> (A)           | 9.5                |
|                 | 0.71                       | -0.03                      | 461.1        | 20.1        | Fe <sub>3</sub> O <sub>4</sub> (B)           | 20.1               |
|                 | 0.07                       | 0.23                       | 189.6        | 26.22       | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)  | 26.22              |
|                 | 0                          | 0.06                       | 327.4        | 39.99       | $\alpha$ -Fe                                 | 39.99              |
|                 | 1.38                       | 1.48                       |              | 4.19        | spm Fe <sup>3+</sup>                         | 4.19               |
| 1-1-Fe-Zn-spent | 0.27                       | -0.09                      | 482.0        | 20.83       | Fe <sub>3</sub> O <sub>4</sub> (A)           | 20.83              |
|                 | 0.65                       | 0.15                       | 427.7        | 35.53       | Fe <sub>3</sub> O <sub>4</sub> (B)           | 35.53              |
|                 | 0.01                       | 0.15                       | 219.6        | 12.72       | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (I)   | 12.72              |
|                 | 0.26                       | -0.32                      | 185.3        | 9.08        | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)  | 9.08               |
|                 | 0.06                       | -0.03                      | 109.1        | 9.80        | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III) | 9.80               |
|                 | 0.01                       | 0.94                       |              | 5.36        | spm Fe <sup>3+</sup>                         | 5.36               |
|                 | 0.49                       | 0.57                       |              | 6.67        | spm Fe <sup>3+</sup>                         | 6.67               |
| 2-1-Fe-Zn-spent | 0.33                       | 0.18                       | 474.1        | 8.05        | Fe <sub>3</sub> O <sub>4</sub> (A)           | 8.05               |
|                 | 0.62                       | 0.01                       | 437.7        | 30.56       | Fe <sub>3</sub> O <sub>4</sub> (B)           | 30.56              |
|                 | 0.61                       | -0.08                      | 222.1        | 6.66        | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (I)   | 6.66               |
|                 | 0.27                       | 0.19                       | 189.7        | 33.17       | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)  | 33.17              |
|                 | -0.08                      | 0.14                       | 109.2        | 10.16       | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III) | 10.16              |
|                 | 0.11                       | 0.62                       |              | 6.06        | spm Fe <sup>3+</sup>                         | 6.06               |
|                 | 0.37                       | 0.54                       |              | 5.34        | spm Fe <sup>3+</sup>                         | 5.34               |
| 3-1-Fe-Zn-spent | 0.30                       | -0.07                      | 487.5        | 13.79       | Fe <sub>3</sub> O <sub>4</sub> (A)           | 13.79              |
|                 | 0.61                       | 0.05                       | 450.3        | 51.71       | Fe <sub>3</sub> O <sub>4</sub> (B)           | 51.71              |
|                 | 0.35                       | -0.17                      | 192.8        | 22.25       | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)  | 22.25              |
|                 | 0.32                       | -0.07                      | 107.9        | 100         | $\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III) | 10.2               |
|                 | 0.43                       | 0.64                       |              | 2.05        | spm Fe <sup>3+</sup>                         | 2.05               |

|            |      |       |       |       |                                    |       |
|------------|------|-------|-------|-------|------------------------------------|-------|
| 4-1-Fe-Zn- | 0.27 | 0.04  | 483.7 | 16.5  | $\text{Fe}_3\text{O}_4(\text{A})$  | 16.5  |
| spent      | 0.60 | -0.10 | 445.3 | 50.86 | $\text{Fe}_3\text{O}_4(\text{B})$  | 50.86 |
|            | 0.44 | 0.11  | 188.4 | 19.78 | $\chi\text{-Fe}_5\text{C}_2$ (II)  | 19.78 |
|            | 0.69 | 0.18  | 127.6 | 7.79  | $\chi\text{-Fe}_5\text{C}_2$ (III) | 7.79  |
|            | 0.25 | 0.98  |       | 5.08  | spm $\text{Fe}^{3+}$               | 5.08  |

### 3.2.4 TEM

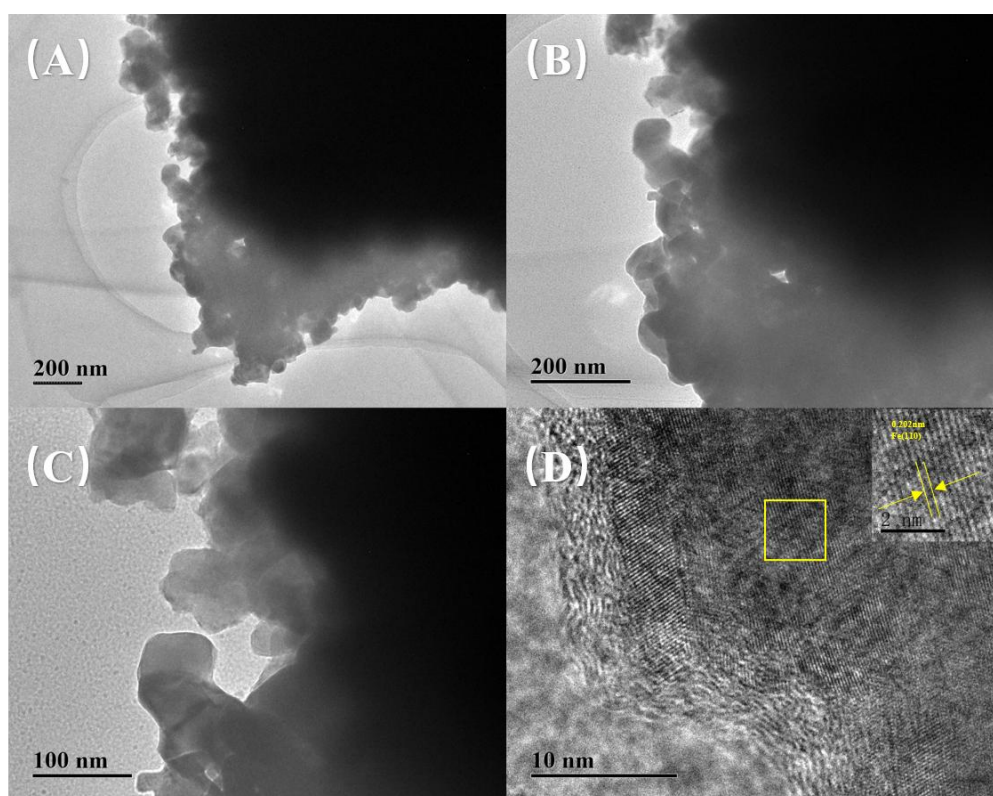


Figure 9. TEM images of fresh produced catalysts of Fe

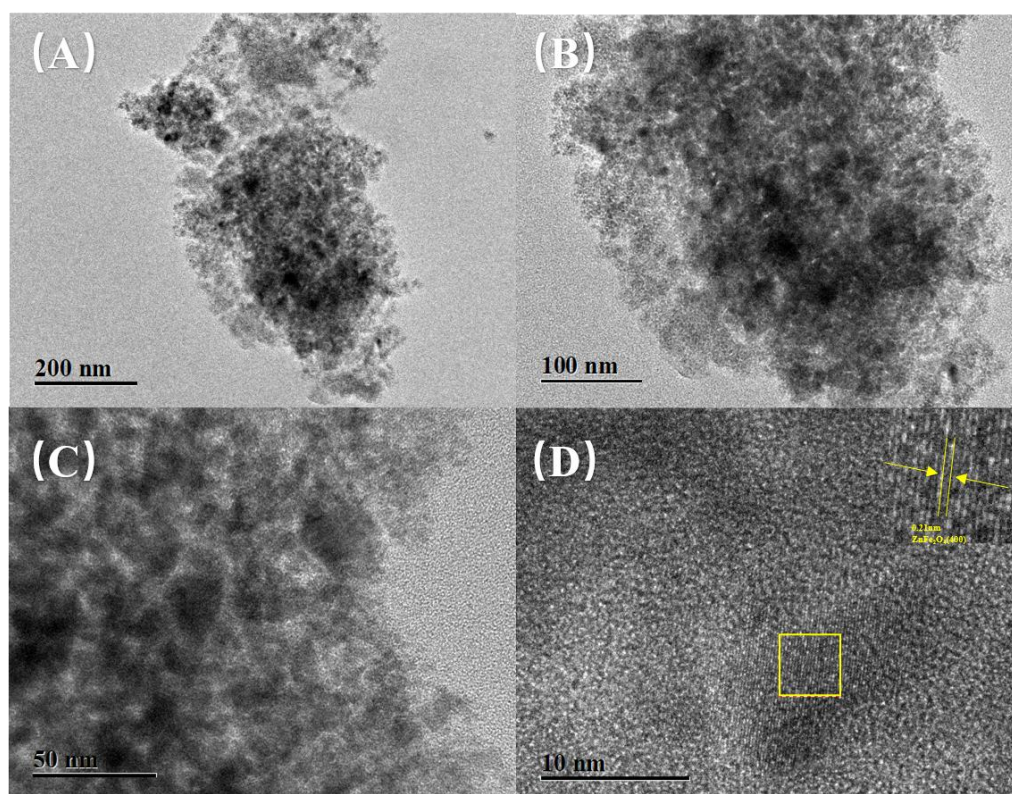


Figure 10. TEM images of after calcination produced catalysts of 2-1-Fe-Zn

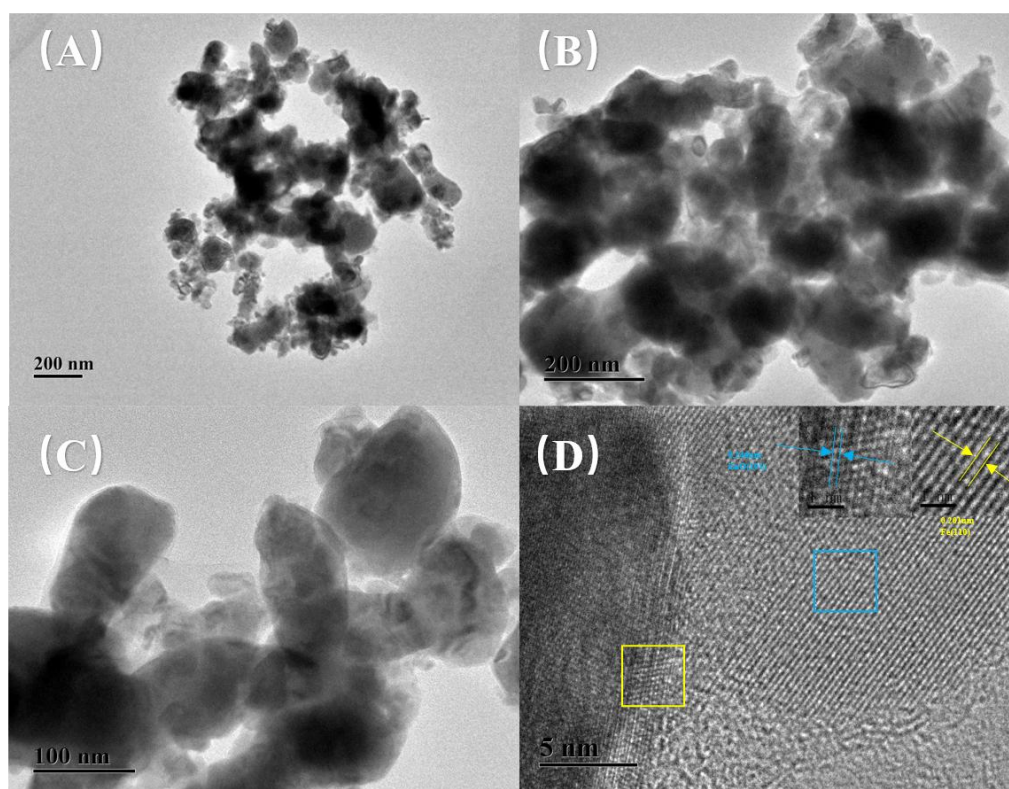


Figure 11. (A–C) TEM and (D) HRTEM images of fresh catalysts of 2-1-Fe-Zn

The morphology of some catalysts was observed using transmission electron microscopy (TEM). Transmission electron microscopy images reveal that all catalyst samples exhibit uniformly dispersed active components. As shown in Figures 9-11, the images depict a fresh Fe catalyst, a 2-1-Fe-Zn catalyst of after calcination, and a fresh 2-1-Fe-Zn catalyst, respectively. Figure 9 reveals that the Fe catalyst exhibits significant agglomeration, consistent with the BET results. The HRTEM image in Figure 5D reveals highly crystalline  $\alpha$ -Fe nanoparticles (with a calculated interplanar spacing of 0.202 nm, corresponding to the (110) crystal plane). Figure 10 shows the calcined 2-1-Fe-Zn catalyst, where improved dispersion is clearly visible. The HRTEM image in Figure 10D reveals highly crystalline  $\text{ZnFe}_2\text{O}_4$  nanoparticles (with a calculated interplanar spacing of 0.21 nm corresponding to the (400) plane). Figure 11 shows the fresh 2-1-Fe-Zn catalyst. Comparing Figures 11 and 9, the fresh 2-1-Fe-Zn catalyst exhibits smaller particle sizes, demonstrating improved dispersion of the active phase. The HRTEM image in Figure 11D reveals highly crystalline ZnO nanoparticles (with a calculated interplanar spacing of 0.246 nm, corresponding to the (101) plane) and highly crystalline  $\alpha$ -Fe nanoparticles (with a calculated interplanar spacing of 0.201 nm, corresponding to the (110) plane). Corresponding to the XRD results, this indicates that  $\text{ZnFe}_2\text{O}_4$  was reduced to Fe and ZnO.

The elemental composition of fresh Fe catalysts and 2-1-Fe-Zn catalysts was further analyzed using transmission electron microscopy/energy dispersive spectroscopy (TEM/EDS) elemental mapping techniques, as shown in Figures 12 and 13. Energy-dispersive X-ray spectroscopy analysis indicates the presence of Fe, Zn, and O elements in the 2-1-Fe-Zn catalyst, exhibiting uniform spatial distribution.

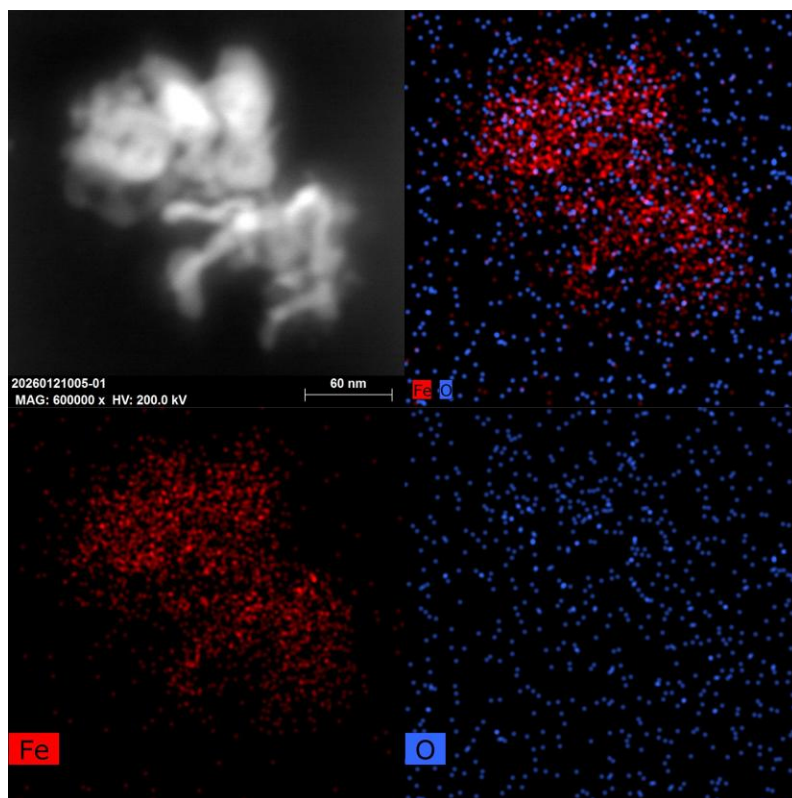


Figure 12.EDS mapping analysis of Fe catalyst showing the presence of Fe in the catalyst.

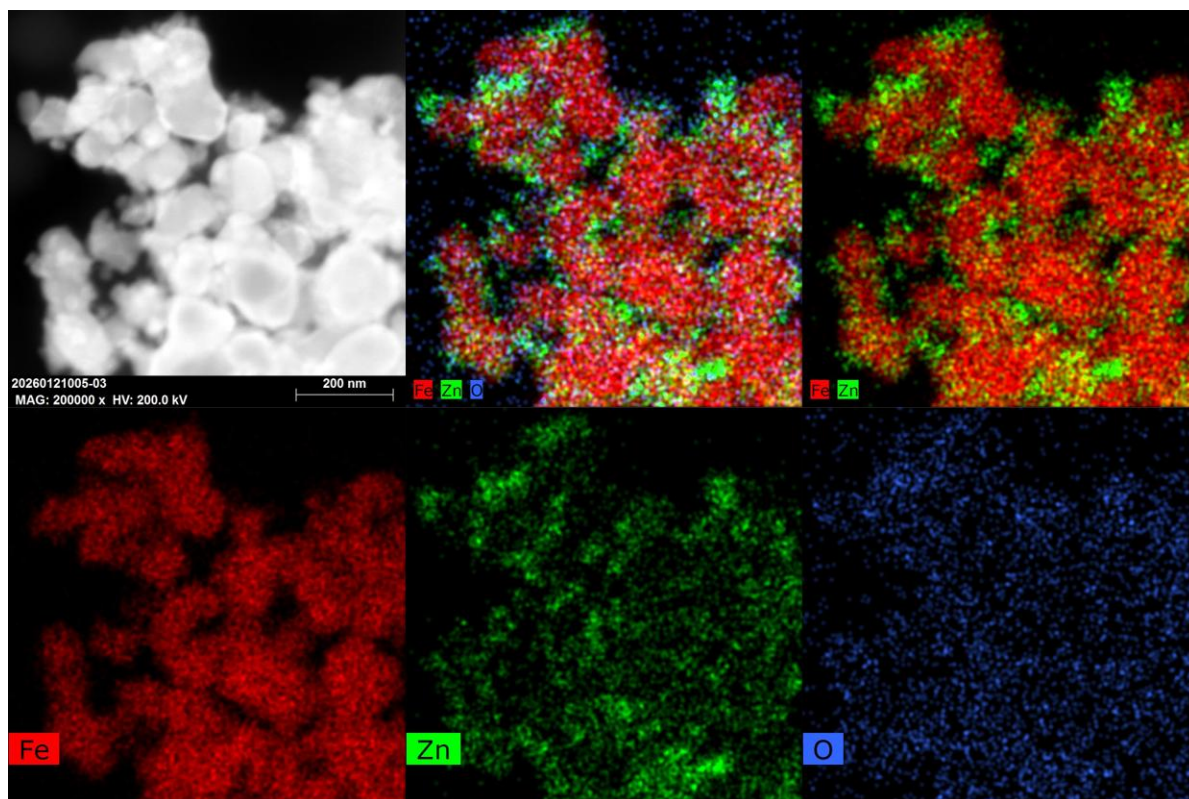


Figure 13. EDS mapping analysis of the 2-1-Fe-Zn catalyst showing the presence of

all the elements Fe、 O and Zn in the catalyst.

### 3.2.5 XPS

To gain deeper insight into the surface microstructure and electron transfer states of the new catalyst, we performed XPS analysis on freshly prepared catalyst material. Figure 14 shows the Fe 2*p* XPS spectra for each catalyst. In the deconvoluted Fe 2*p* spectra of all catalysts, two main peaks and two satellite peaks are observed, corresponding to the spin-orbit doublet Fe<sup>3+</sup> 2*p*<sub>1/2</sub> and Fe<sup>3+</sup> 2*p*<sub>3/2</sub> states, respectively. In the Fe catalyst, a peak appears at 710.60 eV, while the peaks in the x-1-Fe-Zn catalysts are all located near 710.5 eV, which are typical peak positions for Fe<sup>3+</sup>. It can also be observed that after Zn addition, the peak positions all shift toward lower binding energies, with the 2-1-Fe-Zn complex exhibiting the lowest binding energy, whose peak appears at 710.47 eV. Figure 13 displays the Zn 2*p* XPS spectra for each catalyst. It is clearly evident that no Zn 2*p* peak appears in the Fe catalyst, while all x-1-Fe-Zn catalysts exhibit two distinct peaks. The main peak occurs near 1021.3 eV, corresponding to the characteristic diffraction peak position of Zn<sup>2+</sup>. This confirms the simultaneous presence of both ZnO and Fe<sub>2</sub>O<sub>3</sub> within the catalysts. Corresponding to the XRD results, a spinel structure of ZnFe<sub>2</sub>O<sub>4</sub> was observed.

In comparison, the binding energies in the Zn 2*p* spectrum of the x-1-Fe-Zn catalyst have shifted toward higher binding energies, indicating a potential electron transfer from Zn<sup>2+</sup> to Fe<sup>3+</sup>. Simultaneously, Fe<sup>3+</sup> gains electrons, leading to enhanced reaction rates. The Zn 2*p* peak in the 2-1-Fe-Zn catalyst exhibits the highest binding energy, indicating that Fe<sup>3+</sup> in this catalyst has acquired more electrons. This may also explain why this catalyst demonstrates the highest reaction rate. This may also be why this catalyst performs best. By fitting the O 1*s* peak, characteristic peaks at 533.32 eV, 531.71 eV, and 529.79 eV were assigned to lattice oxygen, oxygen vacancies, and surface hydroxyl groups.

Simultaneously, by calculating the area of convolutionable peaks, it was found that the peak area corresponding to oxygen vacancies in the Fe catalyst was 955, while the peak areas corresponding to oxygen vacancies in the x-1-Fe-Zn (x=1, 2, 3, 4)

catalysts were 1029.25, 1258.51, 1021.99, and 1073, respectively. The 2-1-Fe-Zn catalyst exhibited the largest peak area. A larger oxygen vacancy peak area indicates a higher number of oxygen vacancies in the catalyst. Numerous experiments have demonstrated that an increase in oxygen vacancies promotes the Fischer-Tropsch reaction[19].

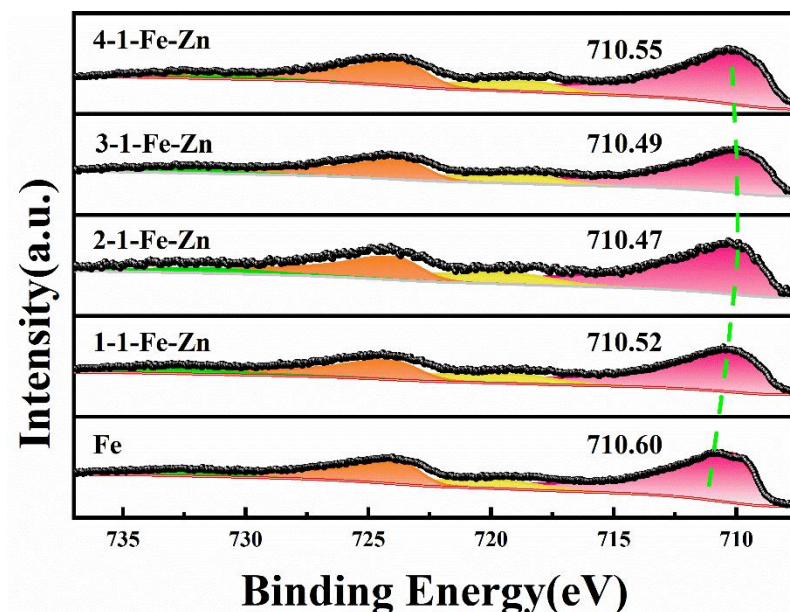


Figure 14.XPS of the catalysts Fe 2*p*

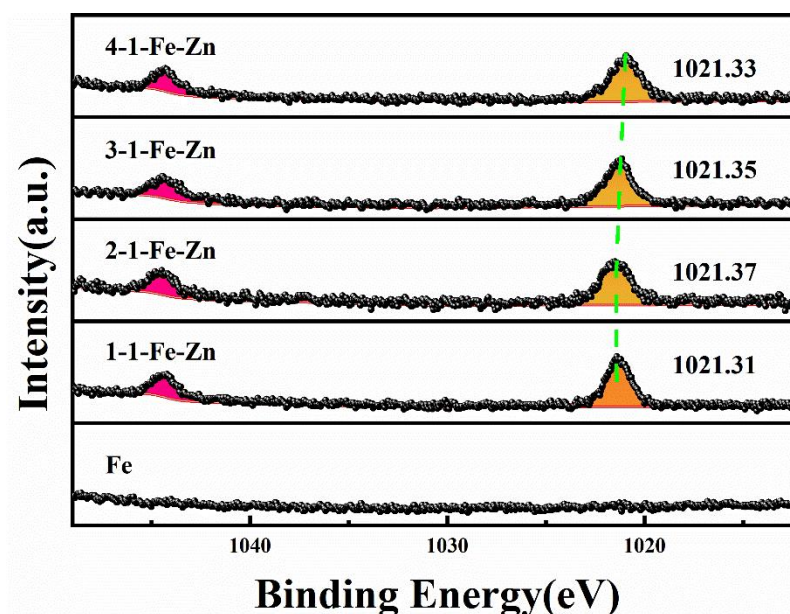


Figure 15.XPS of the catalysts Zn 2*p*

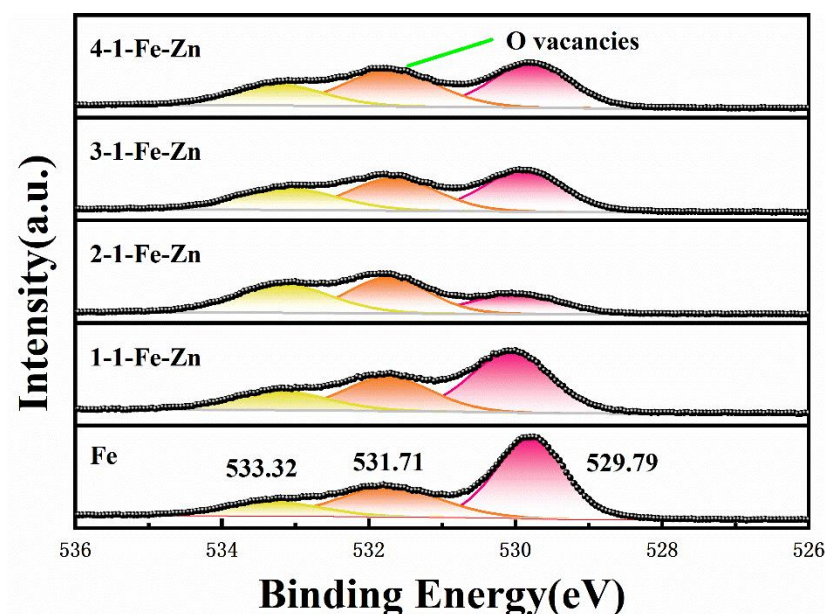


Figure 16.XPS of the catalysts O1s

### 3.2.6 H<sub>2</sub>-TPR

The prepared catalyst was characterized using hydrogen-temperature-programmed reduction (H<sub>2</sub>-TPR) to investigate the reduction behavior of active metal species within the catalyst. As shown in Figure 17, using Fe catalyst reduction as a reference, the reduction of Fe<sub>2</sub>O<sub>3</sub> typically occurs in three stages: a reduction peak at 300–400°C corresponds to Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> reduction, a peak at 420–580°C corresponds to Fe<sub>3</sub>O<sub>4</sub> → FeO reduction, while the peak observed between 580–800°C corresponds to the reduction of FeO → Fe<sup>0</sup>. As clearly shown in Figure 17, the catalyst exhibits two reduction peaks, which result from the coalescence of the reduction peak appearing between 420–580°C and the reduction peak appearing between 580–800°C.

It can be observed that compared to the Fe catalyst, the reduction temperature of the x-1-Fe-Zn catalysts is significantly lower, indicating enhanced reducibility. Specifically, among the x-1-Fe-Zn catalysts, the 2-1-Fe-Zn catalyst exhibits the lowest reduction temperature, meaning it demonstrates the greatest improvement in reducibility.

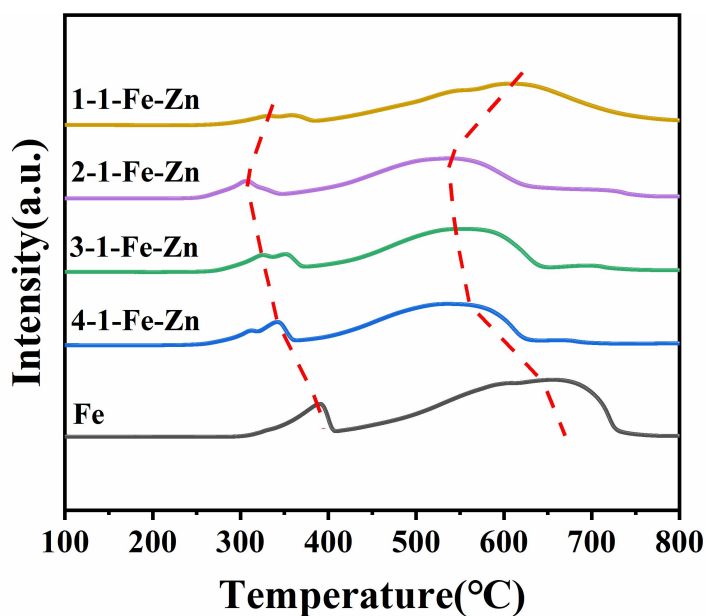


Figure 17.  $H_2$ -TPR curves of the as-prepared catalysts.

### 3.2.7 CO-TPD

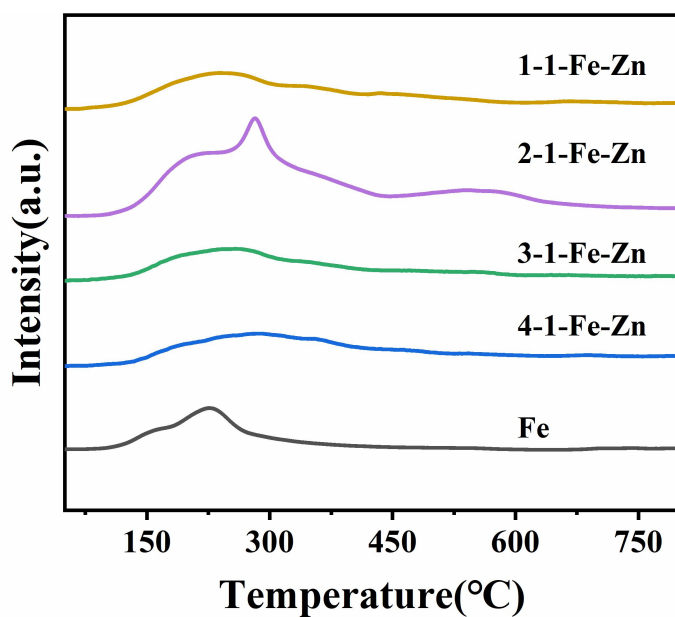


Figure 18. CO-TPD curves of as-prepared catalysts.

Figure 18 illustrates the adsorption behavior of CO on iron-based catalysts. The desorption peak observed around 200°C corresponds to the weak adsorption of CO on the iron oxide surface. Desorption peaks generated at higher temperatures correspond to CO adsorption on the iron carbide surface, indicating dissociative CO adsorption. Concurrently, it is clearly observable that the 2-1-Fe-Zn catalyst exhibits the largest desorption peak area, demonstrating enhanced reducibility and carburizing capability.

Evidently, the formation of  $\text{ZnFe}_2\text{O}_4$  significantly increases the Fe-Zn interactions within the catalyst.

### 3.3 Discussion

Iron-based catalysts have garnered significant attention due to their water-gas shift (WGS) activity, which enables them to maintain considerable reactivity even under low  $\text{H}_2/\text{CO}$  ratios. Simultaneously, iron carbides (eg.  $\chi\text{-Fe}_5\text{C}_2$ ) have garnered significant attention as active phases in Fischer-Tropsch synthesis (FTS) due to their ability to enhance the yield and selectivity of  $\text{C}_{5+}$  hydrocarbons. They not only effectively promote CO hydrogenation and C-C coupling reactions but also reduce the formation of  $\text{CO}_2$  byproducts during the reaction process.

Analysis of nitrogen isothermal adsorption-desorption isotherms yields the BET specific surface area of the catalyst. Calculations indicate that the BET specific surface area of the Zn-doped catalyst increases significantly, reaching a maximum at a Fe/Zn molar ratio of 2:1. This may be attributed to the extensive formation of  $\text{ZnFe}_2\text{O}_4$ , whose structure enhances the catalyst's specific surface area by providing more active sites. This may be one reason why the 2-1-Fe-Zn catalyst exhibits the best Fischer-Tropsch behavior.

Particle size and dispersion are critical factors for enhancing catalyst activity[20]. TEM analysis clearly shows that after Zn addition, the catalyst particle size decreases and dispersion significantly improves. This corresponds to the peak shapes observed in XRD and is consistent with the Fischer-Tropsch behavior of the catalyst.

The formation of iron carbide is related to the reducibility of the catalyst. The formation of the active phase of iron carbide is essentially a multistep process driven by the reducibility of the catalyst. Specifically, iron oxide (such as  $\text{Fe}_2\text{O}_3$ ) is reduced to active metallic iron under suitable conditions. This metallic iron serves as the starting point for the carbonization reaction, interacting with carbon to ultimately form a highly catalytic metal-carbon composite structure. The  $\text{H}_2$ -TPR results reveal that the formation of  $\text{ZnFe}_2\text{O}_4$  reduces the reduction temperature[21], thereby

enhancing the catalyst's reducibility. The lowest reduction temperature and strongest reducibility are achieved at a Fe/Zn ratio of 2:1.

Iron carbides not only play a crucial role in enhancing catalytic activity but also directly regulate the distribution of reaction products. During Fischer-Tropsch synthesis (FTS), the formation of iron carbides promotes chain-growth reactions, thereby increasing the production of long-chain hydrocarbons. Multiple studies consistently indicate that when the proportion of iron carbide phase in iron-based catalysts reaches a higher level, the selectivity of C<sub>5+</sub> hydrocarbon products shows a significant upward trend. Particularly in gas-solid catalytic reaction environments, iron carbides can effectively suppress the formation of byproducts such as CH<sub>4</sub> and CO<sub>2</sub>, thereby enhancing the yield of C<sub>5+</sub> products. The incorporation of zinc (Zn) significantly increases the catalyst's specific surface area by forming a ZnFe<sub>2</sub>O<sub>4</sub> spinel structure. This effectively suppresses agglomeration of the active components while exposing more surface active sites. These factors collectively promote the extensive formation of iron carbides.

Iron carbides, with their outstanding structural stability and catalytic activity, make them an ideal choice for regulating product selectivity. Among various iron carbides, Hägg iron carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>) exhibits a particularly pronounced promoting effect on C-C coupling reactions. Based on Mössbauer spectroscopy-based phase composition analysis, the relative content of  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> increased in the x-1-Fe-Zn series catalysts prepared by introducing Zn into pure Fe catalysts without Zn addition. Among these, the 2-1-Fe-Zn catalyst exhibited the highest  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> proportion, which increased significantly from 26.22% to 49.99%.

The increase in  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> phase content is closely related to its enhanced ability to promote the formation of long-chain hydrocarbons. Compared to the Fe catalyst without Zn addition, the significantly higher  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> content in the 2-1-Fe-Zn catalyst directly correlates with the following improvements in catalytic performance: enhanced CO conversion rate, increased selectivity for C<sub>5+</sub> products, and simultaneously suppressed CH<sub>4</sub> selectivity.

Systematic XRD phase analysis of the catalyst further revealed the structural role

of Zn: XRD results of calcined samples indicated that Zn addition induced the formation of a  $\text{ZnFe}_2\text{O}_4$  spinel structure, with its content peaking at a Fe/Zn molar ratio of 2:1. The XRD pattern of the fresh catalyst after reduction treatment indicates that the preformed  $\text{ZnFe}_2\text{O}_4$  underwent phase separation, converting into metallic Fe and ZnO. The XRD patterns of the post-reaction catalysts reveal that a significant amount of unreacted iron phases remain in the Fe catalyst without Zn addition. This finding is corroborated by Mössbauer spectroscopy analysis. This phenomenon may stem from severe agglomeration of Fe phases within the pure Fe catalyst, preventing certain Fe species from effectively participating in the reaction. Conversely, the incorporation of Zn significantly suppresses this agglomeration, thereby enhancing the dispersion of the active phase. Furthermore, only in the post-reaction XRD pattern of the 2-1-Fe-Zn catalyst can the diffraction peak characteristic of  $\text{Fe}_5\text{C}_2$  be clearly observed, whereas this signal is weak or indistinct in other catalysts. This corresponds to the Mössbauer spectroscopy results indicating that the 2-1-Fe-Zn catalyst contains the highest proportion of  $\chi\text{-Fe}_5\text{C}_2$ .

XPS results indicate that compared to the pure Fe catalyst, the Zn-doped catalyst exhibits enhanced electron-donating ability, with the 2-1-Fe-Zn catalyst demonstrating the strongest electron-donating capacity. The Fe 2p<sub>3/2</sub> binding energy of  $\text{Fe}^{3+}$  decreased from 710.6 eV to 710.47 eV. This indicates increased electron density around the iron species. The enhanced electron density promotes the formation of  $\chi\text{-Fe}_5\text{C}_2$ . This corresponds to the 2-1-Fe-Zn catalyst containing the highest amount of  $\chi\text{-Fe}_5\text{C}_2$  in the Mössbauer spectrum.

## 4.CONCLUSION

This study aims to investigate the effect of the Fe/Zn molar ratio on the catalyst performance in the Fischer-Tropsch synthesis (FTS). Multiple catalysts with atomically uniform distribution were prepared via the coprecipitation method. Through characterization techniques such as XRD, Mössbauer spectroscopy, N<sub>2</sub> adsorption-desorption (BET), XPS, and hydrogen-temperature-programmed reduction (H<sub>2</sub>-TPR). The addition of Zn was found to suppress the agglomeration of Fe species, resulting in smaller catalyst particles. Furthermore, Fe/Zn catalysts prepared via the coprecipitation method formed a spinel structure of ZnFe<sub>2</sub>O<sub>4</sub>, significantly enhancing the catalyst's specific surface area, reducibility, and the proportion of  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>. This active phase enhances selectivity for long-chain hydrocarbons. Catalytic performance evaluation in a fixed-bed reactor demonstrates that the 2-1-Fe-Zn Fischer-Tropsch catalyst exhibits markedly superior behavior compared to other catalysts. These findings not only elucidate the regulatory mechanism of Zn additives but also provide key parameters for the rational design of industrial-scale iron-based Fischer-Tropsch synthesis catalysts. This is expected to advance the development of efficient, low-carbon emission FTS technology. Future research may further extend to catalyst stability optimization and scale-up preparation, accelerating its industrial application.

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