

In situ XAFS research on the formation mechanism of $(\text{Fe}_x\text{Co}_y)_2\text{C}$ for higher alcohol synthesis

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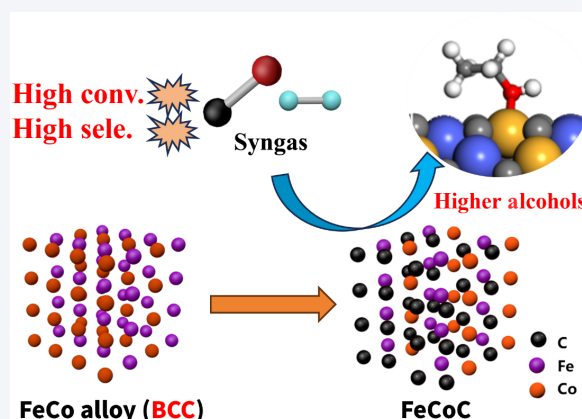
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 Cite this article: Nano Research, 2026, 19, 94908663. <https://doi.org/10.26599/NR.2026.94908663>

ABSTRACT: Higher alcohol synthesis (HAS) via the Fischer–Tropsch process from syngas is a promising technology for advancing renewable energy applications. This method serves as an effective substitute for fossil fuels and contributes to reducing greenhouse gas emissions. The FeCo bimetallic alloy carbide $(\text{Fe}_x\text{Co}_y)_2\text{C}$ has been shown to optimize the dual active interface and promote the production of higher oxygenates. However, understanding the dynamic interactions between metallic components under reaction conditions remains a significant challenge. In this study, we evaluate FeCoK and FeCo catalysts produced through precipitation, as well as the FeK/CoK catalyst created via physical mixing, for their performance in HAS. These catalysts exhibit notable differences in activity and product selectivity. Our investigation into the structure–performance relationship indicates that FeCoK, with $(\text{Fe}_x\text{Co}_y)_2\text{C}$ as its active site, demonstrates the highest activity and selectivity for alcohol production. To further elucidate the formation mechanism of the FeCo alloy carbide, we conduct *in situ* X-ray absorption fine structure (XAFS) tests. The results reveal that Co in the FeCo alloy adopts a body-centered cubic structure, differing from the more common Fischer–Tropsch catalyst structures (face-centered cubic or hexagonal close-packed). Further research into the carburization of the FeCo alloy proposes two essential conditions for the formation of $(\text{Fe}_x\text{Co}_y)_2\text{C}$ via the regular thermochemical method: The carburization must originate from the alloy, and an alkali promoter must be present.



KEYWORDS: higher alcohol synthesis, *in situ* X-ray absorption fine structure (XAFS), active site reconstruction

1 Introduction

Syngas, a customizable mixture of CO and H₂ derived from nonpetroleum resources, is a crucial intermediate for synthesizing high-value chemicals and fuels through catalytic processes [1–4].

Received: November 21, 2025; **Revised:** February 24, 2026

Accepted: March 23, 2026

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Higher alcohols, which contain more carbon atoms than methanol, are essential compounds in the chemical, pharmaceutical, and energy industries, with diverse applications. They function as clean fuels, fuel additives, value-added chemicals in fine chemical synthesis, and precursors in pharmaceutical manufacturing [5]. The technology for higher alcohol synthesis, utilizing the Fischer–Tropsch synthesis (FTS) pathway, not only effectively substitutes traditional fossil fuel-based processes and reduces greenhouse gas emissions but also promotes the recycling of waste resources [6]. This approach is integral to achieving energy transition and environmentally sustainable development [7–10]. FTS is considered a foundational technology for converting syngas

into gasoline, diesel, waxes, and olefins [11–13]. When reaction conditions and the structure of active sites are optimized, FTS can be tailored to produce alcohols with high selectivity [14]. Current mainstream research on catalysts for higher alcohol synthesis (HAS) primarily focuses on cobalt- and iron-based systems. Conventional Fe- and Co-based catalysts encounter trade-offs between activity, selectivity, and stability [15, 16]. Fe catalysts demonstrate a high probability of chain growth but experience carbide phase segregation, which leads to excessive methane production and rapid deactivation [17, 18]. By contrast, Co catalysts exhibit superior stability with FTS activity. However, their strong hydrogenation propensity limits selectivity [19–22]. Recently, attention has shifted to bimetallic systems, particularly advanced metal-carbide composite catalysts [23, 24]. Layered double hydroxides (LDH) have emerged as promising precursors for reduced or carburized bimetallic carbide catalysts, as atomic-scale interface engineering allows for high-density dual-active-site configurations [25–27]. The incorporation of alkaline metal promoters significantly enhances the catalytic performance of FTS. These promoters, with distinct electron donor capacities and electronegativities, serve as both electronic and structural modifiers of catalyst behavior [28]. Based on this research, Gong et al. reported an effective method for maximizing the interface of dual active sites by designing the structure of K-promoted alloy carbides derived from the FeCo LDH precursor. The well distributed alloy carbide, $(\text{Fe}_x\text{Co}_{1-x})_2\text{C}$, demonstrates exceptional activity [29]. However, the mechanistic understanding of their enhanced performance remains incomplete, highlighting the need for rigorous structure–activity relationship studies.

Given the limitations of conventional characterization techniques, the rapid development of X-ray absorption fine structure has emerged as an advanced method for investigating the structure–activity relationships of catalysts during the reaction process [30, 31]. Its exceptional capability for probing atomic and electronic local structures, along with its capabilities for *in situ* monitoring under reaction conditions and tolerance to structural disorder, makes it invaluable for elucidating bimetallic alloying, bulk reconstruction, and catalytic mechanisms [32, 33].

In this study, FeCoK, FeCo, FeK/CoK, FeK, and CoK catalysts were evaluated for HAS. Characterization techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) were employed to analyze the structure of the catalysts at various states. To further elucidate the formation mechanism of $(\text{Fe}_x\text{Co}_{1-x})_2\text{C}$, *in situ* X-ray absorption fine structure (XAFS) experiments were designed to track the dynamic atomic-scale structural evolution during reduction and carburization. Further research into the carburization of the FeCo alloy proposes two essential conditions for the formation of $(\text{Fe}_x\text{Co}_{1-x})_2\text{C}$ using the regular thermochemical method.

2 Experimental

2.1 Catalyst synthesis

The FeCoK catalyst was synthesized using cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., 98.5%) and iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., 98.5%) as metal precursors.

A mixed solution with a concentration of 0.5 M and a Fe/Co molar ratio of 1:1 was prepared by dissolving the nitrates in deionized water. The precipitant solution (0.4 M of K^+) was prepared by dissolving potassium hydroxide (K_2CO_3 , Sinopharm Chemical Reagent Co., Ltd., 99%) in a molar ratio of 2:1 in deionized water. Both the salt and alkali solutions were simultaneously added to 50 mL of deionized water under vigorous stirring at 60 °C, maintaining a constant pH of 9.5. After the suspension was aged at 60 °C for 2 h, the resulting FeCoK precursor was collected via centrifugation, washed three times with deionized water, and dried at 80 °C for 24 h. The precursor was then calcined in a muffle furnace under static air at 350 °C for 4 h to obtain the final FeCoK catalyst. The K element in FeCoK originates from the residual K^+ during the catalyst preparation.

For the synthesis of the FeCo catalyst, the precursor salt solution was identical to that of FeCoK. However, the alkali in the precipitant solution was replaced with ammonium carbonate (Sinopharm Chemical Reagent Co., Ltd., 99.7%) and ammonia water (Sinopharm Chemical Reagent Co., Ltd., 28%). The preparation procedure for FeCo was the same as for FeCoK, except that the precipitant pH was maintained at 7.5. The physically mixed FeK/CoK catalyst was synthesized by separately preparing CoK and FeK catalysts using the same method as FeCoK. The calcined CoK and FeK powders were then physically blended in a 1:1 Co/Fe molar ratio to obtain the FeK/CoK catalyst.

2.2 Catalyst characterization

XRD was performed on a Rigaku Ultima 4 X-ray diffractometer using $\text{Cu K}\alpha$ radiation (40 kV, 40 mA), scanning from 10° to 90° with a step length of 2°. XPS measurements were conducted on a Thermo Scientific $\text{K}\alpha$ spectrometer using $\text{Al K}\alpha$ ($h\nu = 1486 \text{ eV}$) radiation. Prior to XPS measurements, the samples underwent ion etching to remove surface adsorbates and oxide layers. All binding energies were calibrated using the C 1s peak at 284.6 eV. TEM and high-resolution TEM (HRTEM) measurements were performed on a JEOL-JEM 2011 electron microscope at an accelerating voltage of 200 kV. STEM with energy dispersive X-ray spectroscopy (EDS) line scanning and elemental mapping measurements were conducted on a FEI-TALOS-F200X electron microscope, also at 200 kV.

The XAFS measurement was conducted at the BL20U1 Hard branch of the energy material beamline (E-line) and BL05U at the Shanghai Synchrotron Radiation Facility, operating at a storage energy of 3.5 GeV and a beam current of 200 mA (top-up). The flux of the incident X-ray was approximately $10^{12} \text{ photons}\cdot\text{s}^{-1}$, and the energy calibration was performed using Fe and Co foils. Typically, 7.0 mg of catalyst was uniformly mixed with 50 mg of LiF by grinding in an agate mortar and then pressed into a pellet 10 mm in diameter. A custom cell (Fig. S1 in the Electronic Supplementary Material (ESM)), capable of withstanding pressures up to 3 MPa and temperatures up to 500 °C, was used for the *in situ* test. Prior to the XAFS measurement, the cell system was purged with $50 \text{ mL}\cdot\text{min}^{-1} \text{ H}_2$ (99.999%) to eliminate residual air. The XAFS data for the sample was collected at room temperature and labeled RT. Following this, an *in situ* reduction test was conducted by heating the sample to 300 °C at a rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in hydrogen, also at a flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$. Time-resolved spectra were recorded throughout the process. Once the spectrum stabilized, the gas flow was switched to $80 \text{ mL}\cdot\text{min}^{-1}$ syngas ($\text{H}_2/\text{CO} = 2$) and the temperature was decreased to 230 °C to initiate the carburization test. Fe and Co K-edge spectra were alternately collected to

minimize temporal interference, enabling atomic-level tracking of structural evolution during the dynamic reduction and carburization processes.

2.3 Catalyst evaluation

The HAS reaction was performed in a fixed-bed reactor (8 mm in diameter) using a bed containing 1 g of calcined catalyst (40–60 mesh) diluted with 3 g of quartz sand (40–60 mesh). Before the reaction, the catalyst was activated *in situ* under flowing H_2 at 300 °C for 5 h. The reactor temperature was then lowered to 120 °C, and syngas was introduced to pressurize the system to 7 MPa, at which point the reaction commenced. The effluent gas passed sequentially through a hot trap (120 °C) and a cold trap (0 °C) for product separation. The gas composition was analyzed online using an Agilent 7890B gas chromatograph: Permanent gases (N_2 , H_2 , CO, CH_4 , CO_2) were quantified using a thermal conductivity detector (TCD) and a carbon molecular sieve column (TDX⁻¹) with Ar as the carrier gas, and C_1 – C_7 hydrocarbons were analyzed using a flame ionization detector (FID) and a KCl-modified alumina capillary column (19095P K25). Condensed products collected from the traps were analyzed offline using a Shimadzu GC instrument: Aqueous products were analyzed using two Porapak Q columns, with H_2O and methanol detected by TCD and C_1 – C_5 oxygenates detected by FID; liquid oil products were analyzed using an HP⁻¹ column with FID detection and N_2 as the carrier gas; solid wax products were dissolved in carbon disulfide (CS_2) and analyzed using an MXT⁻¹ column with FID detection and N_2 as the carrier gas. Data on catalytic performance was collected during stable operation, which was achieved after at least 12 h on stream. The mass balance, carbon balance, and oxygen balance were rigorously calculated and consistently maintained above 95%, with excellent catalyst reproducibility confirmed through repeated experiments under identical conditions.

3 Results and discussion

3.1 Catalyst performance

FeCoK was evaluated for HAS performance alongside CoK, FeK, FeK/CoK, and FeCo for comparison. As shown in Fig. 1(a), under conditions of $H_2/CO = 2$, 230 °C, and a gas hourly space velocity of 6000 mL·g⁻¹·h⁻¹, FeCoK demonstrated the highest catalytic activity, achieving a CO conversion rate of 50.7%. By contrast, FeCo without K as a promoter exhibited a slight decrease in CO conversion. Interestingly, the CO conversion rates for FeK and FeK/CoK were nearly identical. Given that CoK shows minimal catalytic activity

with a CO conversion of only 3.5%, we can infer that the observed activity primarily derives from the effects of Fe. The selectivity of the catalysts, presented in Fig. 1(b), indicates that FeCoK achieved superior selectivity for higher oxygenates and olefins, with oxygenate selectivity at 42.0% and total selectivity for value-added chemicals (higher oxygenates and olefins) reaching 63.0%. Moreover, the fraction of $C_{2+}OH$ in the oxygenates exceeded 98.1%, with the highest selectivity for ethanol, as shown in Fig. 1(c). The performance of FeCoK aligns with our previous research, where its exceptional catalytic activity and selectivity in HAS derive from the formation of $(Fe_xCo_y)_2C$ [29].

3.2 Catalyst characterization

To further validate the active site structure, we employed a range of characterization techniques to examine the catalyst's structural evolution. Figure 2(a) presents the XRD patterns of FeCoK at various stages, labeled fresh, reduced, and spent, to denote the states after calcination, reduction, and reaction, respectively. The characteristic diffraction peaks of FeCoK-fresh fall between those of Fe_3O_4 (PDF#75-1372) and Co_3O_4 (PDF#43-1003), confirming the successful synthesis of the composite FeCo oxide $(Fe_xCo_y)_3O_4$. Following hydrogen treatment at 300 °C, the diffraction pattern corresponded to the FeCo alloy phase (PDF#03-4131) with a body-centered cubic (BCC) structure, showing no additional peaks, which indicates that Fe and Co remained unseparated after reduction. For the spent sample, the $(Fe_xCo_y)_2C$ alloy carbide was verified to be the main phase postreaction, which is consistent with previous findings [29]. The XPS results (Figs. 2(b) and 2(c)) reveal characteristic signals for the metal states of Fe (706.7 eV) and Co (777.9 eV) following hydrogen reduction. In the spent sample, the oxidation states (Fe at 710.9 eV, Co at 779.5 eV) and the metal states (Fe at 706.7 eV, Co at 777.9 eV) decreased, whereas the carbide states (Fe at 707.4 eV, Co at 778.3 eV) emerged, contributing to the most intense peak. The TEM image shows a spherical nanoparticle morphology and a typical size distribution with an average particle size of 19 nm, consistent with the result of 15 nm based on the XRD data using the Scherrer formula (Fig. S2 in the ESM). The corresponding STEM-EDS elemental mapping profiles (Fig. 2(d)) indicate a uniform spatial distribution of Fe and Co in the spent sample. Line scanning of Fe, Co, and C along the yellow arrow in the STEM image shows that the contents of Fe and Co in the selected areas exhibit the same variation trend, further demonstrating the close contact between Fe and Co at similar concentrations. Combined with the XRD results, the homogeneous elemental dispersion at subnanometer resolution reinforces the formation of FeCo bimetallic carbide with atomic level interface integration.

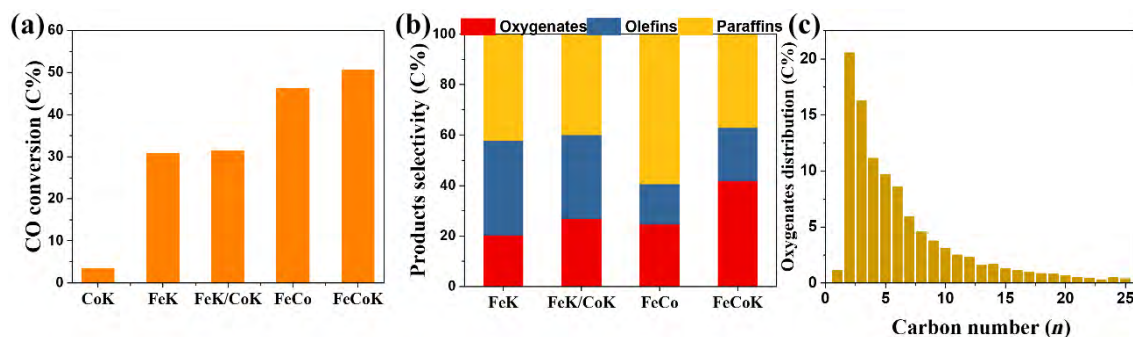


Figure 1 Catalytic performance of different catalysts for higher alcohols synthesis. (a) CO conversion. (b) Products selectivity (CO_2 -free). (c) Oxygenates distribution of FeCoK. Reaction conditions: $H_2/CO = 2$, 7 MPa, 6000 mL·g⁻¹·h⁻¹, 230 °C.

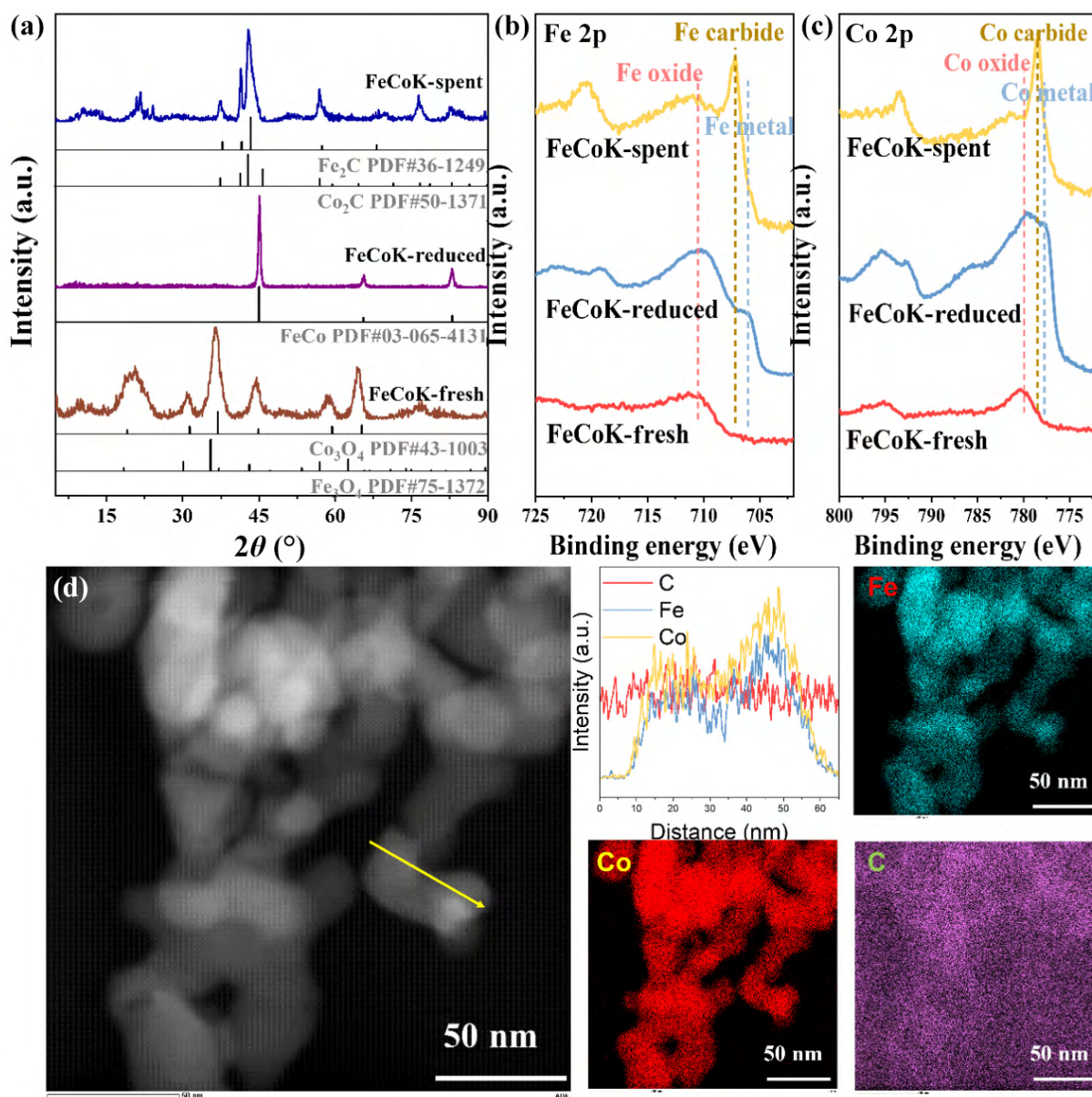


Figure 2 Structure characterization of FeCoK at different stages. (a) XRD patterns. (b) XPS of Fe 2p. (c) XPS of Co 2p. (d) High-angle annular dark-field scanning transmission electron microscopy image of spent sample. EDS line scanning, and EDS mappings of Fe, Co, and C.

To clarify the intrinsic origin of the significantly enhanced performance of the FeCoK catalyst for HAS, we conducted *in situ* XAFS characterization to investigate its structural evolution under activation conditions. The Fe K-edge XANES spectra of FeCoK, shown in Fig. 3(a), indicate that the fresh sample exhibits a structure similar to that of Fe_3O_4 . Following treatment in hydrogen for 20 min, the absorption edge of Fe aligned with that of FeO, and the spectrum fell between that of the initial sample and Fe foil (Fig. S3(a) in the ESM), suggesting that the sample was reduced to a state close to FeO. However, the strong scattering peak at approximately 2.2 Å, as shown in Fig. 3(b) (Fe-Re-20 min), which indicates the presence of metal-metal bonds, reveals that some iron was reduced to metallic Fe. As reduction continues, the Fe XANES spectrum stabilizes after 50 min, with the curves at 70 and 90 min overlapping to the point where they are nearly indistinguishable in the figure. The close similarity between the XANES spectra of Fe foil and Fe-Re-90 min confirms that the Fe in FeCoK was reduced

to the metallic state. Furthermore, the k-space oscillation spectrum of Fe-Re-90 min (Fig. 3(c)) closely resembles that of Fe foil, with only minor intensity differences observed even in the multiple scattering regions.

During the *in situ* reduction of FeCoK, absorption data for Fe and Co was collected alternately. As Fig. 3(d) illustrates, the Co K-edge XANES spectrum prior to reduction (Co-RT) aligns with that of Co_3O_4 . After 10 min of reduction, the absorption spectrum resembles that of CoO, indicating that cobalt in FeCoK has been reduced to a state close to CoO. Further reduction occurs with extended reduction time, as evidenced by the continuous shift of the Co absorption edge toward lower energy (Fig. S3(b) in the ESM). At 60 and 80 min of reduction, the Co XANES spectra exhibit no further changes, confirming that the reduction endpoint has been reached. At this stage, the XANES spectrum below 7725 eV resembles that of Co foil, whereas the curves in the extended X-ray absorption fine structure (EXAFS) are quite

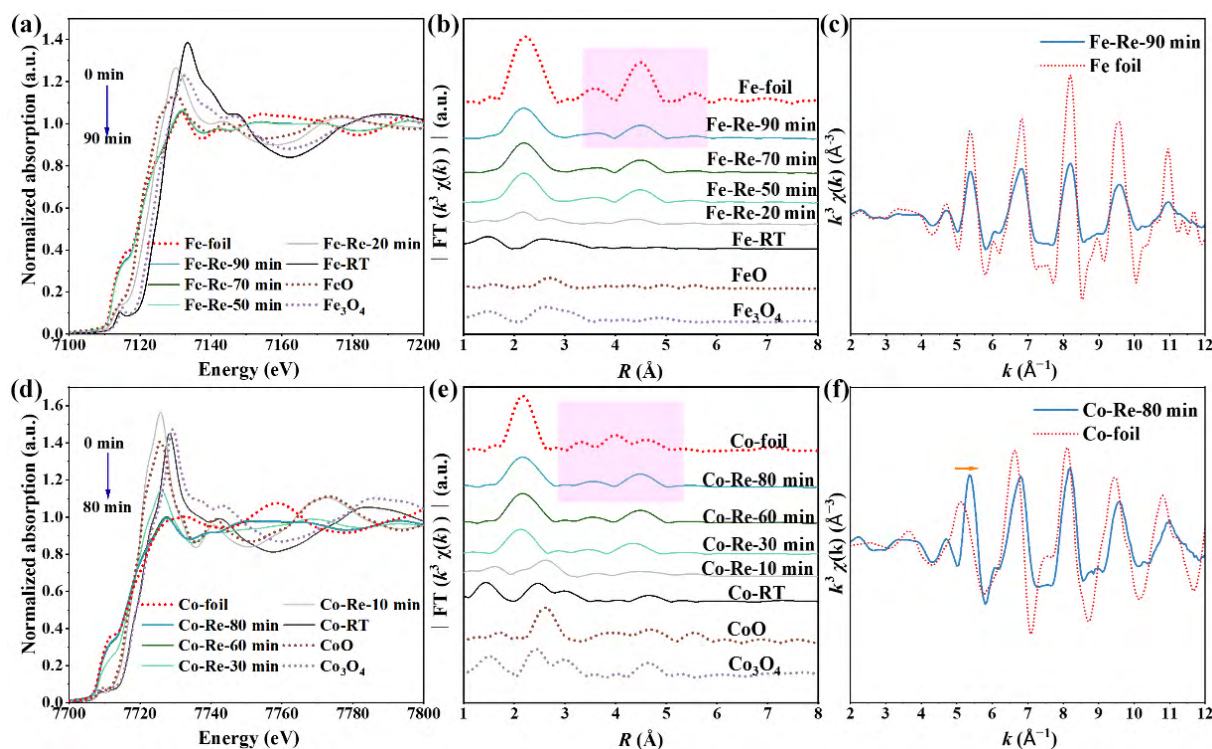


Figure 3 The XAFS results of Fe and Co during *in situ* reduction of FeCoK in hydrogen. (a) Normalized Fe K-edge XANES spectra. (b) Fourier transform of Fe K-edge EXAFS spectra. (c) Fe K-space oscillations. (d) Normalized Co K-edge XANES spectra. (e) Fourier transform of Co K-edge EXAFS spectra. (f) Co K-space oscillations. Reduction conditions: 300 °C, 0.1 MPa, 50 mL·min⁻¹ (H₂). RT, room temperature.

different. The R space shown in Fig. 3(e) provides additional information about the chemical environment of cobalt. Compared to CoO, Co-Re-10 min shows a distinct peak (approximately 2.2 Å) attributed to the Co-Co/Fe bond in the metallic state, resulting from partial reduction to metallic Co. As reduction continues (Co-Re-30 min), the single peak corresponding to the metallic phase intensifies in the range of 2–3 Å, whereas features associated with Co-Co and Co-O bonds in CoO disappear after 30 min, the spectra remain unchanged until the end of the reduction. The single scattering peak in the range of 2 to 3 Å, characteristic of Co-foil, indicates that cobalt has been reduced to a metallic state. However, noticeable differences in peak intensity and width appear. In addition, the Fourier transform of the Co K-edge EXAFS spectra reveals that the sample during the stable stage (30 to 80 min) differs from that of Co-foil in the 3–6 Å range. Furthermore, the $k^3\chi(k)$ oscillations in the k -space of Co after 80 min of reduction (Fig. 3(f)) display phase shifts and distinct patterns compared to Co foil. These discrepancies suggest that the structure of Co in the reduced FeCoK may differ from that of Co-foil. To further investigate the fine structural differences in the Co absorption spectrum between the final state of reduced FeCoK and Co foil, the Fourier transform of the Co K-edge EXAFS spectra was fitted to examine the coordination environment. As is well known, Co typically exhibits a face-centered cubic (FCC) or hexagonal close-packed (HCP) structure with 12 coordination after reduction in hydrogen, with all 12 adjacent Co atoms equidistant from the central atom [32, 34–36]. Co foil, used as a reference in the XAFS test, shows a single fitting path with a coordination number (CN) of 12 at a distance of 2.49 ± 0.01 Å (Table 1 and Fig. S4(a) in the ESM). By comparison, the reduced FeK/CoK sample also exhibits a well-fitting result and

similar coordination information to Co foil (Table 1 and Fig. S4(b) in the ESM). However, the fitting curve does not adequately match the experimental EXAFS data of reduced FeCoK (Co-Re-80 min) when a single Co-Co/Fe path is applied (Fig. S5(a) in the ESM). XRD analysis indicates that the main phase in the reduced sample is an FeCo alloy with a BCC structure, which is the common crystalline phase of Fe after hydrogen reduction [37]. In the BCC structure, the CN of the nearest atom at the corner of the cube cell is 8, whereas the CN of the second nearest atom at the center of the neighboring unit cell is 6. Therefore, two paths, Fe-Fe/Co1 and Fe-Fe/Co2, can be used to fit the EXAFS spectrum of Fe foil, and these paths also align well with the experimental data for the Fe K-edge in reduced FeCoK (Fe-Re-90 min) and the reduced FeK/CoK catalyst (Table 1 and Fig. S6 in the ESM). Similarly, when the EXAFS spectrum of Co-Re-80 min is fitted with two paths, the fitting curve closely matches the original data (Fig. S5(b) in the ESM). Table 1 summarizes the fitting results for the Co and Fe XAFS spectra of FeCoK during the *in situ* reduction test. Considering the adjacent atomic numbers of Co and Fe, distinguishing between Co-Co and Co-Fe coordination based on interatomic distance is challenging. The fitting results indicate that both Fe and Co exhibit a BCC-like local structure, with bond lengths in the nearest and next-nearest coordination shells closely matching those of Fe foil (2.46 and 2.84 Å, respectively). Notably, the coordination information for Co-Re-80 min and Fe-Re-90 min is lower than that of the corresponding Co and Fe foil, likely due to the smaller particle size of the sample. Therefore, we can conclude that during the formation of the FeCo alloy, the BCC structure of Fe facilitates the substitution of some Co atoms for Fe atoms, resulting in a uniform alloy with a BCC crystal phase.

Following the reduction treatment, the atmosphere was changed

to syngas and pressurized to 1.0 MPa to facilitate the carburization of the FeCoK catalyst. As Figs. 4(a) and 4(c) show, exposure to high-pressure syngas caused the XANES absorption edges of both Co and Fe to shift toward higher energy levels (Fig. S7 in the ESM), stabilizing after 40 min with no significant spectral changes. This shift indicates an increase in the chemical valence of the metals, which is likely due to the formation of metal–carbon bonds. The Fourier transform in the R space clearly illustrates the evolution of the carburization process (Figs. 4(b) and 4(d)). Upon contact with high-pressure syngas, the spectra for Fe-Carb-20 min and

Co-Carb-10 min show a notable weakening of the single scattering peak associated with metal–metal coordination in the FeCo alloy at 2.2 Å. Instead, a new scattering peak corresponding to metal–carbon bonds emerges at 1.92 Å for both Fe and Co. In addition, another higher intensity scattering feature at 2.7 Å appears with higher intensity, attributed to complex metal–metal interactions within the carbide structure. As carburization continues, the intensity of the peaks related to both metal–carbon and metal–metal bonds increases significantly. By the end of the test, the spectra for Fe-Carb-120 min and Co-Carb-110 min

Table 1 Fitting result of Fe and Co EXAFS spectra of different catalyst during *in situ* reduction. Samples labeled as “fresh” use a k range of 3–12 Å^{−1} and R range of 1–3.5 Å. Samples labeled as “reduced” and “spent” use a k range of 3–11.5 Å^{−1} and R range of 1–3 Å

Sample	Path	C.N.	R (Å)	$\sigma^2 \times 10^{-3}$ (Å ²)	ΔE_0 (eV)	R -factor
Co foil(0.76)	Co–Co	12*	2.49 ± 0.01	6.2	7.0 ± 0.4	0.002
Fe foil(0.73)	Fe–Fe1	8.0	2.46 ± 0.02	5.0	5.3 ± 2.7	0.004
	Fe–Fe2	6.0	2.85 ± 0.01	5.1	5.3 ± 2.7	
FeCoK-Co-reduced	Co–Fe/Co1	4.5 ± 0.7	2.44 ± 0.01	6.4	5.0 ± 2.4	0.009
	Co–Fe/Co2	3.9 ± 0.8	2.86 ± 0.02	10.0	5.0 ± 2.4	
FeCoK-Fe-reduced	Fe–Co/Fe1	4.9 ± 0.7	2.44 ± 0.01	7.6	2.5 ± 2.1	0.005
	Fe–Co/Fe2	4.8 ± 0.8	2.84 ± 0.01	10.0	2.5 ± 2.1	
FeK/CoK-Co-reduced	Co–Co	10.8 ± 0.6	2.49 ± 0.03	6.0	8.4 ± 0.6	0.003
FeK/CoK-Fe-reduced	Fe–Fe1	5.8 ± 3.6	2.41 ± 0.02	10.0	-5.5 ± 6.7	0.025
	Fe–Fe2	6.6 ± 1.7	2.77 ± 0.03	3.0	-5.5 ± 6.7	

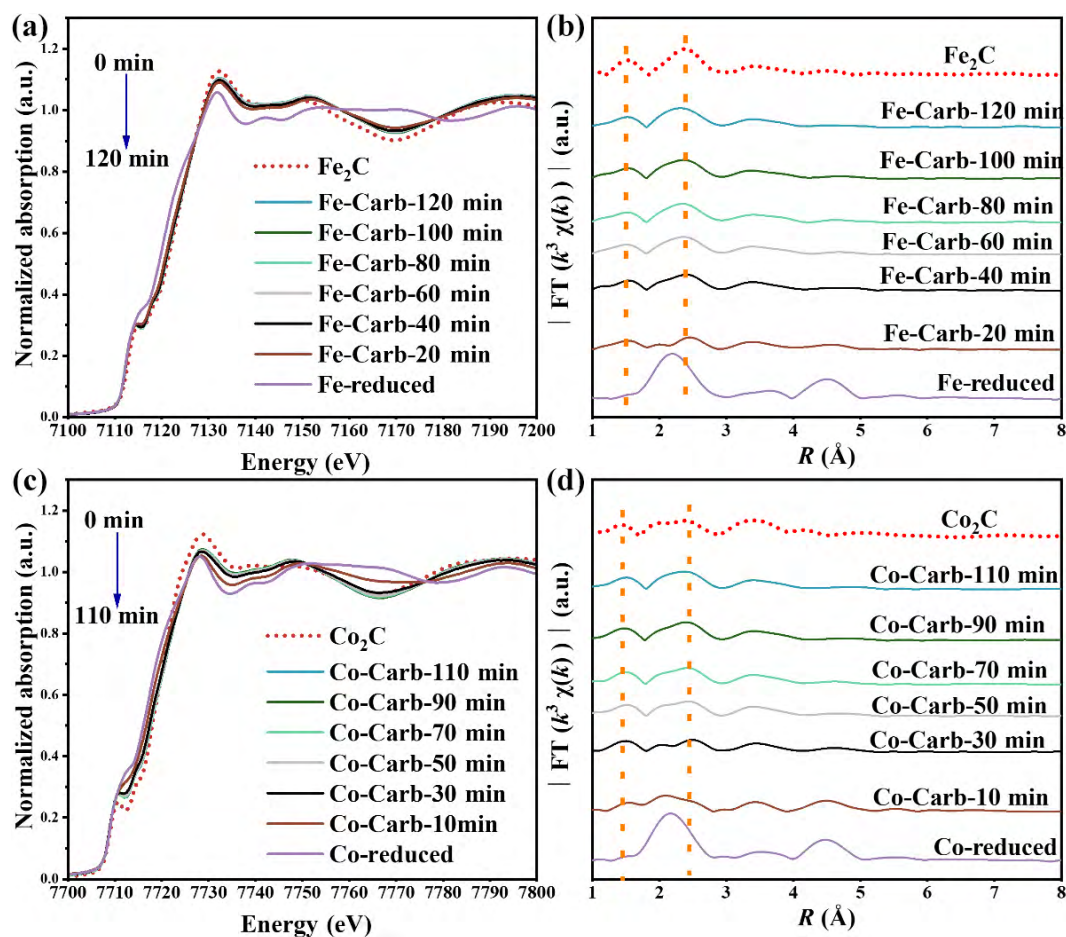


Figure 4 The XAFS result of Fe and Co during *in situ* carburization of FeCoK in syngas. (a) Normalized Fe K-edge XANES spectra. (b) Fourier transform of Fe K-edge EXAFS spectra. (c) Normalized Co K-edge XANES spectra. (d) FT of Co K-edge EXAFS spectra. Carburization conditions: 230 °C, 1 MPa, 80 mL·min^{−1} (H₂/CO = 2).

resemble those of their carbide counterparts (Fe_2C and Co_2C), confirming the conversion of the FeCo alloy into metal carbide under high-pressure syngas.

To further clarify the structure–performance relationship, XRD analysis was conducted to identify the active phases of different catalysts (Fig. S8 in the ESM). The active phase in FeCoK was confirmed to be alloy carbide, $(\text{Fe}_x\text{Co}_y)_2\text{C}$, whereas FeCo remained as the FeCo alloy without significant carburization. In the physically mixed FeK/CoK, the active phases were identified as separate Fe_2C and Co_2C . This suggests that the differences in performance among FeCoK, FeCo, and FeK/CoK can be primarily attributed to variations in their active phases. Although both the FeCo alloy carbide and FeCo alloy exhibit high CO conversion rates, they differ markedly in product selectivity. The metal-based FeCo alloy tends to produce more paraffins, whereas the alloy carbide demonstrates superior selectivity for olefins and alcohols. By contrast, the separated iron carbide and cobalt carbide in the physically mixed FeK/CoK result in a higher production of olefins than alcohols, as well as lower conversion activity.

More evidence emerges from the structural evolution of FeCo and FeK/CoK. The XRD patterns (Fig. S9 in the ESM) reveal that the main phases of FeK/CoK after reduction are FCC-Co and BCC-Fe. The *in situ* XAFS analysis of FeK/CoK during reduction (Fig. S10 in the ESM) shows that the reduced FeK/CoK (Co-Re-80 min) exhibits a structure identical to that of the 12-coordination Co foil rather than the BCC structure with 8 (or 14) coordination. Due to the lack of intimate contact between Fe and Co, no FeCo alloy forms in the physically mixed catalyst during reduction. The separation of metallic Fe and Co subsequently leads to the independent formation of iron carbide and cobalt carbide during the following carburization, rather than alloy carbide. In terms of the FeCo catalyst, the reduction results are similar to those of FeCoK, with the FeCo alloy as its main phase (Fig. S9 in the ESM). The XAS features of Fe and Co are also consistent with those of FeCoK (Fig. S11 in the ESM), indicating the BCC structure of Fe and Co after reduction. However, the carburization of the FeCo alloy does not occur during subsequent treatment in syngas. The *in situ* XAS test results (Fig. S12 in the ESM) indicate that the EXAFS spectra retain their metallic characteristics even after being treated in high-pressure syngas for 120 min. Previous research has concluded that alkali metals, such as Na and K, act as electron

promoters, effectively facilitating the carburization of Fe and Co [38–40]. During catalyst activation, electron rich Fe active centers, formed via the electron donating effect of K^+ , promote the dissociative adsorption of CO. The mechanism involves back donation of electron density into the CO $2\pi^*$ antibonding orbital, which weakens the C–O bond and lowers the dissociation barrier, thereby facilitating CO cleavage into surface carbon species [41–43]. Under the high CO partial pressure and low temperature conditions reported by Emiel de Smit et al., where the carbon chemical potential is inherently elevated, the adsorption and accumulation of C further increase the local carbon chemical potential. This drives carbon diffusion into the iron lattice and promotes carburization, establishing a reaction microenvironment conducive to the nucleation of high-carbon ϵ -carbide (Fe_2C) [44]. Furthermore, by analogy with the role of alkali metals in modulating transition metal carbide surface energies, K_2O selectively adsorbs on specific high-activity crystal planes of ϵ - Fe_2C (e.g., (002) and (100)). This effectively reduces their surface free energy, suppresses transformation to χ - Fe_5C_2 or θ - Fe_3C , and thus maintains the thermodynamic stability and structural integrity of this metastable phase under reaction conditions [45]. Therefore, the presence of K accounts for the differences in carburization features between FeCoK and FeCo.

Based on the research presented, we can outline the evolutionary pathways from the FeCo precursor to the alloy, carbide, and alloy carbide. Figure 5 illustrates two forms of oxidized FeCo precursors: The nonintimate contact forms Fe_3O_4 and Co_3O_4 , obtained via physical mixing, and the atomically interacting Fe and Co in the FeCo composite oxide $(\text{Fe}_x\text{Co}_y)_3\text{O}_4$, where $x + y = 1$, prepared through coprecipitation. During coprecipitation, Fe and Co are uniformly dispersed in the salt solution as metal cations, which is essential for the subsequent formation of composite oxide, alloy, and alloy carbide. Upon reduction in hydrogen, $(\text{Fe}_x\text{Co}_y)_3\text{O}_4$ converts into the FeCo alloy with a BCC structure. By contrast, in the physically mixed material, Fe and Co remain separate, reducing to BCC Fe and FCC Co, respectively. The formation of the alloy via thermochemical reduction necessitates atomic level contact between Fe and Co in the oxide precursor. During subsequent treatment with syngas, the presence of K facilitates the carburization of the FeCo alloy into alloy carbide $(\text{Fe}_x\text{Co}_y)_2\text{C}$. Without the alkali promoter, the alloy retains its metallic state. Similarly, under the

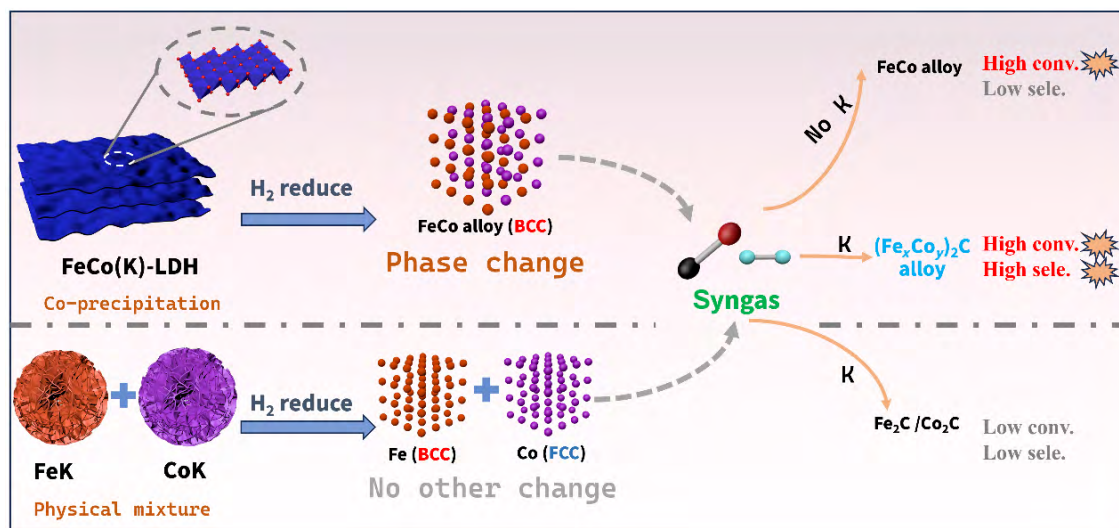


Figure 5 The evolution paths from FeCo precursor to the alloy, carbide, and alloy carbide.

influence of K, BCC Fe and FCC Co are separately carburized into Fe_2C and Co_2C , whereas carburization does not occur in the absence of K. Therefore, two key conditions are crucial for the formation of the FeCo alloy carbide through the conventional thermochemical method: First, the source of carburization must originate from the alloy, and second, an alkali promoter must be present.

3.3 DFT calculation

To gain fundamental insights into the superior catalytic performance of alloy carbide catalysts, density functional theory calculations were conducted to systematically compare the complete reaction pathways for ethanol synthesis via FTS on $(\text{Fe}_x\text{Co}_{1-x})_2\text{C}$ (orange curve) and Fe_2C (blue curve) model catalysts, with particular focus on the activation energy barriers and energy changes at each step. As illustrated in Fig. 6, the two catalysts exhibit distinctly different energetic profiles during CO adsorption, C–O bond cleavage, carbon chain growth, and product formation. Regarding CO adsorption and C–O bond activation, the energy change for CO adsorption from the initial state to the $^*\text{CO}^*\text{CO}$ state on $(\text{Fe}_x\text{Co}_x)_2\text{C}$ is -3.44 eV, slightly stronger than -3.26 eV on Fe_2C , indicating that Co incorporation enhances the chemisorption capability of the surface and facilitates reactant enrichment. Subsequently, the conversion from $^*\text{CO}^*\text{CO}$ to the $^*\text{CH}_2\text{CO}$ intermediate, which involves partial C–O bond scission, hydrogenation, and carbon chain initiation, represents the key step of the overall reaction. On Fe_2C , this step requires overcoming a high activation barrier of 1.92 eV, with the intermediate stabilized at 0.63 eV below the former state, forming a deeply trapped adsorption configuration. In sharp contrast, $(\text{Fe}_x\text{Co}_x)_2\text{C}$ exhibits a significantly reduced barrier of 1.49 eV, accompanied by a shallower adsorption well of only 0.35 eV for the $^*\text{CH}_2\text{CO}$ intermediate. This characteristic combination of low barrier and weak adsorption originates from the synergistic electronic effect of Fe–Co bimetallic sites with their spatial proximity optimizing the transition state geometry, thereby accelerating CO activation and enabling facile intermediate transformation, consistent with the experimentally observed high CO conversion over FeCoK catalysts. In terms of product selectivity, $(\text{Fe}_x\text{Co}_x)_2\text{C}$ preferentially stabilizes the $^*\text{CH}_2\text{CHOH}$ intermediate rather than $^*\text{CH}_2\text{CH}_2\text{O}$, leading to higher ethanol selectivity. Conversely, Fe_2C favors the formation of methanol intermediates with extremely low reaction barriers, resulting in substantial methanol byproduct generation. Evidently, the ethanol formation pathway on $(\text{Fe}_x\text{Co}_x)_2\text{C}$ is thermodynamically and kinetically superior to that on Fe_2C .

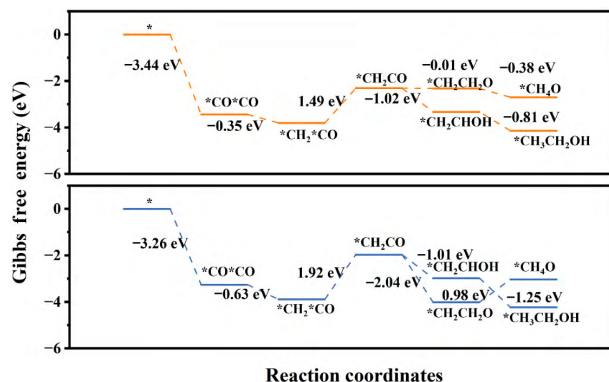


Figure 6 Free energy profiles of the $(\text{Fe}_x\text{Co}_x)_2\text{C}$ (orange) and the Fe_2C (blue) during syngas into ethanol.

4 Conclusions

In this study, the catalysts FeCoK, FeCo, and FeK/CoK were evaluated in HAS, revealing distinct differences in CO conversion rates and product selectivity due to variations in their active phases. The FeCoK catalyst, featuring an FeCo alloy carbide as its active phase, demonstrated the highest catalytic activity and superior selectivity for alcohols and olefins. By contrast, the FeCo catalyst, which has an FeCo alloy as its active site, exhibited lower CO conversion but greater selectivity for paraffins. The physically mixed FeK/CoK, with separate Fe and Co carbides as its active phase, resulted in the lowest CO conversion and moderate selectivity for alcohols. To investigate the evolution of these catalysts, *in situ* XAS characterization was conducted. The Co component in the FeCo alloy was confirmed to have a BCC structure, where the most common crystal form of cobalt is FCC, with the BCC structure seldom reported in the application of CO hydrogenation. As BCC is a common crystal type of Fe, it acts as an advantageous structure for inducing the formation of a BCC FeCo alloy. Subsequent carburization further validated the formation of the FeCo alloy carbide. Based on these observations, we propose a mechanism for the formation of the FeCo alloy carbide via a thermochemical route, emphasizing two critical conditions: The carburization must originate from an alloy precursor, and an alkali promoter, such as K, is essential. These findings offer fundamental insights for designing high-performance dual-active-site catalysts, providing solutions to energy scarcity and environmental challenges through optimized catalytic systems.

Electronic Supplementary Material: Supplementary material (images of *in situ* cell, TEM images, EXAFS fitting parameters, XAFS spectra, XRD patterns, DFT details, and so on) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908663>

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

We gratefully acknowledge financial support from the National Key Research and Development Program of China (No. 2022YFA1503801), the National Natural Science Foundation of China (Nos. 12305375 and 22402219), and Shanghai Science and Technology Development Funds (No. 23ZR1471400). We also thank the BL20U1 and BL05U beamlines of the Shanghai Synchrotron Radiation Facility (SSRF) for providing beam time and setup for the XAFS and *in-situ* experiments.

Declaration of competing interest

The authors declare no competing financial interest.

Author contribution statement

B. H. Q. and Y. W. carried out the synthesis, catalyst test, and characterization of catalysts. Y. J. and K. G. conceived and supervised the project and designed the study. Z. Q. D., X. L. Z., J. S.

C., S. S., and F. F. S. reproduced some experiments and provided helpful discussion. B. H. Q. and B. B. M. wrote and revised the paper.

Use of AI statement

None.

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