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Effect of pretreatment conditions on Fe-ZSM-5 properties and performance for Fischer-Tropsch synthesis

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Abstract

Iron supported on ZSM-5 is a widely studied catalyst for Fischer-Tropsch synthesis (FTS). Iron is activated with H₂, CO, or a mixture of CO and H₂ prior to FTS, resulting in phase transformations that make it challenging to understand structure-property relationships. In this work, we demonstrate that increasing the pretreatment temperature of Fe-Na-ZSM-5 reduces CO conversion irrespective of the reductant, but the product selectivity, iron particle size, composition, CO adsorption properties, and zeolite structure is dependent on both the pretreatment temperature and reductant. Pretreatment of Fe-Na-ZSM-5 in H₂ induces sintering of iron particles, increasing C₂-C₄ olefins and C₅₊ hydrocarbons selectivity from 19.0% and 14.0% at 350 °C to 28.2% and 25.4% at 770 °C, respectively. Conversely, CO pretreatment facilitates carbide formation, coke deposition, and CH₄ formation.

1.0 Introduction

Iron-based catalysts are widely used for the conversion of carbon monoxide (CO) to hydrocarbons via Fischer Tropsch synthesis (FTS), offering advantages such as high activity, hydrocarbon selectivity, limited methane (CH₄) selectivity, and improved water-gas shift activity compared to other active FTS metals like cobalt.¹⁻³ Iron-based catalysts are often pretreated with hydrogen (H₂), CO, or a CO-H₂ mixture at temperatures ranging from 250 to 800 °C to activate the catalyst, leading to the formation of iron oxides and/or carbides with the desired performance.⁴⁻⁶ Bian et al.⁷ studied precipitated iron oxides (Fe₂O₃) and reported that the surface area of CO-pretreated Fe₂O₃ remained similar to the as-synthesized catalyst, but the surface area of the H₂-pretreated sample was five times lower, potentially due to sintering. Ding et al.⁸ observed that H₂-pretreated iron supported on silica (Fe-Mn-K-SiO₂) exhibited a higher surface area than CO or CO-H₂ pretreated catalysts, possibly attributed to pore blockage by carbonaceous species.

The complexity of the *in situ* transformation of iron adds to the importance of selecting appropriate pretreatment conditions, as iron undergoes conversion into combinations of metallic iron (Fe⁰), iron oxides (Fe₃O₄, FeO), and/or carbides (Fe₅C₂, Fe₃C, Fe₇C₃) during pretreatment. Because FTS is a structure sensitive reaction,^{9, 10} understanding how the pretreatment conditions affect the reactor performance is critically important.¹¹⁻¹⁴ Existing studies on the effect of pretreatment conditions on the performance of iron-based catalysts have primarily focused on precipitated iron,^{7, 15-20} promoted precipitated iron,^{8, 18, 21-23} and iron supported on silica.²⁴⁻²⁸ SBA-15 has been used because of high surface area (700 – 1040 m²/g) and a narrow pore-size distribution (5 – 30 nm) that enables introduction of iron nanoparticles within the pores of the support, minimizing iron migration to the outer surface, and subsequent aggregation during pretreatment and reaction.^{27, 29} Similar characteristics are present in ZSM-5 zeolites, with the added benefit of tunable acidity that can be leveraged to control FTS performance.^{30, 31} Although ZSM-5 is an extensively studied support for iron-based catalysts, studies on the effect of pretreatment conditions on iron-supported on ZSM-5 (Fe-ZSM-5) are lacking. This can be seen in the **Table 1** summary of collected Fe-based catalysts and pretreatment conditions that have been studied for FTS.^{7, 8, 15, 18-27 32, 33}

Understanding the effect of FTS pretreatment conditions on Fe-ZSM-5 can be challenging because when CO is used as the reductant, CO dissociation results in carbon deposition, reduction of surface area, and in turn, decreased FTS activity.¹⁷ In contrast, pretreating Fe-ZSM-5 with H₂ accelerates the growth of iron particles, diminishing active sites.^{15, 16, 18} The pores of the zeolite can be blocked by deposited carbon during reaction or sintered iron particles. For example, Marchetti et al.³⁴ reported that pretreating iron supported on zeolite L in H₂ resulted in sintering due to iron oxide migration and agglomeration on the external surface of the zeolite.³⁴

In this study, we support iron on Na-ZSM-5, denoted as Fe-Na-ZSM-5, and systematically vary the pretreatment conditions to better understand their effect on FTS performance. We use H₂ and CO as pretreatment gases in the temperature range of 300 to 770 °C to encompass the conditions

that are typically used for FTS pretreatment. We find that CO conversion decreases with increasing pretreatment temperature, irrespective of the reductant. For the H₂ pretreated samples, increasing the pretreatment temperature increases the selectivity towards C₂-C₄ olefins and C₅+ hydrocarbons, which we attribute to iron nanoparticle growth. Transmission electron microscopy (TEM), particle size distribution (PSD) analysis, and X-ray diffraction (XRD) illustrate that pretreatment with H₂ induces reduction of Fe₂O₃ to metallic iron, and there is observed sintering as the pretreatment temperature increases. In contrast, CO pretreatment does not result in sintering, but we observe Fe carburization and coke deposition which promotes methane (CH₄) formation. Our findings provide important insight into how pretreatment conditions affect iron particle size, phase, and zeolite properties, and in turn, FTS performance, guiding the selection of appropriate FTS pretreatment conditions for Fe-ZSM-5 catalysts.

Table 1. Reported studies on the effect of reduction conditions of iron-based catalysts for FTS.

Catalyst	Pretreatment Conditions			Reaction Temp (°C)	Highest CO Conversion	
	Gas	Temp (°C)	Time (h)		Pretreatment Gas/Product	Iron Phase Post-Pretreatment
Fe ₂ O ₃ ⁷	CO, H ₂	300	6	250	CO/C ₃ -C ₅	Fe ⁰ , χ -Fe ₅ C ₂ , ϵ' -Fe _{2.2} C
Fe/Si/K ¹⁵	CO, H ₂ -CO	270, 300	24	270	CO/C ₂ +	χ -Fe ₅ C ₂ , ϵ' -Fe _{2.2} C
Fe/Cu/K ¹⁸	H ₂ , CO, H ₂ -CO	250 - 310	8, 24	250	CO/olefins and C ₅ +	Fe ⁰ and surface carbon
Fe/K ¹⁹	CO, CO-H ₂	350	24	270	CO-H ₂ /olefins and C ₅ +	Fe ₅ C ₂
Fe/Mn/K ²¹	H ₂ , CO, H ₂ -CO	250 - 400	4, 8	320	CO/C ₂ -C ₄ olefins	Fe ₅ C ₂
Fe/Mo and Fe ²²	H ₂ , CO, H ₂ -CO	280, 350	12	280	CO/NA	Fe ⁰ , Fe ₃ O ₄ , x-Fe ₅ C ₂
Fe/Mn ²³	H ₂ , CO, H ₂ -CO	275 - 300	24	275	CO/CO-H ₂ /olefins and C ₅ +	-
Fe/Mn/K/SiO ₂ ⁸	H ₂ , CO, H ₂ -CO	265	24	260	CO/olefins and C ₅ +	Fe ₅ C ₂ and carbonaceous species
Fe/NS ²⁴	H ₂ , CO, H ₂ -CO	750	24	270	CO/C ₆ -C ₁₄	Likely χ -Fe ₅ C ₂ or θ -Fe ₃ C
Fe/K/Si/Cu ²⁵	H ₂ , CO, H ₂ -CO	270	24	270	CO/Total hydrocarbons	Fe ₃ O ₄ , χ -Fe ₅ C ₂ , ϵ' -Fe _{2.2} C
Fe/SBA-15 ²⁶	H ₂ , H ₂ -CO	330, 415	0	-	H ₂ /Total hydrocarbons	Fe ₃ O ₄ , Fe ²⁺
Fe/SBA-15 ²⁷	H ₂ , H ₂ -CO	430	26	430	H ₂ /Total hydrocarbons	α -Fe, Fe ²⁺ , Fe ₃ O ₄

2.0 Methods

Synthesis of Fe-Na-ZSM-5. The ZSM-5 zeolite was synthesized using tetrapropylammonium hydroxide (TPAOH, 25 wt.%), Ammonium nitrate (NH₄NO₃), aluminum nitrate nonahydrate

($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), tetraethyl orthosilicate (TEOS), and sodium hydroxide (NaOH) which were all purchased from Alfa Aesar and used without further purification. First, 6.25 g of TEOS and 6.10 g of TPAOH were mixed in a Teflon container and stirred at 80 °C for 24 hours. After 24 hours, 0.23 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.12 g of NaOH were dissolved in 2 g of distilled water to form a solution. The solution was added dropwise into the mixture in the Teflon container. The resultant gel with a molar ratio of $1\text{SiO}_2:0.01\text{Al}_2\text{O}_3:0.25\text{TPAOH}:0.05\text{Na}_2\text{O}:8.3\text{H}_2\text{O}$ was then transferred to an autoclave and crystallized at 170 °C for 24 hours. The obtained solid product was washed three times using deionized water and collected by centrifugation at 13000 rpm for 10 min. After washing, the sample was left to dry overnight in the oven at 100 °C. The dried sample was calcined at 550 °C for 10 hours to remove the TPAOH template. Then Na-form ZSM-5 (Na-ZSM-5) with Si/Al ratio 50 was obtained as the final product.

The iron supported zeolite catalyst was synthesized via the wetness impregnation method using iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and distilled water. To obtain a 5 wt.% loading of iron, 0.362 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 0.138 g of distilled water. The solution was added dropwise into 0.95 g of Na-ZSM-5 while stirring. The resulting mixture was left to dry at 30 °C, followed by calcination at 550 °C for 5 hours at 5 °C/min. The obtained catalyst was designated as Fe-Na-ZSM-5.

Temperature Programmed Reduction and Desorption (H_2 -TPR, CO-TPR, and CO-TPD).

Temperature programmed reduction using either H_2 or CO (H_2 -TPR and CO-TPR), and CO temperature programmed desorption (CO-TPD) experiments were performed using a Micromeritics AutoChem II analyzer. For the H_2 -TPR experiment, the Fe-Na-ZSM-5 catalyst was degassed in helium flow of 20 mL/min at 300 °C with a ramp rate of 10 °C/min for 1 hour. After which the sample was cooled to 35 °C, followed by introduction of H_2 at 40 mL/min and ramped to 900 °C at 10 °C/min. The same procedure was used for CO-TPR except with the replacement of H_2 by 20 mL/min CO.

For CO temperature programmed desorption (CO-TPD) experiments, the catalysts were pretreated under 10% H_2 in Ar at 350 °C, 450 °C, 550, and 770 °C with a ramp rate of 10 °C/min for 2 h before pulsing CO over the catalyst at 35 °C. After CO adsorption, the sample was purged with helium and heated to 900 °C at a ramp rate of 5 °C/min. The same procedure was used for the CO pretreated samples with the replacement of H_2 with CO and reduction temperatures of 300 °C, 490 °C, and 750 °C.

Fischer-Tropsch Synthesis Reactor Studies. For the reactor studies, the Fe-Na-ZSM-5 catalyst was pressed into pellets and grinded between 212 - 315 μm . 50 mg of the catalyst was loaded into a stainless-steel reactor using quartz wool to fix the catalyst in place. The catalyst was pretreated with 40 mL/min H_2 or 20 mL/min CO at the prescribed temperatures with a ramp rate of 10 °C/min at 50 psig and held for 2 h. After pretreatment, the reactor was pressurized to 300

psig under the reductant gas and Ar flow and switched to the bypass loop. The bypass was pressurized to 300 psig with a combination of the reactant gases, composed of 20 mL/min H₂, 10 mL/min CO and 15 mL/min Ar to achieve H₂/CO = 2. The reaction was run for 12 hours, and an in-line Agilent gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) were used to evaluate the concentration of gases exiting the reactor. The conversion was calculated using the Ar internal standard to account for the decreasing molar volume due to reaction using the inlet molar flowrate of CO as the basis for the calculation. The selectivity for the carbon-containing products was calculated on a moles of carbon basis. All carbon balances close to 98±0.8%.

Transmission Electron Microscopy (TEM). Images of the pretreated Fe-Na-ZSM-5 catalysts were collected using a FEI Tecnai G2-F20 transmission electron microscope with a 200 kV accelerating voltage. Before imaging, the sample was either pretreated in 40 mL/min H₂ at 350 °C, 450 °C, 550 °C, or 770 °C for 2 hours with a ramp rate of 5 °C/min, or in 20 mL/min CO for 2 hours at 300 °C, 490 °C, or 750 °C with a ramp rate of 5 °C/min.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) was performed using a Discovery series TGA under a nitrogen flowrate of 25 mL/min. The sample holder was loaded into the equipment and tared, before loading the sample with a mass of 5 - 10 mg. The sample was heated to 110 °C with a ramp rate of 20 °C/min and held for 10 minutes to degas, before ramping to 850 °C with a ramp rate of 15 °C/min.

X-ray diffraction (XRD). Before collecting the XRD measurements, the catalysts were affixed to a Nylon loop (0.1 mm ID) with a light coating of viscous oil. XRD data were collected on a Rigaku XtaLAB Synergy-S diffraction system equipped with a HyPix-6000HE HPC detector. CuK α radiation ($\lambda = 1.54184$ Å) was generated by a PhotonJet-S microfocus source at 50 kV, and 1 mA. At room temperature (293 K) and with a sample-to-detector distance of 34 mm, two combination ω - ϕ “Gandolfi” scans were performed, each for 300 s: 1) ω from -62.00 to 31.00 degrees and ϕ rotated through 720 degrees, at $\theta = -42.00$ and $\kappa = 70.00$ degrees; 2) ω from -30.00 to 61.00 degrees and ϕ rotated through 720 degrees, at $\theta = 41.22$ and $\kappa = -70.00$ degrees. The crystallinity of the zeolites in the as-synthesized catalysts were calculated using a method reported by Mohamed et al.³⁵ For each of the sample, the method compares the relative areas of the XRD peaks at $2\theta = 22-25^\circ$. The as-synthesized Na-ZSM-5 is used as the 100% crystallinity reference.

Mössbauer Analysis. ⁵⁷Fe Mössbauer spectroscopy was used to investigate the iron phases present in the Fe-Na-ZSM-5 catalyst before and after pretreatment in H₂ vs CO at each pretreatment temperature. The samples were prepared in Delrin Mössbauer sample cups under ambient conditions and frozen in liquid N₂, with an inner Delrin cup added before freezing. Low-temperature measurements at 80 K were performed using a SeeCo. MS4 Mössbauer

spectrometer integrated with a Janis SVT-400 T He/N₂ cryostat, and isomer shifts were referenced to α -Fe at 25 °C. Spectral data were analyzed using WMoss (SeeCo), with raw data (black dots) and fits (black line), including individual components represented by colored hyperfine patterns. The fitting errors were $\delta \pm 0.02$ mm/s and $\Delta EQ \pm 3\%$, while quantification errors for multicomponent fits were $\pm 3\%$. Abbreviations used include full width at half maximum (FWHM), isomer shift (δ), electric quadrupole splitting (ΔE_Q), and internal magnetic field ($H_{int}(kG)$).

BET Surface Area Measurements. N₂ physisorption experiments were performed using a Micromeritics ASAP 2020 sorption analyzer at -196 °C. Prior to the analysis, all samples were degassed at 350 °C for 2 hours under vacuum and 97 points were analyzed. The surface area of the samples was determined using the Brunauer-Emmett-Teller (BET) method.

X-ray Absorption Fine Structure (XAFS). *In situ* XAFS measurements were conducted to investigate the structural changes of iron during temperature programmed reduction (TPR), pretreatment, and FTS. The measurements were performed at 8-ID (ISS) beamline at the National Synchrotron Light Source (NSLS-II), Brookhaven National Laboratory. The description of the beamline can be found in the literature.³⁶ The monochromator energy was calibrated by setting the position of the Fe foil X-ray absorption spectroscopy (XAS) spectrum derivative maximum to 7112 eV. The fluorescence signal from the sample was collected using a photodiode equipped with a Mn filter. The as-synthesized Fe-Na-ZSM-5 was diluted with boron nitride in a 1:5 ratio. The mixture was grinded together and pressed to form pellets. Then the pellets were grounded and sieved at a 212 - 315 μ m mesh size before loading into a quartz glass capillary tube with 1.5 mm outer diameter and 10 μ m wall thickness. The loaded tube was mounted within a custom designed Claussen cell. *In situ* CO-TPR and H₂-TPR were performed while XAFS data of Fe K-edge were collected. CO and H₂ flowrate were 3 and 6 mL/min respectively, maintaining the 1:2 CO:H₂ ratio (20 mL/min CO and 40 mL/min) used for H₂-TPR, CO-TPR, and during pretreatment prior to FTS reaction in the main reactor.

Ex situ XAFS data were collected for iron oxide standards (Fe₂O₃, Fe₃O₄, FeO, and Fe). Before the measurements, the iron standards were diluted in boron nitride to obtain 5 wt.% of the standards, similar to the weight percent of iron present in Fe-Na-ZSM-5. Iron carbide references were synthesized *in situ* using a method reported by De Smit et al.³⁷ Diluted Fe₂O₃ was loaded into the capillary tube and mounted on the custom-designed Claussen cell. 3 mL/min of CO was introduced into the system, and the temperature was ramped to 350 °C for Fe₅C₂ and 450 °C for Fe₃C synthesis at a ramp rate of 2 °C/min and held for 2 hours. In situ XAFS data were collected during the carbide synthesis. For all the measurements, the incident and transmitted X-ray signals were recorded using ionization chambers, while fluorescence signals were captured with a passivated implanted planar silicon (PIPS) detector. Calibration against the standards and data analysis were performed using the Demeter 0.9.26 package (Athena).

The MCR analysis of the *in situ* XANES data was carried out using the pyMCR package described in the literature and is consistent with our previous work.^{38, 39} Briefly, the number of components necessary to reproduce the XANES spectral series for each dataset was determined based on the autocorrelation analysis of the singular vectors obtained using the singular value decomposition of the corresponding data matrices. Then, the alternating least squares MCR fitting was applied to the data using the appropriate reference spectra as starting solutions. The fitting was carried out with non-negativity constraints on both spectral and concentration profiles, a normalization constraint on the concentrations such that the sum of all component concentrations adds up to unity at each time point, as well as additional cut-off constraint that removes component contributions if it is below 0.02, which was found to improve the stability of the fitting. The converged results were then used for the analysis.

3.0 Results and Discussion

3.1 FTS Performance of the Pretreated Fe-Na-ZSM-5 Catalysts.

FTS performance as a function of pretreatment conditions over Fe-Na-ZSM-5 is shown in **Figure 1** with tabulated values included in **Table S1**. The samples are denoted as H₂-T for the H₂-pretreated samples, and CO-T for the CO-pretreated samples, where T represents the pretreatment temperature. In accordance with the H₂ temperature programmed reduction (H₂-TPR) in **Figure S1(a)** which shows three peaks centered at ca. 350, 550 and 770 °C, we pretreated Fe-Na-ZSM-5 in H₂ at each of the three temperatures and labeled the catalysts H₂-350, H₂-550, and H₂-770. 450 °C pretreatment temperature (H₂-450) is also included because it is a commonly used pretreatment temperature for iron-based catalysts during FTS.^{40, 41} For the H₂-pretreated catalysts in **Figure 1(a)**, increasing the pretreatment temperature from 350 °C to 770 °C decreases the CO conversion from 10.8 to 3.4%. We hypothesize that sintering of iron particles reduces available active iron surface area and phase transitions to less-active Fe result in the decrease in measured activity. For the product distribution, increasing the pretreatment temperature under H₂ increases C₂-C₄ olefins and C₅₊ hydrocarbons, whereas C₂-C₄ paraffins and CH₄ decrease. These findings are consistent with sintering, where previous literature reports indicating that large Fe nanoparticles promote formation of C₅₊ hydrocarbons,^{24, 42, 43} and smaller iron particles are associated with increased CH₄ selectivity.⁴³ As shown in **Table S1**, increasing pretreatment temperature generally decreases CO₂ selectivity from 31.1 % in H₂-350 to 22.9% in H₂-770.

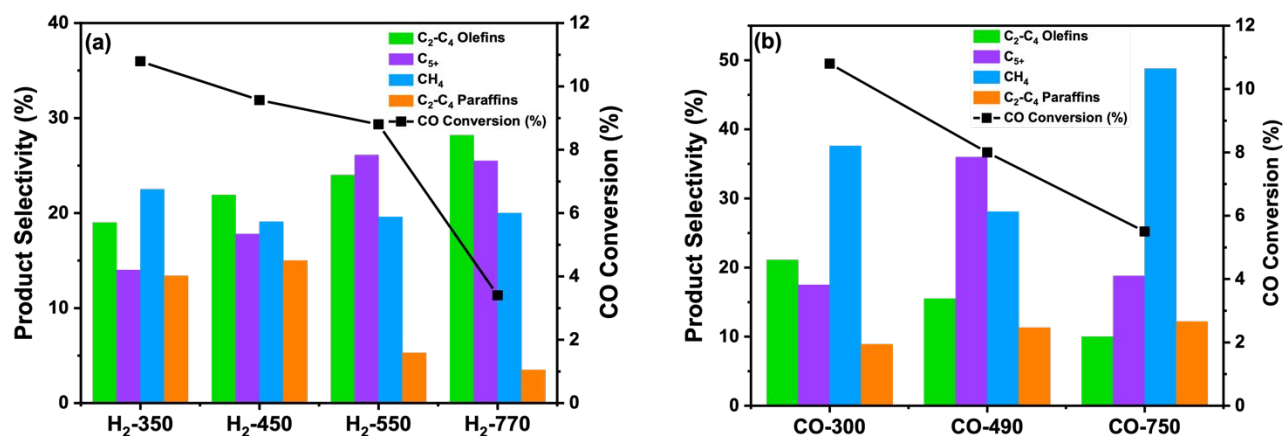


Figure 1. CO conversion and hydrocarbon selectivity averaged between 9 - 12 hours on stream of Fe-Na-ZSM-5 pretreated in H₂ (a) and CO (b) at temperatures ranging from 300 - 770 °C. Reaction conditions: catalyst mass = 50 mg, temperature = 300 °C, pressure = 300 psig, H₂/CO = 2, H₂ = 20 mL/min, CO = 10 mL/min, and Ar = 15 mL/min as internal standard.

Figure 1(b) shows the FTS performance of the CO-pretreated samples, with three pretreatment temperatures selected (300, 490, and 750 °C), in accordance with CO temperature programmed reduction (CO-TPR) in **Figure S1(b)**. Similar to the H₂-pretreated samples, increasing the pretreatment temperature also results in decreasing CO conversion from 10.8 to 5.5%, likely

because of sintering, iron phase transformations, and/or carbon deposition. Although increasing CO pretreatment temperatures enhances carburization, which can be favorable for FTS, the higher temperatures may lead to carbon deposition, which blocks active sites and decreases activity.^{13, 44} The product selectivity in **Figure 1(b)** shows a trend with C₂-C₄ olefins and paraffins, where olefins decrease and paraffins slightly increase with increasing pretreatment temperatures. At the highest pretreatment temperature, CH₄ selectivity dominates possibly due to the removal of deposited carbon as CH₄. The CO-pretreated samples have lower CO₂ selectivity when compared to the H₂-pretreated samples, showing values of 14.8, 9.3, and 10.1% for CO-300, CO-490, and CO-750, respectively. Understanding the observed trends in FTS performance requires deeper investigation into the structure of the catalysts after pretreatment.

3.2 Structural Properties of the Pretreated Fe-Na-ZSM-5 Catalysts.

The effect of pretreatment temperature on the iron particle size is first investigated using transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) in **Figure 2**. The particle size distribution (PSD) of the H₂-pretreated samples in **Figure 2(a-d)** shows a shift towards higher values with increasing pretreatment temperatures, indicating Fe sintering is occurring. These findings are in agreement with literature, and could be contributing to the decreased FTS activity in **Figure 1(a)**.^{7, 15, 17, 18, 45-47} In contrast, there is no significant increase in iron particle size for the CO-pretreated samples in **Figure 2(e-g)**, possibly due to carburization and carbon deposition stabilizing the Fe nanoparticles, consistent with observations by other researchers.^{7, 10, 45} For the highest temperature pretreated sample, CO-750, carbonaceous layers are observed around the iron particles in the TEM image (**Figure 2(h)**), which is further supported by the TGA in **Figure 2(i)** showing a sharp decrease in mass, suggestive of coke removal. This trend is not observed in the H₂-pretreated catalysts in **Figure S2**, indicating that carbon deposition is not contributing to the decrease in activity of the H₂-pretreated catalysts with increasing temperature. However, because the CO-pretreated samples do not exhibit significant sintering, the decrease in CO conversion with increasing pretreatment temperature is attributed to changes in the Fe phase and carbon deposition.

Following the observed iron sintering and coke deposition on the pretreated catalysts, the effect of the pretreatment temperature on the surface area, porosity, and pore volume of ZSM-5 is measured with N₂ physisorption and included in **Table 2**. After iron impregnation, the initial surface area and total pore volume of the parent Na-ZSM-5, initially measured as 352 m²/g and 0.66 cm³/g, respectively, decreases to 331 m²/g and 0.61 cm³/g. This decrease is attributed to the obstruction of zeolite pores by the iron nanoparticles, leading to decreased accessible zeolite surface area.⁴⁸ For the H₂-pretreated samples at the lowest pretreatment temperature (H₂-350), the surface area and total pore volume decrease to 295 m²/g and 0.55 cm³/g, respectively. For H₂-450 and H₂-550, the surface area and pore volume exhibit slight changes. At the highest pretreatment temperature (H₂-750), the surface area decreases to 161 m²/g, and the total pore and micropore volumes decrease. The substantial reduction in the surface area of H₂-770 is attributed to sintering of iron particles obstructing zeolite pores, thereby blocking accessible N₂ adsorption

area, or decomposition of the zeolite structure under the high temperature conditions. For the CO-pretreated samples, as the pretreatment temperature increases the BET surface area decreases from 294 to 205 m²/g likely due to the blocking of zeolite pores by deposited carbon.

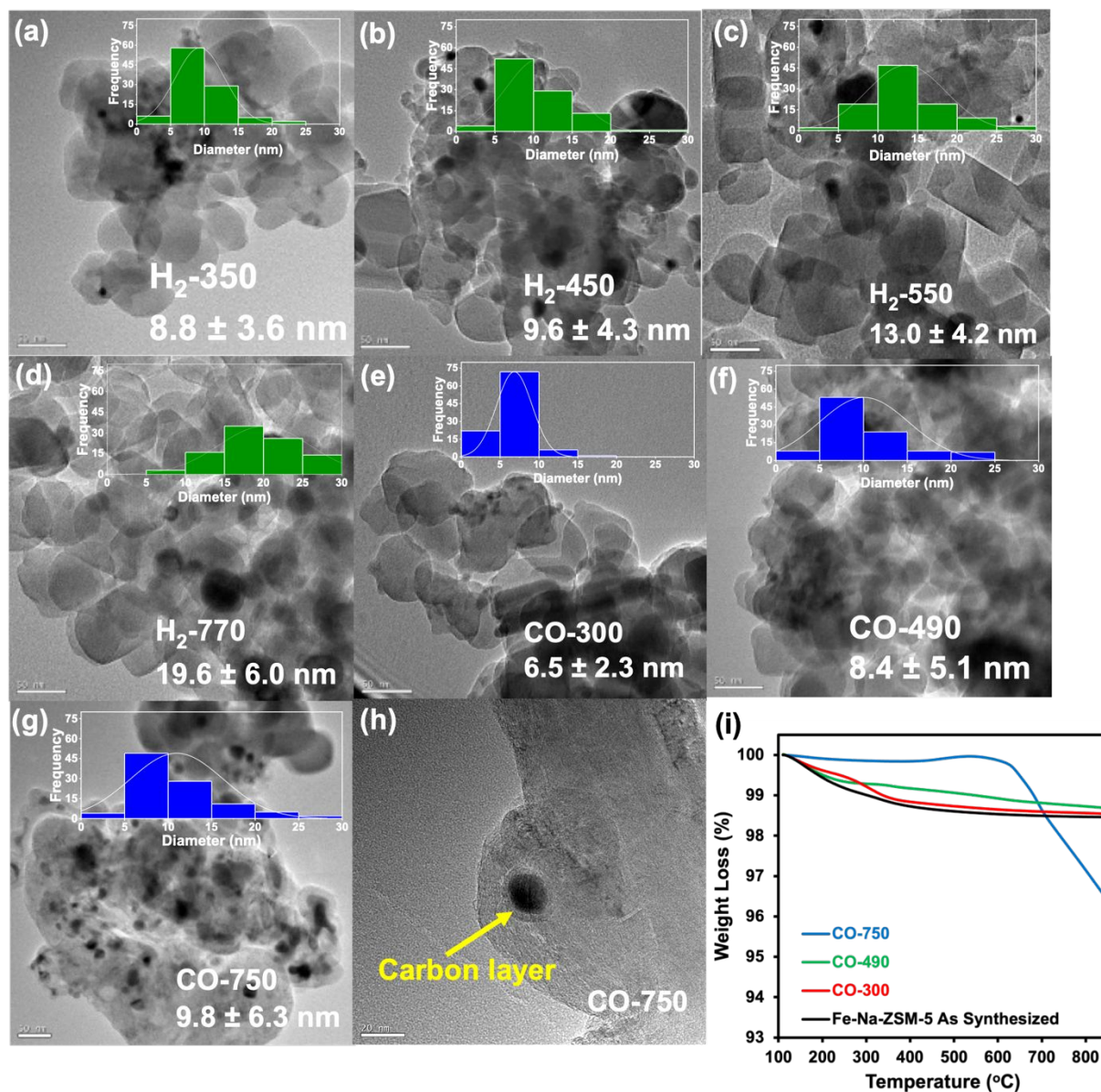


Figure 2. Transmission electron microscopy (TEM) images, and particle size distribution (PSD) of Fe-Na-ZSM-5 pretreated in H₂ at 350 °C (a), 450 °C (b), 550 °C (c), 770 °C (d), and in CO at 300 °C (e), 490 °C (f), and 750 °C (g – h). Thermogravimetric analysis (TGA) of the CO-pretreated samples (i). TGA of the H₂-pretreated samples is in **Figure S2** of the SI. The PSD was generated using diameter measurements of 100 iron particles from the TEM images.

Table 2. Physical properties of Fe-Na-ZSM-5 pretreated in H₂ and CO as a function of pretreatment temperature with as-synthesized Na-ZSM-5 and Fe-Na-ZSM-5 included as references.

Catalyst	Iron Median Size (nm)	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)	Relative Zeolite Crystallinity (%)
Na-ZSM-5*	NA	352	0.66	0.12	100.0
Fe-Na-ZSM-5*	NA	331	0.61	0.11	88.5
H ₂ -350	8.8 ± 3.6	295	0.55	0.10	90.0
H ₂ -450	9.6 ± 4.3	340	0.63	0.11	87.5
H ₂ -550	13.0 ± 5.2	335	0.59	0.10	83.7
H ₂ -770	19.6 ± 6.0	161	0.39	0.05	81.2
CO-300	6.5 ± 2.3	294	0.57	0.10	91.8
CO-490	8.4 ± 5.1	260	0.50	0.08	83.1
CO-750	9.8 ± 6.3	205	0.58	0.06	82.8

* = As-synthesized samples

X-ray diffraction (XRD) patterns of the pretreated samples in **Figure 3** provide insight into the crystallinity of the ZSM-5 and the iron structure post-pretreatment. The XRD patterns of all the pretreated samples in **Figure 3(a)** show preservation of the bulk crystalline structure of ZSM-5 with characteristic peaks of the MFI zeolite after pretreatment, which is consistent with TEM and studies showing that the bulk crystalline structure of the zeolite remains stable up to 800 °C.⁴⁹ The relative crystallinity of ZSM-5 is calculated from the XRD patterns using a method reported by Mohamed et al.³⁵ with as-synthesized Na-ZSM-5 used as the 100% crystallinity reference. As shown in **Table 2**, increasing the pretreatment temperature leads to a slight decrease of the relative crystallinity of the ZSM-5 zeolite irrespective of the reductant (CO or H₂). This suggests that the bulk crystalline structure of the ZSM-5 is mostly preserved after high temperature pretreatment (≤ 770 °C) with a slight decrease in relative crystallinity.

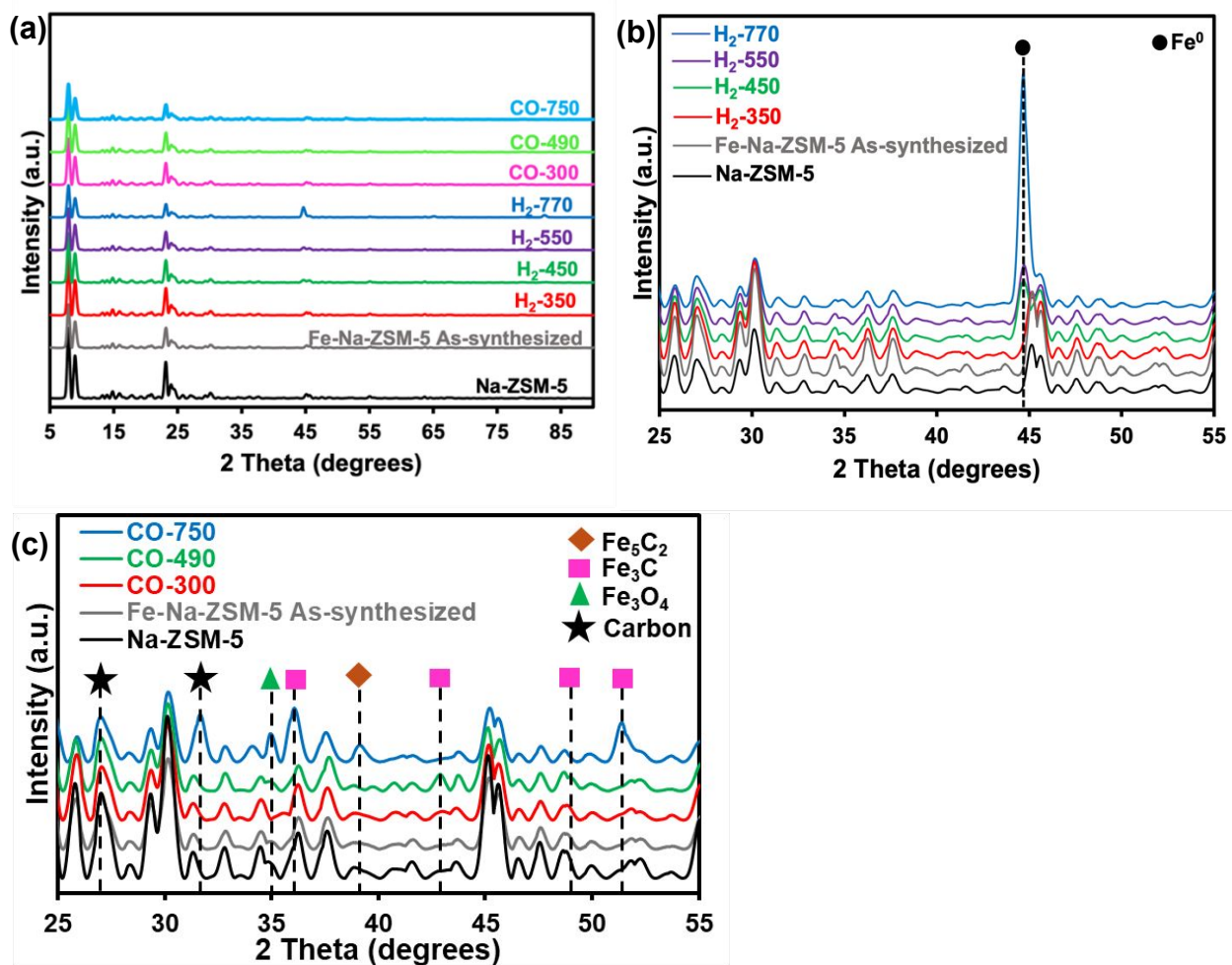


Figure 3. X-ray diffraction (XRD) patterns of Fe-Na-ZSM-5 pretreated in H₂ and CO (a), zoomed in XRD pattern of the H₂-pretreated samples (b), and zoomed in patterns of the CO-pretreated samples (c).

To analyze observable iron species, we provide zoomed in XRD profiles of the catalysts within the 2θ range of 25 - 55° in **Figure 3(b and c)**. Overall, the XRD shows that pretreatment in H₂ leads to the complete reduction of Fe₂O₃ to Fe⁰, also supported by the H₂-TPR in **Figure S1(a)**, while CO pretreatment results in the simultaneous reduction and carburization of Fe₂O₃, which forms iron carbides and reduced oxides. In the case of H₂-770, we observe a significant increase at 44.7°, corresponding to the (110) plane of metallic iron (Fe⁰), suggesting Fe agglomeration begins at 450 °C which is consistent with the TEM images.^{50, 51} This aggregation may be responsible for the very low CO conversion of H₂-770 as seen in **Figure 1(a)**. However, for the CO-pretreated samples in **Figure 3(c)**, agglomeration of Fe⁰ peaks is absent, supporting the hypothesis that iron particles are stabilized during carburization, as suggested by TEM and PSD. Characteristic peaks are observed of Fe₃O₄ (310) at 35°,⁵² iron carbides (Fe₅C₂, Fe₃C) at 36.1, 39.2, and 51.5°,^{53, 54} and carbon at 27.0 and 31.6°. Iron carbides, such as Fe₅C₂ and Fe₃C are active phases for CO conversion, with Fe₅C₂ frequently cited as the phase that promotes hydrocarbon formation.^{37, 40, 41, 55, 56}

The iron phase composition of the pretreated Fe-Na-ZSM-5 samples was analyzed further using Mössbauer spectroscopy, as shown in **Figures 4** and **S3**. The Mössbauer spectra of the high temperature pretreatment samples, H₂-770 and CO-750 are shown in **Figure 4**. The spectra of H₂-770 indicate that the sample primarily contains metallic iron in the form of α -Fe (57%), which agrees with the sintered metallic iron observed by XRD. Additionally, 21% of the iron is present as Fe²⁺ oxo suggesting integration into the zeolite framework due to the high temperature pretreatment. The Mössbauer of the CO-750 sample shows that majority of the iron (65%) is also present as Fe²⁺ oxo, likely due to the high pretreatment temperature, while only about 12% is present as metallic iron. The Mossbauer spectra of CO-300 and CO-490 in **Figure S3** show a complex mixture of iron phases that are predominantly Fe²⁺ including oxides and carbides. The Mossbauer fitting parameters are summarized in **Tables S4** and **S5**.^{40, 57, 58}

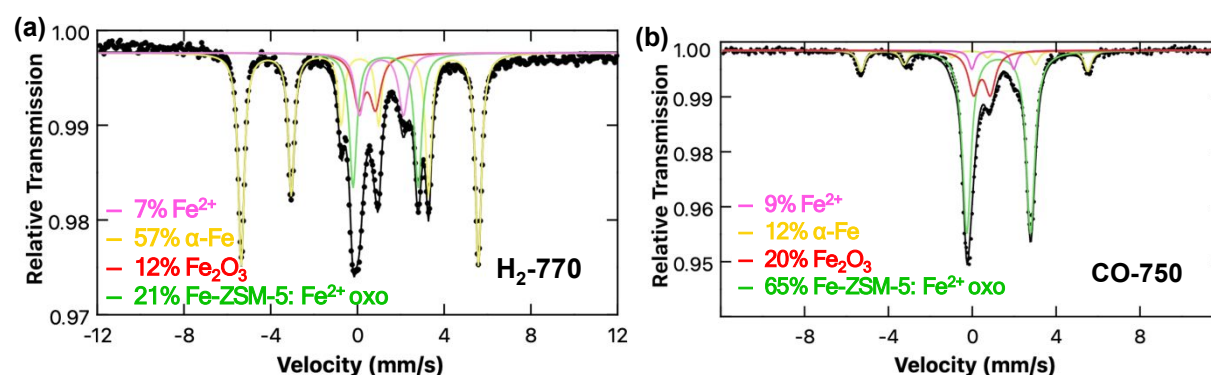


Figure 4. Mössbauer spectra of Fe-Na-ZSM-5 pretreated in (a) H₂ at 770 °C and (b) CO at 750 °C.

3.3 CO Adsorption Properties of the Pretreated Fe-Na-ZSM-5 Catalysts.

To gain a better understanding on the effect of pretreatment conditions on the Fe structure, we include CO temperature programmed desorption (CO-TPD) in **Figure 5**. The CO-TPD of the H₂-pretreated samples in **Figure 5(a)** highlights the effect of iron particle size on CO adsorption. In the CO-TPD of the H₂-pretreated samples, peaks at 190 °C and 260 °C are attributed to desorption of weakly bound CO, while the peak at 464 °C is attributed to strong CO binding, indicative of CO dissociation.⁵⁹⁻⁶¹ At higher pretreatment temperatures (450 – 770 °C), CO preferentially binds weakly, whereas for H₂-350, CO exhibits both weak and strong binding, suggesting the presence of two active sites in H₂-350. The CO-TPD profiles of the H₂-pretreated samples suggest that as pretreatment temperature increases, the CO adsorption and dissociative capacity decrease. This is attributed to the smaller particle size at low pretreatment temperatures, providing more active sites and higher electron density for CO adsorption,⁶² as supported by the FTS data presented in **Figure 1(a)**.

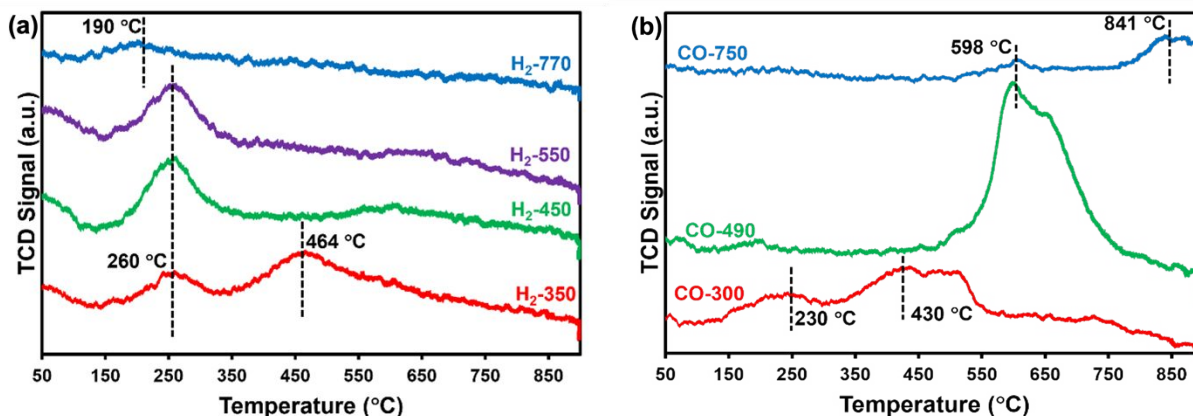


Figure 5. Carbon monoxide temperature programmed desorption (CO-TPD) of the Fe-Na-ZSM-5 catalysts pretreated in H₂ (a) and CO (b) at different temperatures.

The CO-TPD of the CO-pretreated samples shown in **Figure 5(b)** highlights the effect of iron carbide formation and coke deposition on CO adsorption. For the CO-pretreated samples, peaks for weak and strong binding of CO are present in the CO-TPD of CO-300, which is similar to H₂-350. The similarity in the CO adsorption behavior of CO-300 and H₂-350 suggest presence of similar active sites which could be responsible for the similarity in CO conversion as shown in **Figure 1**. Interestingly, the BET surface area and pore volume of these two samples are also similar as shown in **Table 2**.

For the CO-TPD of CO-490 and CO-750, a peak at 598 °C is attributed to the desorption of CO bound to iron carbides.⁶³ The absence of the peak at 598 °C for CO-300 indicates that there is less CO dissociation, and in turn, iron carbide formation at pretreatment temperatures below 490 °C. The lack of peaks over CO-750 is attributed to carbon deposition on the active sites, supported by the TGA in **Figure 2(i)**. In summary, the CO-TPD shows that CO adsorption is weakened by larger iron particle sizes because the desorption profiles of the catalysts with smaller particle sizes, *i.e.* the CO-pretreated samples and H₂-350 exhibit desorption at high temperatures, consistent with findings by Suo et al.⁶⁴

3.4 Structure-Performance Relationships of the Pretreated catalysts.

To investigate the effect of pretreatment on FTS performance, CO conversion versus time on stream (TOS) data for all the pretreated catalysts is included in **Figure 6**. The 12-hour TOS results for H₂-350 and H₂-450 in **Figure 6(a)** exhibit similar trends with high initial activity. After about 4 h on stream, the activity of H₂-350 increases while that of H₂-450 remains relatively stable. The initial decline in activity of both catalysts may be attributed to the transformation of iron oxides and/or metallic iron into iron carbides and deposition of inactive graphitic carbon.^{25, 28, 65} Luo et al²⁵ report that in H₂-pretreated iron catalysts, after the induction period, the formation of iron carbides increases slightly with reaction time, resulting in the gradually increasing CO conversion, agreeing with our observations and previous studies on Fe-Na-ZSM-5.^{40, 41} For the higher pretreatment temperatures (H₂-550 and H₂-770), the catalysts

interestingly do not exhibit the initial decrease in activity, possibly due to sintering and an induction mechanism that is a function of the larger Fe particle size.

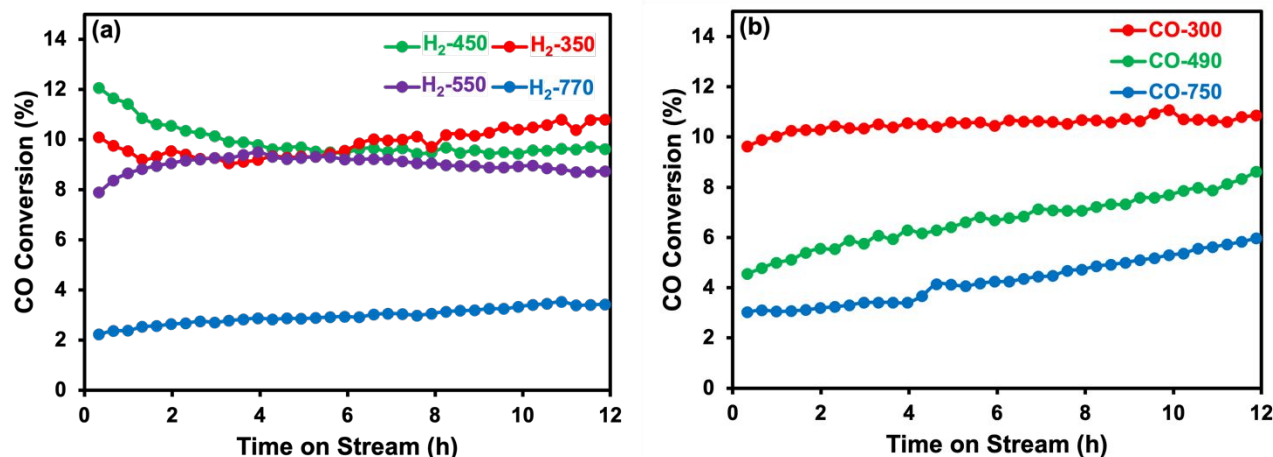


Figure 6. CO conversion versus time on stream of Fe-Na-ZSM-5 as a function of pretreatment temperature in H₂ (a), and in CO (b). Reaction conditions: Catalyst mass = 50 mg, Temperature = 300 °C, pressure = 300 psig, H₂/CO ratio = 2, H₂ = 20 mL/min, CO = 10 mL/min, and Ar = 15 mL/min as internal standard.

The 12-hour TOS results for the CO-pretreated samples in **Figure 6(b)**, show distinct behavior compared to H₂-pretreated samples because there is not a decrease in initial activity. These findings are consistent with those of Xu et al.⁶⁶ where they observe an initial decline in the CO conversion of the H₂ pretreated catalyst, which is absent in the CO and CO/H₂ pretreated catalysts. Our reactor data suggests that CO pretreatment of Fe-Na-ZSM-5 at 490 °C and 750 °C induces a higher degree of carburization and coke deposition on the iron oxide particles, resulting in lower conversion. However, as the reaction proceeds the coke is removed that reveals active sites, which gradually increases the CO conversion.

To elucidate details of the iron structure during pretreatment as a function of pretreatment conditions, X-ray absorption fine structure (XAFS) analysis is conducted on H₂-350, H₂-450, CO-300, and CO-490. The K-edge X-ray absorption near-edge structure (XANES) analysis after pretreatment are shown in **Figure 6** with the insets showing the pre-edge features, and the as-synthesized Fe-Na-ZSM-5 is included as a reference. Spectra for iron standards Fe₂O₃, Fe₃O₄, FeO, and Fe⁰ are included in **Figure S3**. The XANES spectrum of the as-synthesized Fe-Na-ZSM-5 shows a pre-edge feature at 7115 eV and white line at 7134.4 eV consistent with the Fe₂O₃ reference in **Figure S3**, indicating that Fe₂O₃ is present in the Fe-Na-ZSM-5 catalyst before pretreatment. The XANES spectra of all the samples in **Figure 6(a and b)** shift to lower energies after pretreatment in either H₂ or CO at all temperatures. For instance, the white line of H₂-350 appears at 7130.2 eV with pre-edge at 7113.6 eV, which are at lower energies than those of the as-synthesized Fe-Na-ZSM-5 catalyst. For all the samples, the intensity of the higher pretreatment temperatures (H₂-450 and CO-490) are lower compared to the lower pretreatment temperatures, suggesting a higher degree of reduction/carburization.

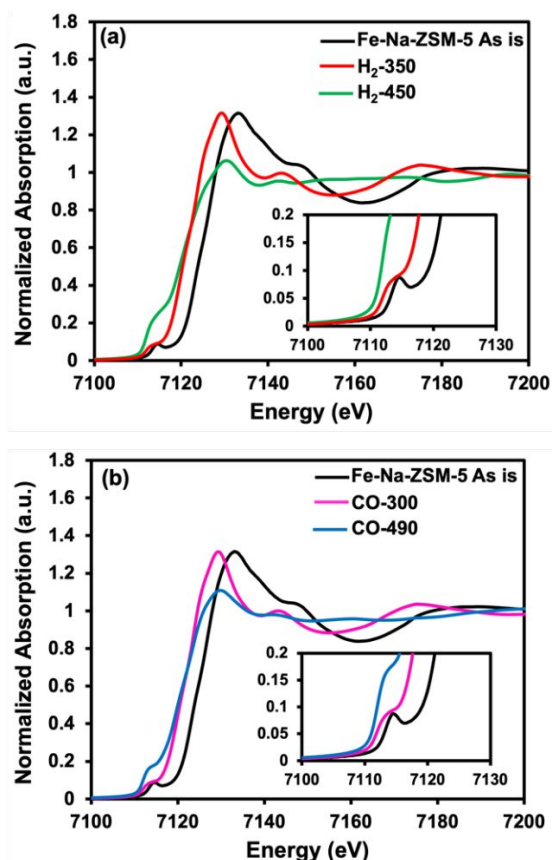


Figure 7. Fe K-edge X-ray absorption near-edge structure (XANES) spectra of H₂-pretreated (a), and CO-pretreated (b) Fe-Na-ZSM-5 samples. The as-synthesized catalyst, Fe-Na-ZSM-5 is included as a reference.

To gain additional insight from the *in situ* XANES data, we applied multivariate curve resolution (MCR) analysis as shown in **Figure 8(a-d)**. The MCR analysis was used to extract the fractions of different Fe species contained in the sample as a function of time during the pretreatment. During the analysis, we attempted to use Fe₂O₃ and Fe₃O₄ spectra as starting solutions, however, the resulting components either converged to the Fe-Na-ZSM-5 spectrum, taken prior to pretreatment, or to a non-physical spectrum. Consequently, these species are excluded from the MCR plots and only the as-is Fe-Na-ZSM-5, metallic Fe, and FeO spectra are used during the analysis. For the low-temperature pretreated samples, H₂-350 and CO-300 as depicted in **Figure 8(a and c)**, the Fe-Na-ZSM-5 initially undergoes gradual reduction, leading to formation of FeO, as evidenced by the concurrent gradual increase in the FeO spectrum. After about 0.8 h, the proportion of FeO within the samples stabilizes and persists until the end of the pretreatment period, indicating that FeO predominates as the primary species after pretreatment. The MCR analysis indicates that FeO is the predominant iron species in H₂-350 and CO-300 after pretreatment.

The comparable fractions of FeO shown by the MCR analysis of H₂-350 and CO-300, alongside the analogous CO-TPD profiles as depicted in **Figure 5**, likely account for the similar CO

conversion observed in **Figure 1**. However, the presence of iron carbides in CO-300 suggested by the additional shoulder in its CO-TPD at ~ 500 °C, likely contribute to the differences in the initial catalyst activity, as evidenced in the TOS data in **Figure 6(a and b)**, as well as differences in product selectivity. We hypothesize that at the onset of the reaction, the predominant FeO in H₂-350 undergoes transformation, forming a mixed phase of iron containing some iron carbides and inactive carbides. After ~ 2 hours on stream, the CO conversion gradually increases, mirroring the TOS pattern of CO-300, which likely already contains iron carbides prior to FTS.

In the MCR analysis of H₂-450 shown in **Figure 8(b)**, the fraction of FeO steadily increases as that of iron oxides in as-synthesized Fe-Na-ZSM-5 gradually decreases. After about 0.7 h, some of the generated FeO undergoes further reduction, forming metallic Fe. The fractional contribution of Fe gradually increases, ultimately becoming the predominant species post-pretreatment. The appearance of Fe seems to coincide with pretreatment temperatures above 400°C, which agrees with the XRD data in **Figure 3(b)**. Similarly, for CO-490 in **Figure 8(d)**, the fraction of iron oxides in the as-synthesized Fe-Na-ZSM-5 gradually decreases during reduction, facilitating the formation of FeO with increasing fractional contribution. However, after ~ 0.7 h, a spectrum indicative of a mixed phase emerges. Here, successful fitting of the data was accomplished by adding an additional spectrum from the end of the *in situ* XANES series to the MCR starting solutions. We hypothesize that the extracted component represents a mixed phase and can be attributed to iron carbides, and some iron oxides which gradually increase in concentration during pretreatment. Overall, the MCR analysis agrees with XRD, suggesting that higher pretreatment temperatures promote reduction and carburization of Fe in Fe-Na-ZSM-5.

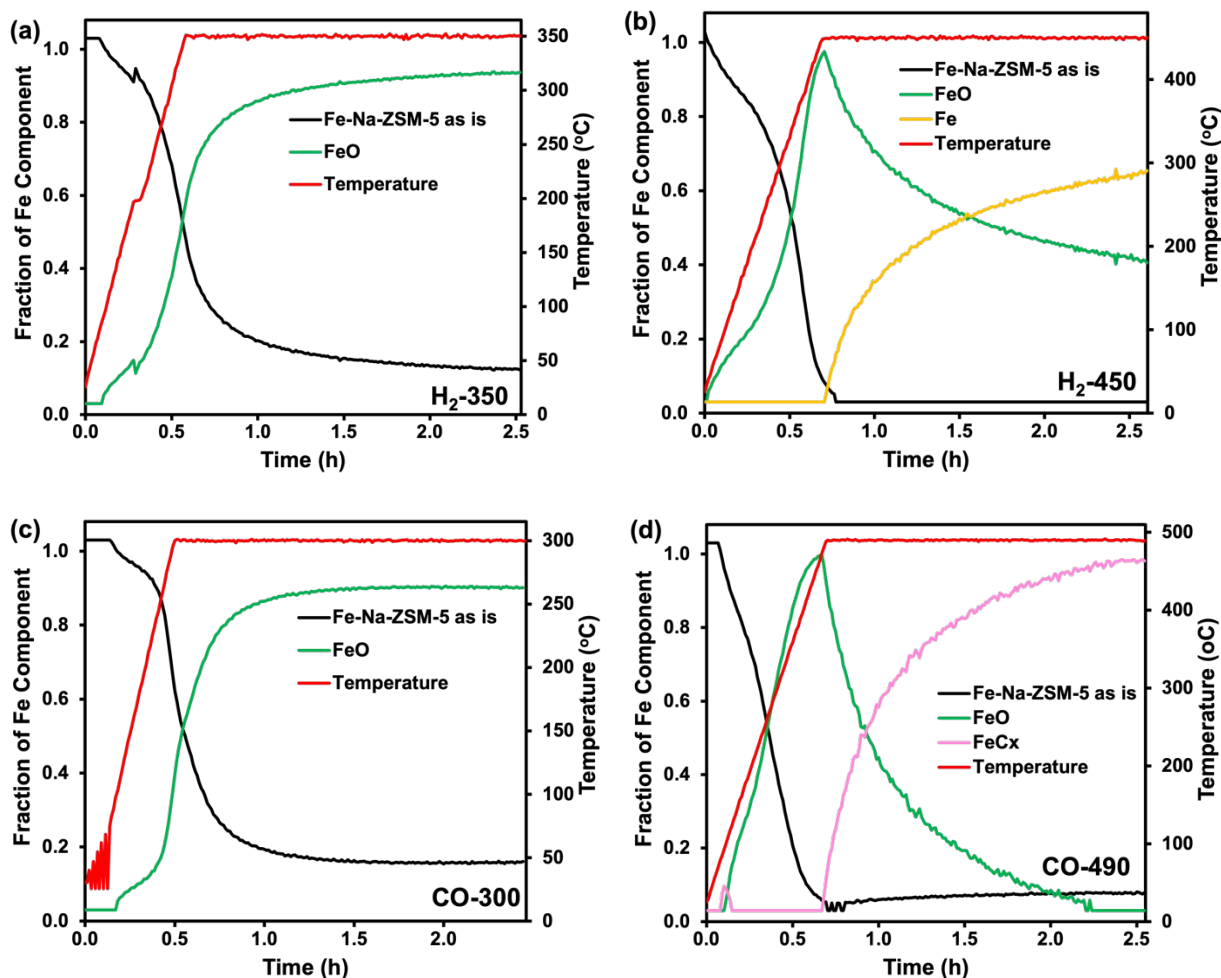


Figure 8. Multivariate Curve Resolution (MCR) analysis of the XANES spectra of Fe-Na-ZSM-5 pretreated in H_2 at 350 °C (a), and 450 °C (b) and in CO at 300 °C (c), and 490 °C (d), with the as-synthesized catalyst, Fe-Na-ZSM-5 included as a reference.

Conclusion

This study explores the effect of pretreatment conditions on the structure and performance of iron supported on ZSM-5 (Fe-Na-ZSM-5) for FTS. The reactor studies and structural characterization show that pretreatment in a H_2 leads to sintering, diminishing CO adsorption capacity and CO conversion at high temperatures, while CO pretreatment induces carbide formation and coke deposition, stabilizing iron particles but lowering CO conversion at higher reduction temperatures. Irrespective of activation gas, the pretreatment temperature significantly affects the initial iron phase and further *in situ* restructuring that occurs as the reaction progresses, yielding comparable trends in the TOS data across all catalysts pretreated with the same gas. However, the variation in the fractions of the iron phases present according to the XAFS data may account for differences in the FTS performance.

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References

1. Keyvanloo, K.; Mardkhe, M. K.; Alam, T. M.; Bartholomew, C. H.; Woodfield, B. F.; Hecker, W. C., Supported iron Fischer–Tropsch catalyst: superior activity and stability using a thermally stable silica-doped alumina support. *ACS Catalysis* **2014**, *4* (4), 1071-1077.
2. Xue, Y.; Liu, Z.; Zhang, Y.; Duan, S.; Chen, J., Effect of the Valence State of Iron in the Precursors on the Fischer–Tropsch Synthesis Performance of an Fe/Fe Foam Catalyst. *Industrial & Engineering Chemistry Research* **2021**, *60* (6), 2410-2417.
3. Abelló, S.; Montané, D., Exploring iron - based multifunctional catalysts for Fischer–Tropsch synthesis: a review. *ChemSusChem* **2011**, *4* (11), 1538-1556.
4. Huo, C.-F.; Li, Y.-W.; Wang, J.; Jiao, H., Insight into CH₄ formation in iron-catalyzed Fischer–Tropsch synthesis. *Journal of the American Chemical Society* **2009**, *131* (41), 14713-14721.
5. Davis, B. H., Fischer–Tropsch synthesis: reaction mechanisms for iron catalysts. *Catalysis Today* **2009**, *141* (1-2), 25-33.
6. Dictor, R. A.; Bell, A. T., Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts. *Journal of Catalysis* **1986**, *97* (1), 121-136.
7. Bian, G.; Oonuki, A.; Koizumi, N.; Nomoto, H.; Yamada, M., Studies with a precipitated iron Fischer-Tropsch catalyst reduced by H₂ or CO. *Journal of Molecular Catalysis A: Chemical* **2002**, *186* (1-2), 203-213.
8. Ding, M.; Yang, Y.; Wu, B.; Wang, T.; Xiang, H.; Li, Y., Effect of reducing agents on microstructure and catalytic performance of precipitated iron-manganese catalyst for Fischer–Tropsch synthesis. *Fuel processing technology* **2011**, *92* (12), 2353-2359.

9. Cano, L.; Cagnoli, M.; Fellenz, N.; Bengoa, J.; Gallegos, N.; Alvarez, A.; Marchetti, S., Fischer-Tropsch synthesis. Influence of the crystal size of iron active species on the activity and selectivity. *Applied Catalysis A: General* **2010**, *379* (1-2), 105-110.
10. Cheng, K.; Virginie, M.; Ordonsky, V. V.; Cordier, C.; Chernavskii, P. A.; Ivantsov, M. I.; Paul, S.; Wang, Y.; Khodakov, A. Y., Pore size effects in high-temperature Fischer-Tropsch synthesis over supported iron catalysts. *Journal of Catalysis* **2015**, *328*, 139-150.
11. Jin, Y.; Datye, A. K., Phase transformations in iron Fischer-Tropsch catalysts during temperature-programmed reduction. *Journal of Catalysis* **2000**, *196* (1), 8-17.
12. Lin, H.-Y.; Chen, Y.-W.; Li, C., The mechanism of reduction of iron oxide by hydrogen. *Thermochimica Acta* **2003**, *400* (1-2), 61-67.
13. Jozwiak, W.; Kaczmarek, E.; Maniecki, T.; Ignaczak, W.; Maniukiewicz, W., Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres. *Applied Catalysis A: General* **2007**, *326* (1), 17-27.
14. Tahari, M. N. A.; Salleh, F.; Saharuddin, T. S. T.; Samsuri, A.; Samidin, S.; Yarmo, M. A., Influence of hydrogen and carbon monoxide on reduction behavior of iron oxide at high temperature: Effect on reduction gas concentrations. *International Journal of Hydrogen Energy* **2021**, *46* (48), 24791-24805.
15. O'Brien, R. J.; Xu, L.; Spicer, R. L.; Davis, B. H., Activation Study of Precipitated Iron Fischer-Tropsch Catalysts. *Energy & Fuels* **1996**, *10* (4), 921-926.
16. Bukur, D. B.; Koranne, M.; Lang, X.; Rao, K.; Huffman, G. P., Pretreatment effect studies with a precipitated iron Fischer-Tropsch catalyst. *Applied Catalysis A: General* **1995**, *126* (1), 85-113.
17. Bukur, D. B.; Lang, X.; Ding, Y., Pretreatment effect studies with a precipitated iron Fischer-Tropsch catalyst in a slurry reactor. *Applied Catalysis A: General* **1999**, *186* (1-2), 255-275.
18. Bukur, D. B.; Lang, X.; Rossin, J. A.; Zimmerman, W. H.; Rosynek, M. P.; Yeh, E. B.; Li, C., Activation studies with a promoted precipitated iron Fischer-Tropsch catalyst. *Industrial & engineering chemistry research* **1989**, *28* (8), 1130-1140.
19. Soled, S.; Iglesia, E.; Fiato, R., Activity and selectivity control in iron catalyzed Fischer-Tropsch synthesis: The influence of iron catalyst phase on slurry Fischer-Tropsch reaction pathways; Selective synthesis of alpha-olefins. *Catalysis Letters* **1990**, *7*, 271-280.

20. Tahari, M. N. A.; Salleh, F.; Saharuddin, T. S. T.; Dzakaria, N.; Samsuri, A.; Hisham, M. W. M.; Yarmo, M. A., Influence of hydrogen and various carbon monoxide concentrations on reduction behavior of iron oxide at low temperature. *international journal of hydrogen energy* **2019**, *44* (37), 20751-20759.
21. Zhang, J.-l.; Ma, L.-h.; Fan, S.-b.; Zhao, T.-S.; Sun, Y.-h., Synthesis of light olefins from CO hydrogenation over Fe–Mn catalysts: Effect of carburization pretreatment. *Fuel* **2013**, *109*, 116-123.
22. Cui, X.; Xu, J.; Zhang, C.; Yang, Y.; Gao, P.; Wu, B.; Li, Y., Effect of pretreatment on precipitated Fe–Mo Fischer–Tropsch catalysts: Morphology, carburization, and catalytic performance. *Journal of catalysis* **2011**, *282* (1), 35-46.
23. Pennline, H. W.; Zarochak, M. F.; Stencel, J. M.; Diehl, J. R., Activation and promotion studies in a mixed slurry reactor with an iron-manganese Fischer-Tropsch catalyst. *Industrial & Engineering Chemistry Research* **1987**, *26* (3), 595-601.
24. Alayat, A.; McIlroy, D.; McDonald, A. G., Effect of synthesis and activation methods on the catalytic properties of silica nanospring (NS)-supported iron catalyst for Fischer-Tropsch synthesis. *Fuel Processing Technology* **2018**, *169*, 132-141.
25. Luo, M.; Hamdeh, H.; Davis, B. H., Fischer-Tropsch Synthesis: Catalyst activation of low alpha iron catalyst. *Catalysis today* **2009**, *140* (3-4), 127-134.
26. De Berti, I. O. P.; Bengoa, J. F.; Stewart, S. J.; Cagnoli, M. V.; Pecchi, G.; Marchetti, S. G., Effect of activation atmosphere in the Fischer–Tropsch Synthesis using a “quasi-model” catalyst of γ -Fe₂O₃ nanoparticles supported on SBA-15. *Journal of Catalysis* **2016**, *335*, 36-46.
27. Cano, L. A.; Cagnoli, M. V.; Bengoa, J. F.; Alvarez, A. M.; Marchetti, S. G., Effect of the activation atmosphere on the activity of Fe catalysts supported on SBA-15 in the Fischer–Tropsch Synthesis. *Journal of Catalysis* **2011**, *278* (2), 310-320.
28. Xu, J.; Bartholomew, C. H., Temperature-programmed hydrogenation (TPH) and in situ Mössbauer spectroscopy studies of carbonaceous species on silica-supported iron Fischer–Tropsch catalysts. *The Journal of Physical Chemistry B* **2005**, *109* (6), 2392-2403.
29. Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D., Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *Journal of the American Chemical Society* **1998**, *120* (24), 6024-6036.

30. Martínez, A.; Lopez, C., The influence of ZSM-5 zeolite composition and crystal size on the in situ conversion of Fischer–Tropsch products over hybrid catalysts. *Applied Catalysis A: General* **2005**, *294* (2), 251-259.
31. Ma, Z.; Porosoff, M. D., Development of tandem catalysts for CO₂ hydrogenation to olefins. *ACS Catalysis* **2019**, *9* (3), 2639-2656.
32. Azizi, H. R.; Mirzaei, A. A.; Kaykhaili, M.; Mansouri, M., Fischer–Tropsch synthesis: studies effect of reduction variables on the performance of Fe–Ni–Co catalyst. *Journal of Natural Gas Science and Engineering* **2014**, *18*, 484-491.
33. Kölbel, H.; Ralek, M., The Fischer-Tropsch synthesis in the liquid phase. *Catalysis Reviews Science and Engineering* **1980**, *21* (2), 225-274.
34. Marchetti, S.; Cagnoli, M.; Alvarez, A.; Bengoa, J.; Mercader, R.; Yeramian, A., Study of the Fe/zeolite-L system: Part I: characterization of iron species and their structural properties. *Applied surface science* **2000**, *165* (2-3), 91-99.
35. Mohamed, R. M.; Aly, H. M.; El-Shahat, M. F.; Ibrahim, I. A., Effect of the silica sources on the crystallinity of nanosized ZSM-5 zeolite. *Microporous and mesoporous materials* **2005**, *79* (1-3), 7-12.
36. Leshchev, D.; Rakitin, M.; Luvizotto, B.; Kadyrov, R.; Ravel, B.; Attenkofer, K.; Stavitski, E., The Inner Shell Spectroscopy beamline at NSLS-II: a facility for in situ and operando X-ray absorption spectroscopy for materials research. *Journal of Synchrotron Radiation* **2022**, *29* (4), 1095-1106.
37. de Smit, E.; Cinquini, F.; Beale, A. M.; Safonova, O. V.; van Beek, W.; Sautet, P.; Weckhuysen, B. M., Stability and reactivity of ϵ – χ – θ iron carbide catalyst phases in Fischer–Tropsch synthesis: Controlling μ C. *Journal of the American Chemical Society* **2010**, *132* (42), 14928-14941.
38. Camp Jr, C. H., PyMCR: A python library for multivariatecurve resolution analysis with alternating regression (MCR-AR). *Journal of Research of the National Institute of Standards and Technology* **2019**, *124*, 1.
39. Liu, R.; Leshchev, D.; Stavitski, E.; Juneau, M.; Agwara, J. N.; Porosoff, M. D., Selective hydrogenation of CO₂ and CO over potassium promoted Co/ZSM-5. *Applied Catalysis B: Environmental* **2021**, *284*, 119787.

40. Agwara, J. N.; Bakas, N. J.; Neidig, M. L.; Porosoff, M. D., Challenges and Opportunities of Fe - based Core - Shell Catalysts for Fischer - Tropsch Synthesis. *ChemCatChem* **2022**, *14* (19), e202200289.
41. Liu, R.; Ma, Z.; Sears, J. D.; Juneau, M.; Neidig, M. L.; Porosoff, M. D., Identifying correlations in Fischer-Tropsch synthesis and CO₂ hydrogenation over Fe-based ZSM-5 catalysts. *Journal of CO₂ Utilization* **2020**, *41*, 101290.
42. Chen, W.; Fan, Z.; Pan, X.; Bao, X., Effect of confinement in carbon nanotubes on the activity of Fischer–Tropsch iron catalyst. *Journal of the American Chemical Society* **2008**, *130* (29), 9414-9419.
43. Park, J.-Y.; Lee, Y.-J.; Khanna, P. K.; Jun, K.-W.; Bae, J. W.; Kim, Y. H., Alumina-supported iron oxide nanoparticles as Fischer–Tropsch catalysts: Effect of particle size of iron oxide. *Journal of Molecular Catalysis A: Chemical* **2010**, *323* (1-2), 84-90.
44. Jóźwiak, W.; Maniecki, T.; Basińska, A.; Goralski, J.; Fiedorow, R., Reduction requirements for Ru/(K) Fe₂O₃ catalytic activity in water-gas shift reaction. *Kinetics and catalysis* **2004**, *45*, 879-889.
45. Chen, J.; Zhao, Q.; Han, X.; Lv, J.; Li, Z.; Huang, S.; Ma, X., Extremely Low CO/H₂ Ratio Activation of a Precipitated Iron Catalyst for Enhanced Fischer–Tropsch Performance. *Energy & Fuels* **2022**, *36* (10), 5384-5392.
46. Bartholomew, C. H., Mechanisms of catalyst deactivation. *Applied Catalysis A: General* **2001**, *212* (1-2), 17-60.
47. de Smit, E.; Weckhuysen, B. M., The renaissance of iron-based Fischer–Tropsch synthesis: on the multifaceted catalyst deactivation behaviour. *Chemical Society Reviews* **2008**, *37* (12), 2758-2781.
48. Romero-Sáez, M.; Divakar, D.; Aranzabal, A.; González-Velasco, J.; González-Marcos, J., Catalytic oxidation of trichloroethylene over Fe-ZSM-5: Influence of the preparation method on the iron species and the catalytic behavior. *Applied Catalysis B: Environmental* **2016**, *180*, 210-218.
49. Pérez-Page, M.; Makel, J.; Guan, K.; Zhang, S.; Tringe, J.; Castro, R. H.; Stroeve, P., Gas adsorption properties of ZSM-5 zeolites heated to extreme temperatures. *Ceramics International* **2016**, *42* (14), 15423-15431.

50. Lin, W.-S.; Lin, H.-M.; Chen, H.-H.; Hwu, Y.-K.; Chiou, Y.-J., Shape effects of iron nanowires on hyperthermia treatment. *Journal of Nanomaterials* **2013**, *2013*, 9-9.
51. Sun, Y.; Gao, P.; Han, Y.; Ren, D., Reaction behavior of iron minerals and metallic iron particles growth in coal-based reduction of an oolitic iron ore. *Industrial & Engineering Chemistry Research* **2013**, *52* (6), 2323-2329.
52. Qu, B.; Zhu, C.; Li, C.; Zhang, X.; Chen, Y., Coupling hollow Fe₃O₄–Fe nanoparticles with graphene sheets for high-performance electromagnetic wave absorbing material. *ACS applied materials & interfaces* **2016**, *8* (6), 3730-3735.
53. Yang, C.; Zhao, H.; Hou, Y.; Ma, D., Fe₅C₂ nanoparticles: a facile bromide-induced synthesis and as an active phase for Fischer–Tropsch synthesis. *Journal of the American Chemical Society* **2012**, *134* (38), 15814-15821.
54. Nikitenko, S.; Koltypin, Y.; Felner, I.; Yeshurun, I.; Shames, A.; Jiang, J.; Markovich, V.; Gorodetsky, G.; Gedanken, A., Tailoring the properties of Fe–Fe₃C Nanocrystalline particles prepared by sonochemistry. *The Journal of Physical Chemistry B* **2004**, *108* (23), 7620-7626.
55. Ma, C.; Zhang, W.; Chang, Q.; Wang, X.; Wang, H.; Chen, H.; Wei, Y.; Zhang, C.; Xiang, H.; Yang, Y., θ -Fe₃C dominated Fe@C core–shell catalysts for Fischer–Tropsch synthesis: Roles of θ -Fe₃C and carbon shell. *Journal of Catalysis* **2021**, *393*, 238-246.
56. Herranz, T.; Rojas, S.; Pérez-Alonso, F. J.; Ojeda, M.; Terreros, P.; Fierro, J. L. G., Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas. *Journal of catalysis* **2006**, *243* (1), 199-211.
57. Yang, X.; Wang, R.; Yang, J.; Qian, W.; Zhang, Y.; Li, X.; Huang, Y.; Zhang, T.; Chen, D., Exploring the reaction paths in the consecutive Fe-based FT catalyst–zeolite process for syngas conversion. *ACS Catalysis* **2020**, *10* (6), 3797-3806.
58. Fierro, G.; Moretti, G.; Ferraris, G.; Andreozzi, G. B., A Mössbauer and structural investigation of Fe-ZSM-5 catalysts: Influence of Fe oxide nanoparticles size on the catalytic behaviour for the NO-SCR by C₃H₈. *Applied Catalysis B: Environmental* **2011**, *102* (1-2), 215-223.
59. Ma, Z.; Ma, H.; Zhang, H.; Wu, X.; Qian, W.; Sun, Q.; Ying, W., Direct conversion of syngas to light olefins through Fischer–Tropsch synthesis over Fe–Zr catalysts modified with sodium. *ACS omega* **2021**, *6* (7), 4968-4976.

60. Li, J.; Cheng, X.; Zhang, C.; Wang, J.; Dong, W.; Yang, Y.; Li, Y., Alkalies in iron - based Fischer-Tropsch synthesis catalysts: distribution, migration and promotion. *Journal of Chemical Technology & Biotechnology* **2017**, 92 (6), 1472-1480.
61. Chen, Y.; Zhang, H.; Ma, H.; Qian, W.; Jin, F.; Ying, W., Direct conversion of syngas to ethanol over Rh-Fe/ γ -Al₂O₃ catalyst: Promotion effect of Li. *Catalysis Letters* **2018**, 148, 691-698.
62. Han, Z.; Qian, W.; Ma, H.; Wu, X.; Zhang, H.; Sun, Q.; Ying, W., Study of the Fischer-Tropsch synthesis on nano-precipitated iron-based catalysts with different particle sizes. *RSC advances* **2020**, 10 (70), 42903-42911.
63. Yang, X.; Zhang, H.; Liu, Y.; Ning, W.; Han, W.; Liu, H.; Huo, C., Preparation of iron carbides formed by iron oxalate carburization for Fischer-Tropsch synthesis. *Catalysts* **2019**, 9 (4), 347.
64. Suo, H.; Wang, S.; Zhang, C.; Xu, J.; Wu, B.; Yang, Y.; Xiang, H.; Li, Y.-W., Chemical and structural effects of silica in iron-based Fischer-Tropsch synthesis catalysts. *Journal of catalysis* **2012**, 286, 111-123.
65. Pour, A. N.; Housaindokht, M. R.; Tayyari, S. F.; Zarkesh, J.; Alaei, M. R., Deactivation studies of Fischer-Tropsch synthesis on nano-structured iron catalyst. *Journal of Molecular Catalysis A: Chemical* **2010**, 330 (1-2), 112-120.
66. Xu, J.; Bartholomew, C. H.; Sudweeks, J.; Eggett, D. L., Design, synthesis, and catalytic properties of silica-supported, Pt-promoted iron Fischer-Tropsch catalysts. *Topics in catalysis* **2003**, 26, 55-71.

Data Availability Statement

The data supporting this article have been included as part of the Supplementary Information.