Title: Nanocrystalline iron–boron catalysts for low-temperature CO hydrogenation: Selective liquid fuel production and structure–activity correlation

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Abstract

Low-temperature Fischer–Tropsch synthesis (LTFTS) is one of the green routes for liquid fuel production. Herein, we prepared nanocrystalline Fe–B catalysts with different particle sizes and microstructures by adjusting the adding sequence of the precursors. In situ carburization of the Fe–B catalysts at 423 K revealed that the adding sequence influenced pronouncedly the rate and degree of carburization. In LTFTS at 423 K, the Fe–B catalysts displayed similar, markedly high selectivity to liquid fuels, with ~48% for C₅–C₁₁ (gasoline fraction) and ~31% for C₁₂–C₂₀ (diesel fraction) hydrocarbons, and low selectivities to CO₂ and CH₄, manifesting the excellent carbon atom economy over the non-noble Fe–B catalysts. Whilst the carburization degree did not affect the product distribution, the activities of the Fe–B catalysts evolved positively with the ϵ -Fe₂C content. Moreover, a good linear relationship was established between the Fe–Fe coordination number and the ϵ -Fe₂C content.

Keywords: Iron–boron; FeCl₃ precursor; Fischer–Tropsch catalyst; Low-temperature synthesis; Liquid fuel; Structure–activity relationship

1. Introduction

Iron occupies a unique position in **Fischer–Tropsch synthesis (FTS)** in that it has the merits of versatility in product control, high water–gas shift activity offsetting the deficit of H_2 in coal- or biomass-derived syngas (a mixture of CO and H_2), and low cost [1–7]. However, because of the poor low-temperature activity of conventional iron catalysts, even the so-called LTFTS process in industry is operated at above 473 K [8,9]. An iron catalyst that is active at much lower temperature is highly attractive, considering that the chain-growth probability increases preferably with the decrease in the reaction temperature [10], which allows the production of value-added hydrocarbons especially liquid fuels in an energy-efficient and straightforward manner needless of complex catalyst formulation.

It should be noted that the high FTS temperature is demanded by the carburization of iron to iron carbide, the active phase in FTS [11], but not by the very exothermic FTS reaction itself [12]. In FTS, to activate the iron catalyst, the CO molecules should dissociate first on iron to give surface carbon atoms, which then combine with iron to form iron carbide. Being limited by the high strength (11.2 eV) of the CO triple bond [13], the carburization process is unfortunately sluggish especially at low temperature [12], thus placing a severe obstacle to the practical application of the iron catalyst in LTFTS below 473 K.

In surface chemistry, there is a consensus that the reactivity of a metal surface depends critically on the coordination number [14]. In principle, surfaces containing atoms of increasing coordinative unsaturation are more reactive [15], which applies as

well to iron in the case of CO dissociation. It has been documented that the dissociation barrier of CO on the most closely packed Fe(1 1 0) surface is substantially higher than those on the more open Fe(1 0 0), (1 1 1), (2 1 0), (2 1 1), (3 1 0), and (7 1 0) surfaces [16–22]. For instance, CO dissociates at >373 K on Fe(1 1 0) surface [17], compared to ~300 K on the step-like Fe(1 1 1) surface [16]. Analogously, CO desorbs without dissociation at 360 K on densely packed *fcc* Fe film, while it dissociates at temperatures just above 300 K on *bcc* Fe film [23]. Recently, we identified that RQ Fe prepared by the rapid quenching metallurgy with an Fe–Fe coordination number of 4.0 displayed excellent FTS activity below 473 K. For this catalyst, ϵ -Fe₂C was verified as the active phase, which is 4.3 folds as active as χ -Fe₅C₂ in LTFTS at 443 K [24], which is consistent with the theoretical prediction by Jiao and co-workers [25], albeit χ -Fe₅C₂ is generally acknowledged as the real active phase for the iron-based catalysts in FTS above 473 K [26–29].

Metal borides prepared by a wet-chemistry approach using borohydride as the reductant usually bear nanosized dimension and consequently, high surface area and activity. The wet-chemistry approach is technically less demanding than the metallurgical approach and very versatile, since many preparation parameters can be adjusted with ease to tailor the composition, morphology, and structure of the resulting metal boride nanoparticles (NPs), thus providing abundant possibilities for the modulation of the catalytic performance [30]. Herein, we report that by adjusting the adding sequence of the FeCl₃ and KBH₄ aqueous solutions, *i.e.*, (i) adding KBH₄ to FeCl₃, the conventionally adopted sequence (the resulting catalyst is denoted as Fe–

B-*c*), (ii) adding FeCl₃ and KBH₄ simultaneously (the resulting catalyst is denoted as Fe-B-*s*), and (iii) adding FeCl₃ to KBH₄, the reversed adding sequence (the resulting catalyst is denoted as Fe-B-*r*), we were able to fabricate Fe-B NPs with different dimensions and microstructures. We found that in LTFTS at as low as 423 K, these Fe-B catalysts were active and showed excellent selectivity to the gasoline- and diesel-fraction liquid fuels. Furthermore, we identified that the activity of the Fe-B catalysts increased with the increase in the content of ϵ -Fe₂C, while the latter displayed a good linear relationship with the Fe-Fe coordination number, indicating that the Fe-Fe coordination number is an unrecognized key parameter that controls the activity of the iron catalysts in LTFTS.

2. Experimental

2.1. Synthesis of the Fe-B NPs catalysts

The Fe-B NPs were synthesized by the facile wet-chemistry approach. For the preparation of Fe-B-*c*, 5.0 ml of 2.0 M KBH₄ aqueous solution containing 0.20 M KOH as the stabilizer was added at a flow rate of 1.0 ml min⁻¹ with a peristaltic pump to 12.5 ml of 0.20 M FeCl₃ aqueous solution in an ice-water bath with vigorous stirring under the blanket of N₂. Then, the slurry was stirred at 273 K for 30 min to ensure complete reduction. The black precipitates were separated from the solution with a magnet, washed three times with deionized water, two times with anhydrous ethanol, and finally stored in anhydrous ethanol for characterization. For in situ carburization and LTFTS testing, the catalyst was additionally washed two times with

polyethylene glycol (PEG200, $M_w = 200$) and stored also in PEG200. During catalyst washing and transfer, care must be taken to ensure that the catalyst was always covered with a layer of liquid to avoid exposure to air.

The Fe–B-*s* catalyst was synthesized by adding KBH_4 (1.0 ml min^{-1}) and FeCl_3 (2.5 ml min^{-1}) simultaneously, and the Fe–B-*r* catalyst was synthesized by adding FeCl_3 (2.5 ml min^{-1}) into KBH_4 . Except for the difference in the adding sequence, other synthesis parameters for these two Fe–B catalysts were kept the same as those for Fe–B-*c*. For comparison, the Fe–B-*r*-873 catalyst was prepared by thermal treatment of Fe–B-*r* at 873 K in N_2 for 2 h.

2.2. Characterization

The bulk composition was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP–AES; Thermo Elemental IRIS Intrepid). N_2 physisorption was performed on a Micromeritics TriStar3000 apparatus at 77 K. The catalysts were transferred to the adsorption glass tube and heated at 383 K under N_2 for 2 h before measurement. The catalyst weight was determined by the difference in the adsorption tube upon completion of the experiment.

H_2 chemisorption was carried out on a Micromeritics 2750 chemisorption system to determine the metal surface area (S_{Fe}) of the as-prepared Fe–B catalysts. The catalysts were pretreated at 423 K for 1.5 h under Ar and cooled down to room temperature. Then, high-purity H_2 was introduced instead of Ar for 1 h to ensure the saturation adsorption of H_2 . The catalysts were then purged with Ar until the signal

returned to the baseline, as monitored by a thermal conductivity detector (TCD), and heated from room temperature to 873 K at a ramping rate of 10 K min⁻¹ under Ar with the flow rate of 30 ml min⁻¹. The area under the desorption curve was integrated, and the number of the moles of desorbed H₂ was quantified by comparing this area with the area of a calibrated H₂ pulse. The S_{Fe} was calculated with the assumption of the H/Fe stoichiometry of 1:1 [31] and the Fe surface atomic density of 1.63×10^{19} atoms m⁻².

The X-ray powder diffraction (XRD) patterns were acquired on a Bruker AXS D8 Advance X-ray diffractometer using Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm) equipped with a LynxEye 1-dimensional linear Si strip detector. The tube voltage was 40 kV, and the tube current was 40 mA. The 2θ range was scanned from 30° to 90° at the speed of 4° min⁻¹. For the acquisition of the time-dependent XRD patterns, the 2θ range was scanned from 37° to 52° at the speed of 1° min⁻¹ on the same diffractometer.

The surface morphology, particle size, and selected-area electron diffraction (SAED) pattern were observed by transmission electron microscopy (TEM) on a JEOL JEM2011 transmission electron microscope operated at 200 kV. The catalysts were dispersed in anhydrous ethanol, sonicated, and dripped onto a carbon film-coated copper grid. Particle size distribution histogram was constructed by randomly measuring about 300 particles. High-resolution TEM (HRTEM) images of the catalyst after carburization were acquired on a FEI Tecnai G2 S-Twin F20 field-emission transmission electron microscope operated at 200 kV.

The Fe K-edge X-ray absorption fine structure (XAFS) data were collected in the transmission mode at room temperature on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). The beamline was equipped with a Si(1 1 1) double crystal monochromator. Ionization chambers were used to detect the incident and transmitted beam signals. The typical electron beam energy was 2.5 GeV, and the current was 200 mA. The extended X-ray absorption fine-structure (EXAFS) spectra were analyzed by the NSRLXAFS 3.0 package according to standard procedures [32]. The k range measured was 0–16.1 $\text{\AA}^{-1}$ (for the Fe foil standard, 0–14.4 $\text{\AA}^{-1}$). The corresponding k^2 -weighted $\chi(k)$ ($k^2\chi(k)$) curves are presented in Fig. S1. The $k^2\chi(k)$ data were Fourier-transformed (uncorrected) using a Kaiser-Bessel window over a k -range of 3.1–13.6 $\text{\AA}^{-1}$ (for the Fe foil, 3.0–13.6 $\text{\AA}^{-1}$) with a resolution of *ca.* 0.1 $\text{\AA}$. The processed $k^2\chi(k)$ data were fitted in the R -space ranging from 1.3 to 2.8 $\text{\AA}$ with ten independent parameters for the Fe–Fe and Fe–B subshells, including two sets of coordination number (N), the nearest distance between absorber and backscatterer atoms (R_0), the thermal disorder factor (σ_T), the static disorder factor (σ_S), and the inner potential correction (ΔE_0). A convolution of Gaussian and exponent function was used to derive the EXAFS formula [33]. Theoretical backscattering amplitudes and phase shifts for the Fe–Fe and Fe–B pairs were calculated using the FEFF8.2 code [34] with α -Fe and Fe₂B as references, respectively. The amplitude reduction factor (S_0^2) was derived by fitting the Fe foil standard.

⁵⁷Fe Mössbauer absorption spectra (MAS) were recorded on a spectrometer constructed by the Key Laboratory of Nuclear Analysis Techniques, Chinese

Academy of Sciences, using a $^{57}\text{Co}/\text{Rh}$ irradiation source in the constant acceleration transmission mode at room temperature. The velocity was calibrated by a 25 μm -thick $\alpha\text{-Fe}$ foil, and the isomer shift (IS) value was referenced to $\alpha\text{-Fe}$ at room temperature. The spectra were fitted using a least-squares fitting routine that models the spectrum as appropriate superpositions of ferromagnetic sextets and superparamagnetic (spm) quadruple doublets with Lorentzian line-shape and constrains in peak width and intensity using the MossWinn 3.0i program. The derived hyperfine parameters, including IS, quadrupole shift for sextet or quadruple splitting for doublet (QS), and magnetic hyperfine field (H), were used for spectral component qualification. Quantification was based on the areas of the absorption peaks assuming the same recoil-free factor for all kinds of iron nuclei.

2.3. Catalytic testing

The as-prepared Fe–B catalysts dispersed in 20 ml of PEG200 were transferred to a 50 ml-capacity stainless steel autoclave (CJF-0.05). PEG200 has been proven to be an excellent solvent in comparison with dodecane, $[\text{Bmim}][\text{BF}_4]$, ethanol, as well as cyclohexanol in iron-catalyzed LTFTS and does not participate in the reaction [12]. The autoclave was purged three times with syngas ($\text{H}_2/\text{CO}/\text{N}_2 = 64/32/4$, volume ratio) to expel air, sealed, and pressurized to 30 bar at room temperature. When the temperature of 423 K was reached, the stirring was commenced with the speed of 800 rpm for 2 h for in situ carburization of the catalyst. The carburized catalyst was separated from the liquid phase by a magnet, washed with anhydrous ethanol and

PEG200 for two times, and then subjected to activity evaluation under reaction conditions identical to those for in situ carburization. The CO conversion was controlled to below 10%, *i.e.*, a pressure drop below 0.40 MPa at 423 K, to obtain the kinetically meaningful activity data by minimizing the possible diffusion limits. After a reaction time depending on the activity of the catalyst, the stirring was terminated, and the autoclave was cooled down to room temperature. H₂, N₂, CO, CH₄, and CO₂ in the gas phase were analyzed on a GC9560 gas chromatograph fitted with a 2 m-long TDX-01 packed column connected to a TCD, with N₂ as the internal standard. The C₁–C₄ hydrocarbons in the gas phase were analyzed on a GC9160 gas chromatograph fitted with a PONA capillary column (50 m × 0.25 mm × 0.50 μm) connected to a flame ionization detector (FID) and correlated with the content of CH₄. The liquid products were extracted by cyclohexane and analyzed on the same GC9160 gas chromatograph using decahydronaphthalene as the internal standard. The catalysts were tested at least in duplicate; results from replicate runs agreed to within ±5%. The activity was calculated as (moles of CO converted)/(moles of iron × h) on the basis of the conversion of CO, the reaction time for reaching that CO conversion, and the total amount of the iron atoms, as there is no authentic method to determine the active surface area of the iron carbide. The hydrocarbon selectivities were calculated on carbon basis. The carbon balance of the FTS products was better than 95%.

3. Results and discussion

3.1. Morphology and structure of the as-prepared Fe–B catalysts

The basic physicochemical properties of the as-prepared Fe–B-*c*, Fe–B-*s*, and Fe–B-*r* catalysts are compiled in Table 1. Fe–B-*r* has the highest specific surface area (S_{BET}) and metallic iron surface area (S_{Fe}) among the Fe–B catalysts, consistent with its smallest particle size observed by TEM (Fig. 1). We found that since the KBH_4 reductant was always in excess during the reversed adding sequence, the reduction proceeded more drastically, which is expected to result in Fe–B-*r* with the smallest particle size and the largest surface area [35]. Table 1 also shows that the atomic percentage of boron increases from Fe–B-*c*, Fe–B-*s*, to Fe–B-*r*. This trend complies with previous findings that the Fe–B [36] and Ni–B materials [37] prepared in the reversed adding sequence contain more boron. The reversed adding sequence affords a basic environment throughout the reduction, which can avoid the acid-promoted hydrolysis of BH_4^- , thus resulting in Fe–B-*r* with the highest boron content [36].

It is interesting that under similar preparation conditions, Ni–B and Co–B metal-metalloid alloys are amorphous in structure [37,38], while the current Fe–B catalysts are polycrystalline, as verified by the SAED patterns (Fig. 1, inset) showing distinct dots and rings ascribable to *bcc* Fe (α -Fe) rather than one halo ring typical for amorphous alloys [30]. In the present case, the $\text{BH}_4^-/\text{Fe}^{3+}$ molar ratio is 4.0. According to the finding of Saida *et al.*, this ratio is sufficient to ensure the amorphous structure of the Ni–B and Co–B alloys, but a $\text{BH}_4^-/\text{Fe}^{2+}$ molar ratio above 8.0 necessitates the formation of amorphous Fe–B alloy [35]. For trivalent ferric ions, an even higher $\text{BH}_4^-/\text{Fe}^{3+}$ ratio is expected for the formation of amorphous Fe–B alloy.

The crystalline structure of the Fe–B catalysts is also confirmed by XRD (Fig. S2). Fe–B-*c* exhibits three diffraction peaks at 2θ of 44.6° , 65.1° , and 82.4° characteristic of α -Fe (JCPDS 06-0696). The diffraction peaks are broadened for Fe–B-*s*, so only the strongest (1 1 0) peak of α -Fe is discerned. The (1 1 0) peak is further attenuated for Fe–B-*r*, implying further lowering of the degree of crystallinity. On the basis of the broadening of the (1 1 0) peak and the Scherrer equation, their crystallite sizes are calculated and summarized in Table 1, which are much smaller than the particle sizes measured by TEM, indicating that the Fe–B catalysts are constituted by nanoparticles of polycrystalline structure.

The Fe K-edge X-ray absorption near-edge structure (XANES) spectra (Fig. 2a) confirm that the Fe–B catalysts have similar electronic property, with the Fe K-edge energy of 7112 eV typical for metallic iron [39]. Fig. 2b displays the non-phase corrected, k^2 -weighted, Fourier-transformed Fe K-edge EXAFS spectra. Consistent with the SAED and XRD results, the crystalline character of the Fe–B catalysts is corroborated by the occurrence of three distinct coordination peaks in the radial distribution function (RDF) curves at distances identical with those of the Fe foil standard, rather than a single coordination peak characteristic of the short-range ordering of the amorphous alloy [40]. On the other hand, the peak amplitudes of the Fe–B catalysts are substantially lower than those of the Fe foil, signifying the reduced coordination number [41]. Table 2 summarizes the structural parameters from the best fit. The good quality of the fitting is validated by the consistency of the simulated $k^2\chi(k)$ curves with the experimental data (Fig. S3). In addition, the ΔE_0 values within

the energy range of ± 10 eV and the small variations in the σ values (Table 2) signify that the fitted R and N values are **credible**, respectively. There are no virtual changes in the average interatomic distance (R_j) of the first Fe–Fe (~ 2.47 Å) and Fe–B (~ 2.13 Å) coordination subshells for these Fe–B catalysts. The appearance of the Fe–B subshell indicates the presence of the bonding of boron with iron in the Fe–B catalysts. The coordination number (N) of the Fe–Fe shell decreases in the order of Fe–B-*c* (5.1) > Fe–B-*s* (4.2) > Fe–B-*r* (3.8), which is significantly smaller than the value of 8.0 for the Fe foil standard.

3.2. Phase composition of the carburized Fe–B catalysts

Prior to the LTFTS reaction, the Fe–B catalysts were activated by in situ carburization at 423 K for 2 h in a batchwise reactor under the LTFTS conditions proposed by Kou and co-workers ($\text{H}_2/\text{CO}/\text{N}_2 = 64/32/4$ by volume, 30 bar at RT, PEG200 as the reaction medium) [12]. The carburized Fe–B catalysts were characterized by XRD and ^{57}Fe MAS. Fig. 3a shows that for Fe–B-*c*, aside from the occurrence of new features at 2θ of 43.0° and 56.9° , the diffraction peaks at 2θ of 44.6° and 82.3° due to α -Fe (JCPDS 06-0696) still dominate after carburization. For Fe–B-*s*, an additional feature at 2θ of 37.3° appears at the expense of α -Fe. For Fe–B-*r*, the features at 2θ of 37.3° , 43.0° , and 56.9° are intensified further; these peaks are assignable to ε -Fe₂C (JCPDS 36-1249), as will be corroborated by ^{57}Fe MAS later. For Fe–B-*r*, there is also a broad bump overlapping with the main peak of ε -Fe₂C at 2θ of 43.0° , which may originate from the coexistence of χ -Fe₅C₂ (JCPDS 36-1248)

of low content and/or small crystallite size.

Fig. 4 presents the HRTEM images of the carburized Fe–B-*r* as a representative of the Fe–B catalysts. The carburized Fe–B-*r* catalyst is nano-dimension and bears the crystalline core–amorphous shell structure. The amorphous shell of low contrast may be due to a boron oxide layer that is carried over from the as-prepared Fe–B-*r* (Fig. 1c) and/or a newly formed carbon layer during the carburization process [42]. In the crystalline core, the lattice fringes with the spacings of 2.09 Å (Fig. 4a) and 2.05 Å (Fig. 4b) assignable to the (1 0 1) plane of ϵ -Fe₂C and the (5 1 0) plane of χ -Fe₅C₂, respectively, are readily visible, which are consistent with the assignments according to XRD. The presence of ϵ -Fe₂C is further validated by the observation of the lattice fringes with a larger spacing of 2.38 Å (Fig. 4b) attributable to the (1 0 0) plane of ϵ -Fe₂C.

Figs. 3b–3d present the time-dependent XRD patterns of the Fe–B catalysts during in situ carburization. It is found that the adding sequence of FeCl₃ and KBH₄ drastically influences the carburization rate of α -Fe to ϵ -Fe₂C. For Fe–B-*c*, ϵ -Fe₂C emerges at *ca.* 30 min of carburization and becomes comparable to α -Fe in diffraction intensity at above 90 min of carburization. For Fe–B-*s*, ϵ -Fe₂C is comparable to α -Fe in intensity only after 20 min of carburization. For Fe–B-*r*, the diffraction peak of α -Fe is virtually diminished after 35 min of carburization, with ϵ -Fe₂C dominating the diffractogram. On the basis of Figs. 3b–3d, the crystallite sizes of ϵ -Fe₂C in the carburized Fe–B-*c*, Fe–B-*s*, and Fe–B-*r* are estimated to be 13.2, 11.9, and 12.8 nm, respectively.

Fig. 5 presents the ^{57}Fe MAS spectra of the carburized Fe–B catalysts as well as the deconvoluted sub-spectra; the corresponding Mössbauer parameters are compiled in Table 3. The assignment of $\varepsilon\text{-Fe}_2\text{C}$ is readily established from three sextets with the H values of *ca.* 140, 170, and 235 kOe [24,43]. Three sextets with the H values of *ca.* 110, 185, and 229 kOe allow the assignment of $\chi\text{-Fe}_5\text{C}_2$ [44]. The assignment of $\alpha\text{-Fe}$ is based on the sextet with the H value of *ca.* 333 kOe [26]. The sextet with the H value of *ca.* 270 kOe is due to $\text{Fe}_{80}\text{B}_{20}$ [45,46]. There is also a doublet with the IS value of *ca.* 0.23 mm s $^{-1}$ and the QS value of *ca.* 1.10 mm s $^{-1}$ attributable to Fe(II) or Fe(III) species [47,48], which may be due to the occurrence of some poorly crystallized iron oxide. By assuming the same recoil-free factors, the contents of $\varepsilon\text{-Fe}_2\text{C}$ in the carburized Fe–B-*c*, Fe–B-*s*, and Fe–B-*r* are quantified as 16.2%, 27.1%, and 31.8%, respectively, and the contents of $\chi\text{-Fe}_5\text{C}_2$ are 16.0%, 22.6%, and 26.1% in the carburized Fe–B-*c*, Fe–B-*s*, and Fe–B-*r*, respectively.

The above XRD and ^{57}Fe MAS results demonstrate that the adding sequence of FeCl_3 and KBH_4 pronouncedly influences the carburization rates of the Fe–B catalysts and the phase compositions of the carburized catalysts. To unveil the main factor that affects $\varepsilon\text{-Fe}_2\text{C}$ formation, correlation of the physicochemical characters of the as-prepared Fe–B catalysts with the content of $\varepsilon\text{-Fe}_2\text{C}$, the excellent active phase in LTFTS [24], was intended. Remarkably, a linear relationship only emerges when plotting the content of $\varepsilon\text{-Fe}_2\text{C}$ against the Fe–Fe coordination number, as illustrated in Fig. 6a. This linear relationship is consistent with the knowledge that the dissociation barrier of CO on metallic iron decreases with the decrease in the coordination number

of iron [16–22], as supported by the time-dependent XRD patterns presented in Figs. 3b–3d, and convincingly evidences the critical role of the highly coordinatively unsaturated iron atoms in ε -Fe₂C formation at low temperature. According to Weckhuysen and co-workers, ε -Fe₂C is thermodynamically stable only at <473 K [49]. However, at low temperature its transformation from α -Fe is severely inhibited by kinetics. While at elevated temperatures, ε -Fe₂C readily evolves into high-temperature phases such as χ -Fe₅C₂ and FTS-inactive θ -Fe₃C [49]. The present work substantiates our recent finding that the key to disentangle this dilemma is to reduce the coordination number of iron [24].

It is interesting that after LTFTS we did not identify χ -Fe₅C₂ on the RQ Fe catalyst with the Fe–Fe coordination number in-between those of Fe–B-*s* and Fe–B-*r* [24]. It is logical to deduce that on RQ Fe the activation barrier for ε -Fe₂C formation is much lower than that for χ -Fe₅C₂ formation. In contrast, the Fe–B catalysts contain an appreciable amount of χ -Fe₅C₂ after in situ carburization at 423 K, which ordinarily forms at ~523 K [49]. It is likely that the presence of boron in the Fe–B catalysts narrows down the energy difference between these two barriers. In order to elucidate the exact role of boron, not only the formation of carbon on the surfaces of iron with and without boron, but also the diffusion of surface carbon to the bulk to form iron carbides (ε -Fe₂C and χ -Fe₅C₂) have to be simulated in detail. Surface reactions have already been challenging for quantum chemistry because of the numerous possible reaction channels and the huge size of the system. The diffusion of carbon requires a molecular dynamics simulation of thousands of trajectories with

properly chosen potential energy surface. Simulating this complicated phase transformation process is challenging for quantum chemistry for the time being [50]. Due to these challenges, a perfect understanding of the role of boron played in χ -Fe₅C₂ formation is difficult at the present stage and calls for further studies.

3.3. LTFTS performance and structure–performance correlation

The catalytic activities of the carburized Fe–B catalysts in LTFTS at 423 K are presented in Table S1. The activity is expressed as moles of CO converted on per mole of iron per hour, for there is no authentic method to determine the active surface area of iron carbide for calculating the intrinsic activity. It is found that the activity compares as 2.1, 4.3, and 6.7 mol_{CO} mol_{Fe}^{−1} h^{−1} on Fe–B-*c*, Fe–B-*s*, and Fe–B-*r*, respectively, showing that the content of ε -Fe₂C markedly influences the LTFTS activity. Notably, the activity of Fe–B-*r* approaches that of RQ Fe (7.2 mol_{CO} mol_{Fe}^{−1} h^{−1}) prepared by the technically demanding rapid quenching metallurgy [24] when compared at similar CO conversion under identical LTFTS conditions (Table S1). On the other hand, Fig. 7 shows that the product distributions are constant on all three Fe–B catalysts, which indicates that the nature of the active phase is **identical** and the difference in the boron content among these catalysts (Table 1) does not induce distinguishable difference in product selectivity. It is worth noting that on the Fe–B catalysts, the selectivities to the unwanted CO₂ and CH₄ are only 6.7% and 4.2% at most, respectively. The main products are the more desirable C₅–C₁₁ hydrocarbons (gasoline fraction, ~48%) and C₁₂–C₂₀ hydrocarbons (diesel fraction, ~31%), and the

selectivity to C₂₁₊ hydrocarbons is less than 5.0%, manifesting the superior utilization efficiency of the carbon atoms in syngas over these Fe–B catalysts in LTFTS. The comparison of the product distributions over the Fe–B catalysts with that over RQ Fe under identical LTFTS conditions (Fig. S4) implies that the presence of B is beneficial to the suppression of the undesired CO₂ and CH₄ byproducts.

Heterogeneous catalysis occurs on catalyst surface. To estimate the surface availability of the LTFTS active phase ϵ -Fe₂C, as a first approximation we assume that the active surface area of ϵ -Fe₂C is proportional to its bulk content determined by ⁵⁷Fe MAS weighted by the S_{Fe} of the as-prepared Fe–B catalysts (Table 1), which is termed as the nominal active surface area (hereafter referred to as “nominal S_{act} ”). Fig. 6b reveals that the activities of the Fe–B catalysts increase linearly with the nominal S_{act} of ϵ -Fe₂C, demonstrating that the activity difference among these catalysts is originated from the difference in the surface abundance of ϵ -Fe₂C, but not due to the difference in the nature of the active phase. On the basis of the activities and the nominal S_{act} values, along with the compositions of the as-prepared Fe–B catalysts (Table 1), we tentatively estimated their turnover frequencies (TOFs). The resulting apparent TOFs are in the same order of magnitude with the values of 9.1, 6.8, and 6.9 s⁻¹ for Fe–B-*c*, Fe–B-*s*, and Fe–B-*r*, respectively. These values are higher than the TOF of $3.58 \times 10^{-3} \text{ s}^{-1}$ reported on a poly(N-vinyl-2-pyrrolidone)-stabilized Ru nanocluster (PVP-Ru) catalyst under similar reaction conditions [51]. However, one cannot make too much of this difference, because the active surface area of the PVP-Ru catalyst was estimated on the basis of the particle size of the Ru nanoclusters

with the assumed truncated hexagonal bipyramid morphology, and the surface occupation by PVP or other impurities was not taken into consideration. Both approximations actually resulted in an apparent TOF of the lower limit for the PVP-Ru catalyst [52].

To validate the generality of the linear relationship unveiled in Fig. 6, two control catalysts were prepared and evaluated. First, Fe-B-*r*-873 was prepared by thermally annealing Fe-B-*r* at 873 K in N₂ for 2 h. EXAFS (Fig. S5 and Table 2) reveals that its Fe-Fe coordination number **increases** to 5.8 due to sintering (Fig. S2). With this value, we can read out the ϵ -Fe₂C content in Fe-B-*r*-873 from Fig. 6a. Coupled with the S_{Fe} of 5.0 m² g⁻¹ of Fe-B-*r*-873 (Table 1), its nominal S_{act} is figured out, and the activity is predicted as 0.39 mol_{CO} mol_{Fe}⁻¹ h⁻¹ by simply referring to Fig. 6b. Under identical LTFTS conditions, we acquired the experimental activity of Fe-B-*r*-873 of 0.45 mol_{CO} mol_{Fe}⁻¹ h⁻¹ (Table S1). Second, RQ Fe with the Fe-Fe coordination number of 4.0 was prepared following our previous work [24]. This catalyst has the S_{Fe} of 31 m² g⁻¹ (Table 1) and the experimental activity of 7.2 mol_{CO} mol_{Fe}⁻¹ h⁻¹ under the same LTFTS conditions (Table S1). On the basis of Fig. 6, we analogously predicted the activity as 6.8 mol_{CO} mol_{Fe}⁻¹ h⁻¹ for RQ Fe. Although the predicted activities are somewhat lower than the experimental ones, the closeness is remarkable, considering the drastic differences between the control catalysts (Fe-B-*r*-873 and RQ Fe) and the as-prepared Fe-B catalysts in structure and/or composition.

Aside from the present and our previous works [24], there are only few works addressing the active phase of the iron-based catalysts in LTFTS. Fan *et al.*

characterized the Fe NPs prepared in a mixture of EG and water after LTFTS at 423 K by XRD, and found that the Fe NPs remained amorphous. After subsequent calcination at 873 K under nitrogen flow, diffractions associated with θ -Fe₃C as well as metallic iron emerged [12]. Because θ -Fe₃C is the only iron carbide that can survive under high temperature, and other iron carbides, if ever formed, would readily evolve into θ -Fe₃C at 873 K [49], one cannot figure out the exact active phase in that case. Chen *et al.* reported that the Fe NPs prepared in water exhibited an activity of 0.83 mol_{CO} mol_{Fe}⁻¹ h⁻¹ in LTFTS at 473 K. After reaction, they identified by ⁵⁷Fe MAS that the catalyst was dominated by oxidized iron, while there were only 13.3% of χ -Fe₅C₂ and 7.1% of ε' -Fe_{2.2}C [46]. Although the activity of ε' -Fe_{2.2}C in LTFTS has not been explored experimentally, considering that its crystallographic structure is similar to that of ε -Fe₂C (both with carbon atoms being situated in octahedral interstices) [11], it is reasonable to propose that ε' -Fe_{2.2}C is analogously more active than χ -Fe₅C₂ [24,25]. Therefore, the low ε' -Fe_{2.2}C content in Fe NPs after reaction may be responsible for its low LTFTS activity.

As an important property of a catalyst, the stability of the Fe-B-*r* catalyst exhibiting the highest activity was examined. Fig. 8 shows that the CO conversion decreased only by 5.3% from the first run to the fifth run. The ~1% per run activity drop may be caused by small material loss due to catalyst attrition in stirred liquid-phase reaction and repetitive catalyst recovery. This possibility, rather than an alteration in the nature of the catalyst during the stability test, is supported by the essentially identical product distributions also depicted in Fig. 8. The XRD pattern of

the Fe–B-*r* catalyst after the stability test (Fig. S6) confirms that ϵ -Fe₂C remains as the dominant phase with the crystallite size of 12.5 nm, which is similar to the size before the stability test, verifying the durability of the Fe–B-*r* catalyst in LTFTS.

4. Conclusions

We have demonstrated that the facile wet-chemistry method is versatile in adjusting the physicochemical properties of the Fe–B catalysts. In LTFTS at 423 K, these catalysts exhibited similar, high selectivity to gasoline- and diesel-fraction liquid fuels, while the best activity was achieved on the Fe–B-*r* catalyst, which is also stable in repeated catalytic runs. An excellent linear relationship between the Fe–Fe coordination number and the ϵ -Fe₂C content, and a linear correlation between the LTFTS activity and the surface abundance of ϵ -Fe₂C, are identified. This work offers a convenient route for the fabrication of cost-effective but high-performance iron-based catalysts for the industrially appealing LTFTS process and highlights the critical role of the Fe–Fe coordination number in the rational design of iron nanomaterials for the LTFTS reaction.

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Figure captions

Fig. 1 TEM images and particle size distribution histograms of the (a) Fe–B-*c*, (b) Fe–B-*s*, and (c) Fe–B-*r* catalysts.

Fig. 2 (a) The normalized Fe K-edge XANES spectra, and (b) the non-phase corrected, k^2 -weighted, Fourier-transformed Fe K-edge EXAFS patterns of the Fe–B catalysts.

Fig. 3 (a) XRD patterns of the Fe–B catalysts after in situ carburization at 423 K for 2 h under the LTFTS conditions. (b), (c), and (d) Time-dependent XRD patterns of the Fe–B-*c*, Fe–B-*s*, and Fe–B-*r* catalysts during in situ carburization under the LTFTS conditions, respectively.

Fig. 4 HRTEM images of the Fe–B-*r* catalyst after in situ carburization at 423 K for 2 h under the LTFTS conditions.

Fig. 5 ^{57}Fe Mössbauer spectra of the Fe–B catalysts after in situ carburization at 423 K for 2 h under the LTFTS conditions.

Fig. 6 Plots of (a) the $\varepsilon\text{-Fe}_2\text{C}$ content versus the Fe–Fe coordination number, and (b) the activity versus the nominal S_{act} of $\varepsilon\text{-Fe}_2\text{C}$ of the Fe–B catalysts. Two points labelled with $\times$ represent the predicted $\varepsilon\text{-Fe}_2\text{C}$ content and activity of the control Fe–B-*r*-873 and RQ Fe catalysts.

Fig. 7 The product selectivities over the Fe–B catalysts in LTFTS. Reaction conditions: $T = 423\text{ K}$, $p = 30\text{ bar}$ at room temperature, $\text{H}_2/\text{CO}/\text{N}_2 = 64/32/4$, 2.5 mmol of Fe, 20 ml of PEG200, stirring rate of 800 rpm, and the CO conversion level of about 9%.

Fig. 8 The CO conversion and product distribution over the Fe–B-*r* catalyst in five successive LTFTS runs. Reaction conditions: $T = 423\text{ K}$, $p = 30\text{ bar}$ at room

temperature, $\text{H}_2/\text{CO}/\text{N}_2 = 64/32/4$, 2.5 mmol of Fe, 20 ml of PEG200, stirring rate of 800 rpm, and reaction time of 35 min.

Table 1 Physicochemical properties of the as-prepared Fe–B-*c*, Fe–B-*s*, Fe–B-*r*, Fe–B-*r*-873, and RQ Fe catalysts.

Catalyst	Composition ^a (atomic ratio)	S_{BET} (m ² g ^{−1})	d^b (nm)	d_{cryst}^c (nm)	S_{Fe} (m ² g _{cat} ^{−1})
Fe–B- <i>c</i>	Fe _{82.5} B _{17.5}	26	50.6	14.4	14
Fe–B- <i>s</i>	Fe _{80.4} B _{19.6}	37	34.6	10.8	23
Fe–B- <i>r</i>	Fe _{71.2} B _{28.8}	71	19.1	9.5	29
Fe–B- <i>r</i> -873	n.m. ^d	22	n.m. ^d	23.1	5.0
RQ Fe	Fe _{92.7} Al _{7.3}	44	n.m. ^d	13.5	31

^a Bulk composition determined by ICP–AES.

^b Mean particle size measured by TEM.

^c Crystallite size calculated from the broadening of the Fe(1 1 0) diffraction peak and the Scherrer equation.

^d Not measured.

Table 2 The structural parameters from the Fe K-edge EXAFS data of the as-prepared Fe-B-*c*, Fe-B-*s*, Fe-B-*r*, and Fe-B-*r*-873 catalysts.^a

Sample	Pair	N	R_0 (Å)	σ_T (Å)	σ_S (Å)	R_j^b (Å)	ΔE_0 (eV)
Fe-B- <i>c</i>	Fe-Fe	5.1	2.39	0.079	0.077	2.47	-3.3
	Fe-B	2.1	2.08	0.082	0.046	2.13	0.5
Fe-B- <i>s</i>	Fe-Fe	4.2	2.40	0.079	0.077	2.48	-4.8
	Fe-B	2.4	2.08	0.082	0.046	2.13	-9.4
Fe-B- <i>r</i>	Fe-Fe	3.8	2.40	0.073	0.072	2.47	-3.8
	Fe-B	2.7	2.09	0.069	0.046	2.14	-3.9
Fe-B- <i>r</i> -873	Fe-Fe	5.8	2.51	0.083	-	2.51	9.1
Fe foil	Fe-Fe	8.0	2.48	0.072	-	2.48	1.9

^a N , coordination number; R_0 , the nearest distance between absorber and backscatterer atoms; R_j , the average interatomic distance; σ_T , the thermal disorder factor; σ_S , the static disorder factor; ΔE_0 , inner potential correction. Errors: N , $\pm 10\%$; R_0 , ± 0.02 Å.

^b $R_j = R_0 + \sigma_S$.

Table 3 ^{57}Fe Mössbauer parameters of the Fe–B-*c*, Fe–B-*s*, and Fe–B-*r* catalysts after in situ carburization at 423 K for 2 h under the LTFTS conditions.^a

Assignment	Parameter	Fe–B- <i>c</i>	Fe–B- <i>s</i>	Fe–B- <i>r</i>
$\varepsilon\text{-Fe}_2\text{C}$ (A)	IS (mm s^{-1})	0.25	0.25	0.25
	QS (mm s^{-1})	0.01	0.05	0.03
	H (kOe)	136	140	140
	A (%)	2.5	4.2	5.1
$\varepsilon\text{-Fe}_2\text{C}$ (B)	IS (mm s^{-1})	0.24	0.24	0.24
	QS (mm s^{-1})	−0.05	−0.02	−0.01
	H (kOe)	175	175	170
	A (%)	8.7	14.6	16.8
$\varepsilon\text{-Fe}_2\text{C}$ (C)	IS (mm s^{-1})	0.16	0.16	0.16
	QS (mm s^{-1})	0.10	0.10	0.10
	H (kOe)	235	235	235
	A (%)	5.0	8.3	9.9
$\chi\text{-Fe}_5\text{C}_2$ (A)	IS (mm s^{-1})	0.18	0.18	0.18
	QS (mm s^{-1})	0.08	0.08	0.08
	H (kOe)	185	185	185
	A (%)	7.2	8.6	10.5
$\chi\text{-Fe}_5\text{C}_2$ (B)	IS (mm s^{-1})	0.25	0.25	0.25
	QS (mm s^{-1})	0.14	0.10	0.10
	H (kOe)	229	229	229

	A (%)	6.6	10.3	10.0
χ -Fe ₅ C ₂ (C)	IS (mm s ⁻¹)	0.30	0.28	0.30
	QS (mm s ⁻¹)	-0.10	-0.10	-0.10
	H (kOe)	109	115	109
	A (%)	2.2	3.7	5.6
α -Fe	IS (mm s ⁻¹)	0.02	0.02	0.01
	QS (mm s ⁻¹)	0.02	0.02	0.03
	H (kOe)	333	332	333
	A (%)	38.6	14.4	14.5
Fe ₈₀ B ₂₀	IS (mm s ⁻¹)	0.14	0.16	0.16
	QS (mm s ⁻¹)	0.01	-0.05	0.03
	H (kOe)	272	269	268
	A (%)	25.9	28.1	18.6
Fe(II)/Fe(III)	IS (mm s ⁻¹)	0.23	0.23	0.29
	QS (mm s ⁻¹)	1.11	1.10	1.12
	A (%)	3.3	7.8	9.0

^a IS: isomer shift (relative to α -Fe); QS: quadrupole shift for sextet or quadruplet splitting for doublet; H : magnetic hyperfine field; A : relative spectral area.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Graphical abstract

Nanocrystalline iron–boron catalysts for low-temperature CO hydrogenation: selective liquid fuel production and structure–activity correlation

Ke Xu ^a, Yi Cheng ^a, Jun Lin ^b, Hao Wang ^a, Songhai Xie ^a, Yan Pei ^a, Shirun Yan ^a, Minghua Qiao ^{a,*}, Zhen Hua Li ^a, Baoning Zong ^{c,*}

Nanocrystalline iron–boron catalysts with high structural unsaturation are highly active and selective for the production of gasoline- and diesel-fraction liquid fuels in low-temperature Fischer–Tropsch synthesis (LTFTS) at 423 K.