

Na promoter synergistic tuning Co-Fe alloy-carbide dual sites: Directing syngas conversion to C₂₊ alcohols

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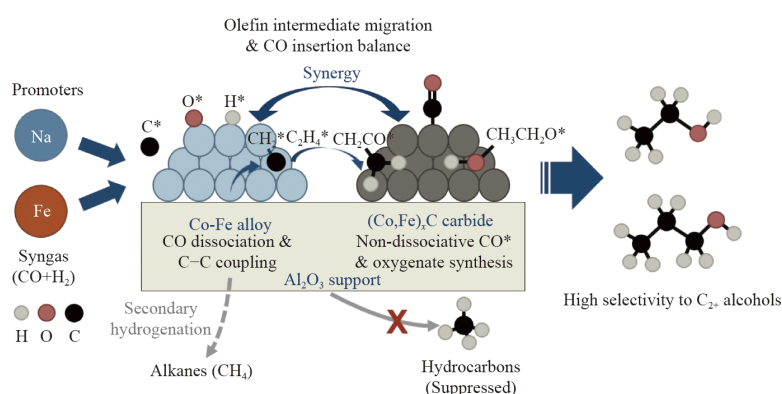
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Abstract: Designing highly efficient catalysts for the direct conversion of syngas to C₂₊ alcohols is crucial for the effective utilization of coal-based resources and the enhancement of national energy security. In this study, a series of Na-modified CoFe/Al₂O₃ catalysts were synthesized *via* the impregnation method, and their catalytic performance in syngas-to-alcohol reactions was systematically evaluated. Multiple characterization

techniques, including XRD, N₂ adsorption-desorption, H₂-TPR, XPS, DRIFTS, *in situ* Raman and Mössbauer spectroscopy, were employed to elucidate the synergistic effects of Na and Fe promoters on the catalyst structure and catalytic behavior. The results demonstrate that Na facilitates the formation of Co-Fe alloy sites during the reaction. Simultaneously, Fe modifies the electronic state of Co species and promotes the transformation of lattice oxygen into adsorbed oxygen, thereby increasing the concentration of surface oxygen vacancies. The synergistic interaction between the alloy and carbide sites enhances the CO insertion capability of olefin intermediates, leading to a significantly improved selectivity towards C₂₊ alcohols. Under the conditions of 260 °C and 2 MPa, the Co1Fe1Na1 catalyst exhibited optimal performance, achieving a total alcohol selectivity of 45%, with C₂₊ alcohols accounting for 94.1%. This study provides novel insights into the rational design of Co-based catalysts for the efficient conversion of syngas to C₂₊ alcohols.

Key words: CO hydrogenation; ethanol; C₂₊ alcohols; Co-based catalysts



With the continuous growth of global energy demand and the increasing awareness of environmental protection, the development of non-petroleum-based energy technologies has become a major focus of scientific and technological advancement worldwide. China's resource endowment, characterized as "rich in coal, poor in oil, and scarce in natural gas," determines that coal will continue to play a dominant role in the national energy structure for a prolonged period^[1-3]. Therefore, to realize the clean and efficient utilization of coal *via* developing coal-derived syngas conversion routes toward value-added chemicals is of great strategic significance. Higher alcohols (C₂₊

alcohols, HAs), defined as alcohols containing two or more carbon atoms, can serve not only as clean fuels and fuel additives but also as important chemical intermediates. It is widely used in the production of plasticizers, detergents and other high-value chemicals^[4-6]. Consequently, the direct catalytic conversion of syngas into higher alcohols has attracted increasing research interests^[7-8].

The direct synthesis of higher alcohols from syngas is a highly complex process involving both dissociative and non-dissociative CO activation steps. From the catalyst design, it is necessary to precisely regulate the synergistic interplay between C-C coupling and C-O insertion, making

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it particularly challenging to balance alcohol formation with carbon-chain growth^[9–10]. Co-based catalysts have received considerable attention due to their strong chain-growth capability and relatively low cost. However, metallic Co⁰ sites exhibit negligible C–O insertion activity, and therefore require the introduction of additional C–O insertion sites to enable efficient higher-alcohol synthesis^[11].

To address this challenge, previous studies have mainly focused on constructing two types of active sites. One strategy is introducing the second metal to form alloy structure. Su et al.^[12] compared monometallic Co and bimetallic CoCu/SiO₂ catalysts and found that the promotional role of Cu manifests in two key aspects: weakening CO/HCO dissociation to suppress the formation of CH_x species, at the same time as controlling the size of surface Co species while inhibiting CH_x insertion, thereby steering the reaction pathway toward alcohol formation. Cao et al.^[13], combining density functional theory and microkinetic modeling, further elucidated the reaction mechanisms of higher-alcohol synthesis over CuCo alloy catalysts and revealed facet-dependent differences in methanol and ethanol formation. However, the susceptibility of active metals to sintering and the coverage of active sites by cobalt carbides during prolonged operation collectively will lead to the phenomenon of catalysts deactivation and a shift of products toward lower carbon numbers over time^[14].

In addition to alloy-based strategies, constructing Co⁰/Co₂C dual active sites represents another effective approach. Li et al.^[15] investigated the role of Co⁰/Co₂C dual sites in syngas-to-higher-alcohol synthesis, demonstrating that modulating the Na promoter content to control the Co⁰/Co₂C ratio is crucial. They found that only within an optimal range can strong synergistic effects be realized, allowing the CO insertion rate to be well balanced with hydrogenation and chain-growth rates—a condition most favorable for oxygenate formation. Promoters also play a pivotal role in facilitating Co₂C formation. Du et al.^[16] reported that CaO promotes the formation of hexagonal close-packed (hcp) metallic Co, which is more prone to transformation into Co₂C under reaction conditions. Zhao et al.^[17] synthesized core-shell Co@Co₂C catalysts and found that Mn enhances surface CO dissociation and disproportionation while partially suppressing H₂ adsorption. It creates a carbon-rich and hydrogen-deficient surface environment, which promotes the transformation of metallic Co into Co₂C and consequently favors the synthesis of higher alcohols and lower olefins. An et al.^[18] further reported that Ga promoters simultaneously enhance both dissociative and non-dissociative CO adsorption, enabling the cooperative regulation of CO insertion and carbon-chain growth. Despite considerable progress in constructing bifunctional active sites, the fundamental nature of the active centers and their dynamic evolution are still not fully understood. This gap in knowledge hinders the rational engineering of catalytic sites for precise product selectivity and raises downstream separation costs.

In this study, we focus on regulating the synergistic interplay between CO insertion and chain growth. A series of Al₂O₃-supported CoFeNa catalysts were prepared *via* impregnation method. By optimizing the Co-Fe-Al ratios, the surface electronic properties of the catalysts were effectively tuned. A combination of XRD, H₂-TPR, *in situ* infrared spectroscopy, *in situ* Raman spectroscopy and Mössbauer spectroscopy was employed to systematically elucidate the roles of Na and Fe promoters in tuning catalyst structure and enhancing catalytic performance. The high selectivity toward ethanol and propanol is attributed to precise control over the transformation pathways of key reaction intermediates.

1 Experimental

1.1 Materials and reagents

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O), sodium nitrate (NaNO₃), and pseudoboehmite were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification. All chemicals were of analytical grade. Hydrogen (H₂), carbon monoxide (CO) and argon (Ar) with a purity of 99.99% were supplied by Air Liquide (Shanghai). Deionized water was produced in the laboratory and used throughout the experiments.

1.2 Catalyst preparation

The Al₂O₃ support was obtained by calcining pseudoboehmite in air at 500 °C for 2 h. All CoFeNa/Al₂O₃ catalysts were prepared by an impregnation method and denoted as Co_xFe_yNa_z, where *x*, *y* and *z* represent the molar ratios of Co, Fe and Na, respectively. Taking the Co1Fe1Na1 catalyst as an example, 7.13 g of cobalt nitrate hexahydrate, 9.86 g of iron nitrate nonahydrate, and 2.07 g of sodium nitrate were dissolved in deionized water to prepare a metal precursor solution with *n*(Co) : *n*(Fe) : *n*(Na) = 1.0 : 1.0 : 1.0.

Subsequently, 10 g of the Al₂O₃ support was added to a 100 mL round-bottom flask, followed by the addition of the above metal solution. The mixture was dried under vacuum using a rotary evaporator until complete solvent removal. The dried sample was then calcined in a muffle furnace at 400 °C for 6 h to obtain the Co1Fe1Na1 catalyst. Using the same procedure, Co1Fe2Na1 and Co2Fe1Na1 catalysts with different *n*(Co) : *n*(Fe) : *n*(Na) molar ratios, as well as the Fe-free Co1Na1 catalyst, were prepared.

1.3 Catalyst characterization

N₂ adsorption-desorption measurements were carried out using a Micromeritics ASAP 2460 automated adsorption analyzer. Prior to measurement, samples were evacuated at

300 °C for 2 h. After degassing, the samples were backfilled with N₂ to atmospheric pressure, removed, and accurately weighed before analysis. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance powder diffractometer using Cu K α radiation ($\lambda = 0.154$ nm), operated at 40 kV and 40 mA. Data were recorded over a 2θ range of 10°–80° at a scanning rate of 10(°)/min.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Shimadzu Axis Supra+ spectrometer using Al K α radiation ($h\nu = 1486.6$ eV) as the X-ray source, with an operating voltage of 15 kV and a current of 10 mA. The C 1s peak at 284.8 eV was used as the binding energy reference.

H₂ temperature-programmed reduction (H₂-TPR) experiments were conducted on a Micromeritics AutoChem II 2920 system. First, 50 mg of catalyst was loaded and heated to 150 °C, followed by purging with helium for 1 h to remove moisture. After pretreatment, the temperature was lowered to 50 °C, and the gas flow was switched to a reducing mixture of 10% H₂/90% Ar. The sample was then heated to 800 °C at a rate of 10 °C/min, while hydrogen consumption was monitored using a thermal conductivity detector (TCD).

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Thermo Fisher Nicolet iS50 FT-IR spectrometer. Under a H₂ atmosphere, the pressure in the reaction cell was first increased to 0.2 MPa and the temperature raised to 420 °C for reduction. After reduction, the temperature was lowered to 260 °C, and the pressure was gradually increased to 2 MPa. Once the pressure reached 2 MPa, a background spectrum was recorded, after which the gas atmosphere was switched to a H₂:CO mixture (2:1). Spectra were collected every 5 min.

In situ Raman spectroscopy was conducted using a Renishaw in *via* Raman spectrometer equipped with an *in situ* reaction cell. A 532 nm laser was used for excitation, and calibration was performed using a single-crystal silicon standard at 520 cm⁻¹.

Mössbauer spectroscopy (MES) measurements were carried out on an LT-MS963rd Mössbauer spectrometer operating in constant-acceleration mode, using a ⁵⁷Co(Rh) source. Spectral fitting and data analysis were performed using MossWinn 4.0 software.

1.4 Catalytic performance evaluation

The catalytic performance for syngas-to-alcohol synthesis was evaluated in a fixed-bed reactor. Typically, 4 g of catalyst (20–40 mesh) was thoroughly mixed with 4 g of quartz sand and loaded into the isothermal zone of the reactor, with quartz sand packed above and below the catalyst bed.

Prior to reaction, the catalyst was reduced at 420 °C and 0.2 MPa under a mixed H₂/Ar atmosphere ($\phi(\text{H}_2):\phi(\text{Ar}) = 2:1$) at GHSV of 4500 mL/(g·h) for 20 h. After reduction, the reactor was cooled to 150 °C under pure Ar. Syngas with a composition of ($\phi(\text{H}_2):\phi(\text{CO}):\phi(\text{Ar}) = 8:4:1$, GHSV of 2000 mL/(g·h)) was then introduced, and the pressure was gradually increased to 2 MPa. Once the target pressure was reached, the temperature was increased to 260 °C at a rate of 0.5 °C/min.

Gaseous products were analyzed online using an Agilent 8890A gas chromatograph. The tail gas flow rate was quantified by the internal standard method using Ar as the internal standard. The concentrations of H₂, CO and CO₂ were determined by a thermal conductivity detector (TCD) equipped with a Haysep Q packed column (6 ft × 1/8 in × 2 mm) and a molecular sieve packed column (8 ft × 1/8 in × 2 mm). Hydrocarbon products (C₁–C₄) were analyzed using a flame ionization detector (FID) with an Al₂O₃ capillary column (30 m × 0.53 mm × 15 μ m).

Liquid products were collected using a cold-trap system and analyzed by gas chromatography-mass spectrometry (GC-MS). The injector temperature was set at 320 °C, with a split ratio of 50:1 and an injection volume of 0.2 μ L. An HT-PONA capillary column (50 m × 0.20 mm × 0.50 μ m) was used with a constant column flow rate of 1.0 mL/min. The ion source temperature, interface temperature, and scan range were set to 230, 290 °C and 20–300 m/z, respectively. Qualitative analysis was performed using the mass spectrometer, while quantitative analysis of hydrocarbons and oxygenates in the oil phase was conducted using an FID detector with the external standard method.

The aqueous-phase products were analyzed by gas chromatography using an HT-FFAP capillary column (50 m × 0.32 mm × 0.50 μ m). The injector temperature was set at 250 °C with a split ratio of 100:1 and an injection volume of 0.2 μ L. The oven temperature program was as follows: 60 °C for 4 min, then ramped to 200 °C at 5 °C/min. The FID detector temperature was 250 °C, with hydrogen and air flow rates of 30 and 400 mL/min, respectively. The compositions of oxygenates in the aqueous phase were quantified using the external standard method.

The calculation formulas for CO conversion, CO₂ selectivity, and product selectivity are given in Eqs. (1)–(3), where x_{CO} represents the CO conversion (%), s_{CO_2} represents the CO₂ selectivity (%), and s_i represents the selectivity of product i .

$$x_{\text{CO}} = \frac{n_{\text{CO}}^{\text{in}} - n_{\text{CO}}^{\text{out}}}{n_{\text{CO}}^{\text{in}}} \times 100\% \quad (1)$$

$$s_{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{out}}}{n_{\text{CO}}^{\text{in}} - n_{\text{CO}}^{\text{out}}} \times 100\% \quad (2)$$

$$s_i = \frac{n_i^{\text{out}}}{n_{\text{CO}}^{\text{in}} - n_{\text{CO}}^{\text{out}} - n_{\text{CO}_2}^{\text{out}}} \times 100\% \quad (3)$$

2 Results and discussion

2.1 Structural characterization of catalysts

The N₂ adsorption-desorption results of the fresh catalysts (Table 1) show that, compared with the Fe-free catalyst, the introduction of Fe species increases the specific surface area and pore volume of the catalysts to varying extents, which is favorable for the improvement of the activity of the reaction. The XRD patterns (Figure 1(a)) indicate that, for the Co1Na1 catalyst, only characteristic diffraction peaks located at 36.8° and 65.2° corresponding to the Co₃O₄ phase (PDF#43-1003) are observed. After the introduction of Fe species, the intensities of Co₃O₄ diffraction peaks in Co1Fe1Na1 and Co2Fe1Na1 catalysts are significantly weakened, while characteristic diffraction peaks of α -Fe₂O₃ (PDF#33-0664) appear at 33.2°, 35.6° and 54.1°. For the Fe-rich Co1Fe2Na1 catalyst, only α -Fe₂O₃ diffraction peaks are detected.

In addition, diffraction peaks corresponding to CoAl₂O₄ (PDF#44-0160) are observed in Co1Fe1Na1 and Co2Fe1Na1 catalysts, indicating enhanced Co-Al interactions with increasing Fe content. However, no characteristic diffraction peaks corresponding to the CoFe₂O₄ spinel are observed in any of the catalysts, indicating that the CoFe₂O₄ spinel phase—which requires strong metal-metal interactions—is not readily formed through impregnation and calcination alone. H₂ temperature-programmed reduction (H₂-TPR) profiles (Figure 1(b)) show that the introduction of Fe species effectively lowers the reduction temperature of Co species. For the Co1Na1 sample, the three of H₂ consumption peaks centered at approximately 347, 425 and 565 °C were observed, the first two being attributed to partial reduction of Co₃O₄ to Co²⁺ and further reduction of Co²⁺ to Co⁰, while the third peak centered at 565 °C was attributed to reduction of CoAl₂O₄^[19–20]. As the Fe/Co ratio increases, the temperature required for complete reduction of Co species gradually decreases from 565 to 481 °C, which indicates that the addition of Fe promotes the reduction process.

The Co 2p XPS spectra (Figure 2(a)) exhibit two main

peaks at approximately 780.0 and 795.5 eV across all catalysts, corresponding to Co 2p_{3/2} and Co 2p_{1/2}, respectively. For the Fe-free Co1Na1 catalyst, the Co species are primarily present as Co²⁺ (782.2 eV, dark red line) and Co³⁺ (780.2 eV, blue line), along with well-defined satellite peaks^[17,21–22]. The introduction of Fe species induces a noticeable shift of Co 2p binding energies toward lower values compared with Co1Na1 catalyst. This shift remains significant with increasing Fe content (from Co2Fe1Na1 to Co1Fe1Na1). Specifically, the Co 2p_{3/2} peak position of Co1Fe1Na1 is shifted by −0.4 eV relative to that of Co1Na1, which confirms electron transfer from Fe species to Co species. As a result, the electron density at Co sites increases, thereby favoring the optimization of CO adsorption.

The Fe 2p spectra (Figure 2(b)) display characteristic peaks attributed to Fe²⁺ (~710.5 eV) and Fe³⁺ (~712.5 eV). With increasing Fe content, the Fe 2p binding energies also similarly shift toward lower values, further confirming the electronic interaction between Co and Fe species, which is crucial for the formation of Co-Fe alloy sites during subsequent reactions. These results indicate electronic transfer and synergistic reduction effects at the Co-Fe interface. The Fe promoter modifies the surface chemical state of Co species *via* electron transfer, increasing the proportion of Co²⁺ while decreasing that of Co³⁺. Meanwhile, Co species are reduced earlier than Fe species and activate H₂ to generate active H*, which subsequently promotes the reduction of Fe³⁺ to Fe²⁺. Furthermore, the electron-donating effect of the Na promoter stabilizes Co²⁺ and Fe²⁺ species.

Table 1 Physical properties of Co1Na1, Co2Fe1Na1, Co1Fe1Na1 and Co1Fe2Na1

Sample	BET surface area S/(m ² ·g ^{−1})	Total pore volume v/(cm ³ ·g ^{−1})
Co1Na1	86.91	0.24
Co2Fe1Na1	90.08	0.23
Co1Fe1Na1	115.08	0.29
Co1Fe2Na1	106.15	0.26

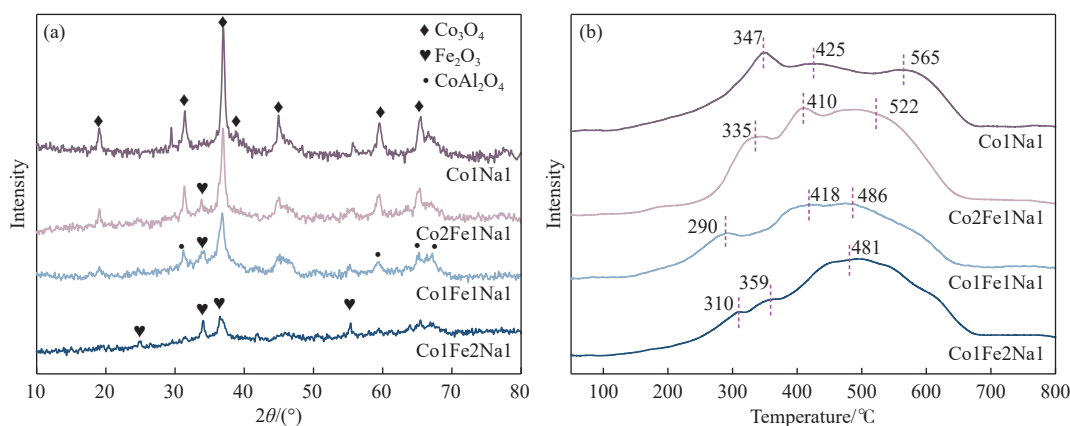


Fig. 1 (a) XRD patterns and (b) H₂-TPR profiles of Co1Na1, Co2Fe1Na1, Co1Fe1Na1 and Co1Fe2Na1

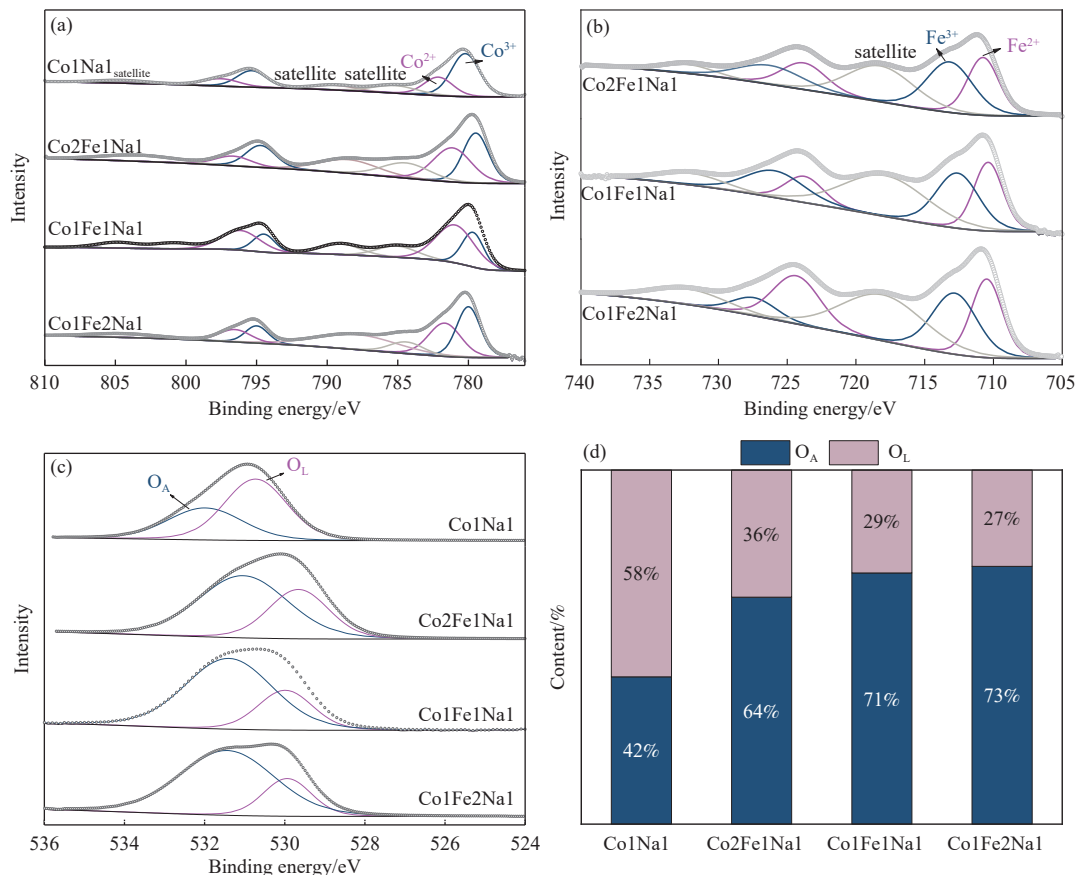


Fig. 2 XPS spectra of (a) Co 2p, (b) Fe 2p, (c) O 1s and (d) proportion of oxygen species of fresh Co1Na1, Co2Fe1Na1, Co1Fe1Na1 and Co1Fe2Na1 catalysts

As the Co/Fe molar ratio decreases, the density of Co-Fe interfacial sites increase, with Co1Fe1Na1 exhibiting the highest proportion of Co²⁺ species. This surface valence-state modulation establishes the foundation for generating Co-Fe alloy-carbide dual active sites and their subsequent synergistic catalysis. Quantitative fitting of the Co 2p_{3/2} peak areas (Table 2) further reveals that the introduction of Fe species significantly alters the surface valence distribution of Co species. Co1Fe1Na1 shows the lowest Co³⁺/Co²⁺ ratio (0.52), indicating a pronounced enrichment of Co²⁺ species on the surface. Combined with the binding energy shift (−0.4 eV), these electron-rich Co²⁺ sites are identified as key precursors for the *in situ* formation of Co₂C active phases during reaction^[15,17]. Their synergy with Fe carbide sites effectively enhances CO insertion into

olefinic intermediates, thereby enabling high selectivity toward ethanol and propanol.

Notably, the O 1s spectra (Figures 2(c) and 2(d)) show that with the introduction and increasing of Fe species, the proportion of lattice oxygen (O_L) decreases significantly, while the fraction of adsorbed oxygen (O_A) increases dramatically from 42% for Co1Na1 to 73% for Co1Fe2Na1. This trend indicates that Fe species induces lattice distortion, promotes the transformation of lattice oxygen into adsorbed oxygen species, and generates abundant oxygen vacancies. These oxygen vacancies enhance the adsorption and activation of oxygenated intermediates, facilitate C–O insertion steps during reaction, and constitute a key factor underlying the high C₂₊ alcohol selectivity of Co1Fe1Na1^[23–24].

Table 2 Atomic percentages and binding energies of surface elements for fresh catalysts

Catalyst	Co ³⁺		Co ²⁺		Fe ³⁺		Fe ²⁺		ΔBE [*] (Co 2p)/eV	ΔBE [*] (Fe 2p)/eV	Co ³⁺ /Co ²⁺
	peak/eV	area	peak/eV	area	peak/eV	peak/eV	peak/eV	peak/eV			
Co1Na1	780.2	8271	782.1	3666	—	—	—	—	0	—	2.3
Co2Fe1Na1	779.5	10143	781.2	10168	712.5	709.9	—	—	−0.6	0	1.0
Co1Fe1Na1	779.7	5790	780.9	11175	712.6	710.4	—	—	−0.4	+0.4	0.5
Co1Fe2Na1	780.0	9463	781.7	8549	712.8	710.5	—	—	−0.2	+0.5	1.1

*: ΔBE (Co 2p) and ΔBE (Fe 2p) are the binding energy offsets relative to Co1Na1 (Co 2p_{3/2}) and Co2Fe1Na1 (Fe 2p_{3/2}) respectively.

2.2 Catalytic performance evaluation

The catalytic performance of different catalysts for syngas-to-alcohol conversion at 260 °C and 2 MPa (Figure 3) reveals that, compared to Co1Na1, the Fe-doped Co1Fe1Na1 catalyst exhibits an increase in CO conversion from 30% to approximately 45%, corresponding to a 50%

enhancement in catalytic activity. A further increase in Fe content confers a subsequent boost in the catalytic activity of Co1Fe2Na1, with the CO conversion rising to approximately 63%. Conversely, increasing the Co content instead (Co2Fe1Na1) results in an even higher CO conversion of 76%, but this is accompanied by a pronounced increase in alkane selectivity.

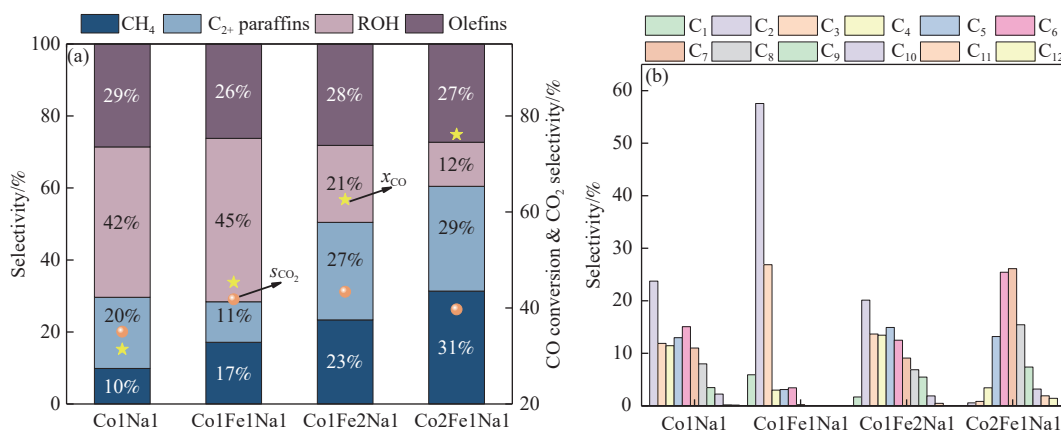


Fig. 3 (a) Catalytic performance for syngas to higher alcohols and (b) carbon number distribution of alcohols over Co1Na1, Co1Fe1Na1, Co1Fe2Na1 and Co2Fe1Na1

Regarding alcohol selectivity, the incorporation of Fe into Co1Fe1Na1 has only a minor effect on the total alcohol selectivity but significantly alters the carbon number distribution of alcohol products, exhibiting excellent selectivity toward C₂₊ alcohols, especially ethanol and propanol. Catalysts with higher Co or Fe molar ratios show markedly different reaction behaviors, with both alcohol and olefin selectivity decreasing significantly. In particular, Co2Fe1Na1 likely possesses stronger chain-growth capability due to its higher Co content, displaying catalytic behavior more similar to low-temperature Co-based F-T synthesis catalysts, characterized by high activity and high alkane selectivity.

In addition, Figure 4 depicts the 300 h stability test of the representative Co1Fe1Na1 catalyst for syngas-to-alcohol reactions. The time-on-stream profiles illustrate the dynamic changes of CO conversion and product selectivity. Although CO conversion decreases during the first 100 h due to dynamic evolution of active sites, it stabilizes at approximately 45% during the subsequent steady-state period from 100 to 300 h. Meanwhile, the total alcohol selectivity remains consistently above 43% (right Y-axis), with no obvious deactivation observed. Quantitative analysis at four sampling points (bar charts) shows that the selectivity distributions of hydrocarbons and total alcohols (ROH) remain nearly unchanged during the steady-state period. These results demonstrate that Co-Fe alloy and carbide sites reach a favorable balance under syngas atmospheres, ensuring the long-term operational stability of the catalyst.

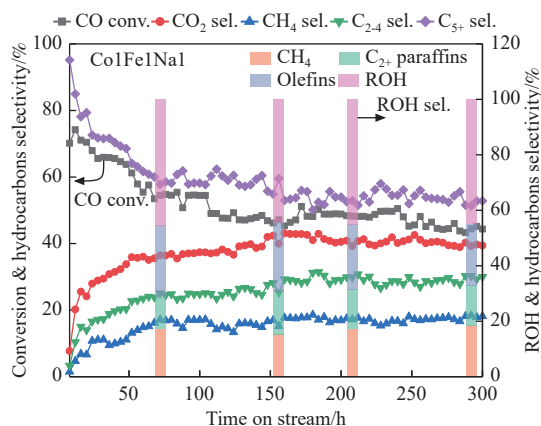


Fig. 4 Long-term stability test of Co1Fe1Na1 catalyst
Reaction conditions: 260 °C, 2.0MPa, H₂/CO=2, GHSV=2000 mL/(g·h).

Note: Lines represent the changes in CO conversion and selectivity of products (CO₂, CH₄, C₂₋₄, C₅₊) over time; Bar charts represent the distribution of hydrocarbon (CH₄, olefins, paraffins) and total alcohol (ROH) selectivities at the sampling points (72, 156, 208 and 292 h).

2.3 Structure–performance relationship and mechanistic insights

To elucidate the origins of the outstanding selectivity of the Co1Fe1Na1 catalyst toward ethanol and propanol, *in situ* Raman spectroscopy was performed.

For the fresh catalyst, an absorption band at 680 cm⁻¹ assigned to α -Fe₂O₃ was observed (Figure 5(a))^[25]. After switching the atmosphere to H₂, a distinct Co₃O₄ band

appeared at 480 cm^{-1} ^[26]. As the reduction temperature increased, the intensities of the Raman bands at 680 and 584 cm^{-1} gradually diminished and nearly vanished at 400 °C , indicating that the surface Co and Fe oxides could be substantially reduced to the metallic state under the reduction temperature (420 °C) employed for catalytic evaluation.

After completion of the reduction, the atmosphere was switched to syngas (Figure 5(b)). The characteristic G and D bands at 1595 and 1350 cm^{-1} , respectively, only began to

emerge gradually after 60 min of reaction^[27], while a vibrational band attributable to Fe–O bonds manifested at 584 cm^{-1} ^[28]. Meanwhile, symmetric stretching vibrations of surface formate species (HCOO^*) were detected at 1031 and 810 cm^{-1} ^[29]. The D band corresponds to amorphous/defective carbon, whereas the G band is associated with graphitized carbon. The amorphous carbon formed at the early reaction stage is related to the generation of active carbide phases, whereas excessive graphitic carbon (strong G band) may cause pore blockage.

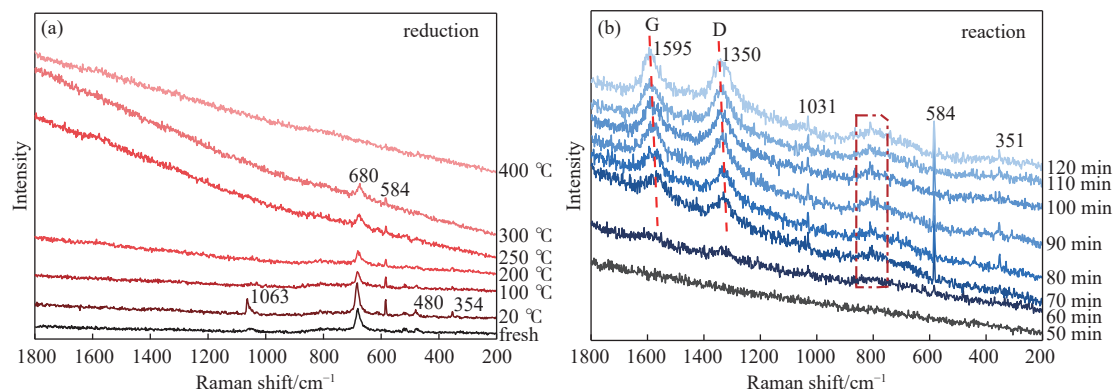


Fig. 5 *In situ* Raman spectra during (a) reduction and (b) CO hydrogenation over Co1Fe1Na1 catalyst

A direct comparison of the *in situ* Raman spectra recorded during reaction for Co1Fe1Na1 (Figure 5(b)) and Co1Fe2Na1 (Figure 6) reveals that the characteristic bands observed for Co1Fe1Na1—including the carbon species at $1595/1350\text{ cm}^{-1}$ and formate species at 1031 cm^{-1} —exhibit significantly higher signal-to-noise ratios, sharper peak shapes, and superior spectral resolution. This observation indicates a more ordered evolution of surface active sites and a more homogeneous distribution of reaction intermediates over Co1Fe1Na1. In contrast, Co1Fe2Na1 shows a much noisier Raman background, likely due to excessive Fe content inducing aggregation of surface active species or structural disorder, thereby limiting effective contact between intermediates and active sites.

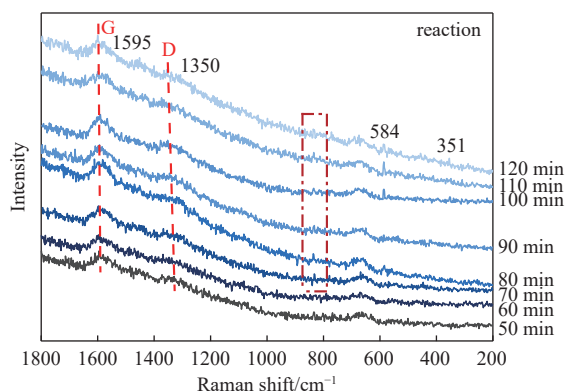


Fig. 6 *In situ* Raman spectra during CO hydrogenation over Co1Fe2Na1 catalyst

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) of Co1Fe1Na1 (Figure 7(a))

reveals that, upon introduction of CO and H_2 , typical gas-phase CO vibration bands at 2178 and 2111 cm^{-1} appear only after 20 min of reaction. Concurrently, infrared absorption bands corresponding to CO_2 (2362 and 2332 cm^{-1}) and CH_2CO^* intermediates (1604 and 1345 cm^{-1}) were detected^[30]. As the reaction proceeded from 20 to 50 min, the intensities of CO_2 and CH_2CO^* bands gradually increased, accompanied by the emergence of distinct bridged CO adsorption bands at 1872 and 1933 cm^{-1} ^[31]. After 50 min, the intensity of CO_2 band decreased, indicating that CO_2 participated in subsequent reactions.

The *in situ* DRIFTS results suggest that olefinic intermediates are readily formed on Co1Fe1Na1 during reaction; however, these intermediates are relatively unstable and can undergo CO insertion *via* non-dissociative adsorption of CO species on metallic Co^0 or Fe^0 sites to form alkoxy intermediates, or react with surface oxygen species to generate $\text{CH}=\text{CH}-\text{O}^*$ species, which are further hydrogenated to ethanol. This reaction pathway effectively suppresses excessive hydrogenation of C–C bonds.

With increasing Fe content (Figure 7(b)), Co1Fe2Na1 exhibits significantly more intense CH_2CO^* adsorption bands at 1603 and 1353 cm^{-1} , weaker CO adsorption bands, and the appearance of a methane-related band at 3014 cm^{-1} ^[32].

These findings indicate that Co1Fe2Na1 possesses a weaker CO insertion capacity, favoring C–C coupling and chain growth, as well as excessive hydrogenation to form alkanes or direct desorption of olefins. This behavior is consistent with the higher C_2 – C_4 alkane/olefin selectivity observed for Co1Fe2Na1 during catalytic performance

evaluation. In contrast, the olefinic intermediates on Co1Fe1Na1 demonstrate higher reactivity toward oxygenate formation while suppressing excessive chain growth, resulting in superior selectivity toward ethanol and propanol.

XRD patterns of the spent Co1Fe1Na1 and Co1Fe2Na1 catalysts (Figure 8(a)) reveal distinct diffraction peaks corresponding to Co_3Fe_7 alloy (PDF#50-0795), as well as Fe_3C (PDF#35-0772) and Co_2C (PDF#05-0704). This indicates that the Na promoter effectively facilitates the formation of Co-Fe alloys during the reaction and induces the generation of Co and Fe carbide phases under syngas atmospheres. Notably, the characteristic diffraction peaks of composite $(\text{Co}_x\text{Fe}_{1-x})_3\text{C}_2$ carbides were successfully identified in Co1Fe1Na1, confirming that Fe incorporation not only modulates electronic properties but also promote the formation of Co-Fe composite active centers under reaction conditions. These composite carbide sites, in intimate contact with alloy sites, synergistically enhance the CO insertion capability of olefinic intermediates^[33].

In addition, diffraction peaks attributable to CoFe_2O_4 spinel were observed in the spent catalysts, although this phase was not detected in the fresh catalysts, indicating that reduction and reaction processes promote Co-Fe interactions. Such interactions are favorable for the

formation of carbides and metallic Co-Fe alloys at active sites, thereby regulating CO adsorption/activation and the formation of key enol intermediates, ultimately optimizing C–C coupling. Raman spectra of the spent catalysts (Figure 8(b)) demonstrate that the Fe_3O_4 -related band (678 cm^{-1}) only on Co1Fe2Na1^[34].

Correspondingly, XPS results of the spent catalysts (Figure 9) further elucidate the electronic evolution of active sites. Compared with Co1Na1, Fe-containing catalysts exhibit a distinct shift of Co $2p_{3/2}$ binding energy toward higher values (+0.4 to +0.7 eV), which is attributed to the formation of Co_2C and the electron transfer from Co species to C species during reaction. Five peaks were identified in the Co $2p_{3/2}$ XPS spectrum, except for two satellite peaks at 789.2 and 785.0 eV, and the characteristic peak at 777.6 eV could be attributed to carbonic Co^[35]. Meanwhile, the fitted XPS spectrum of Fe $2p_{3/2}$ also has Fe C characteristic peak at 706.7 eV^[36]. Besides, the Fe $2p_{3/2}$ binding energy shifts toward lower values, confirming that Fe species maintains a relatively high electron density during reaction. This observation demonstrates dynamic electron transfer between Co species and Fe species, optimizing the balance between CO dissociation and insertion.

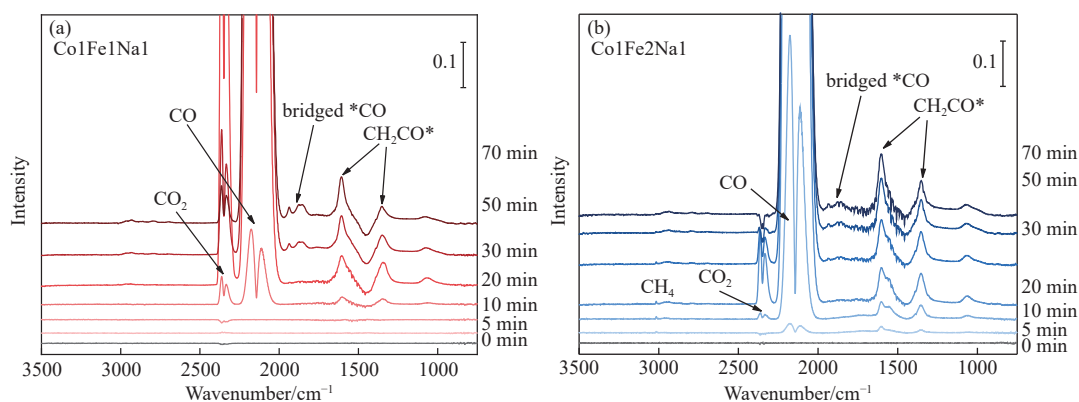


Fig. 7 In situ DRIFTS spectra over (a) Co1Fe1Na1 and (b) Co1Fe2Na1 catalysts during CO hydrogenation

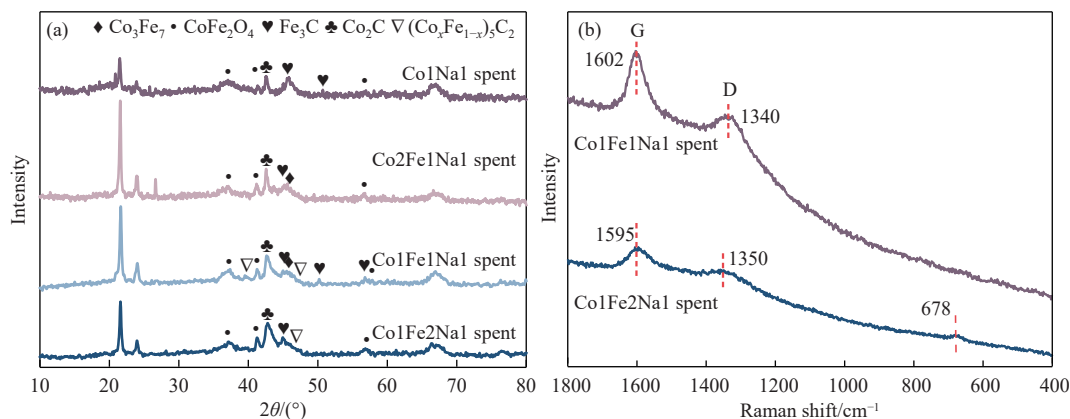


Fig. 8 (a) XRD patterns and (b) Raman spectra of spent Co1Fe1Na1 and Co1Fe2Na1 catalysts

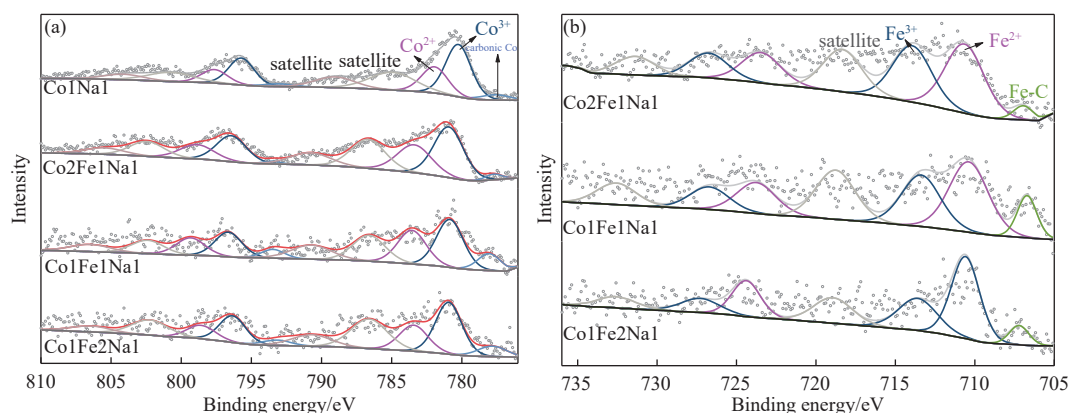


Fig. 9 XPS spectra of (a) Co 2p, (b) Fe 2p of spent Co1Na1, Co2Fe1Na1, Co1Fe1Na1 and Co1Fe2Na1 catalysts

Mössbauer spectra of the spent Co1Fe1Na1 catalyst (Figure 10) show that iron carbide phases mainly consist of χ -Fe₅C₂ and Fe₂C, accounting for approximately 58% of total Fe species (Table 3). Notably, no Fe₃O₄ phase is detected, which is consistent with Raman results. The high content of composite carbide phases provides abundant active sites. Unlike those in F-T synthesis, the (Co_xFe_{1-x})₅C₂ composite carbides formed in syngas-to-alcohol systems are considered to possess Rh-like CO insertion capability^[15], which effectively promotes non-dissociative CO adsorption and insertion. In synergy with alloy sites, these carbides enable highly selective formation of higher alcohols^[33].

Based on comprehensive *in situ* characterizations and post-reaction structural analyses, the structure-performance relationship of CoFeNa/Al₂O₃ catalysts can be summarized as follows: the Na promoter facilitates the formation of Co-Fe alloy sites during reaction, which enhance CO adsorption and dissociation (producing C and O species) and concurrently regulate hydrogenation capability to suppress methane formation. Under syngas atmospheres, Co-Fe alloy sites partially transform into metallic carbide phases (e.g., Co₂C, FeC_x), which strengthen non-dissociative CO adsorption and insertion, promote CO₂ activation to a certain degree, and inhibit the formation of long-chain hydrocarbon formation. The Al₂O₃ support stabilizes

oxygenated intermediates *via* its intrinsic basic environment and modulates the oxidation states of metal sites through oxygen vacancies, thereby optimizing C–C coupling efficiency. Appropriate Co-Fe interactions on Co1Fe1Na1 significantly enhance the CO insertion capability of olefinic intermediates and prevent excessive chain growth, ultimately leading to superior selectivity toward ethanol and propanol.

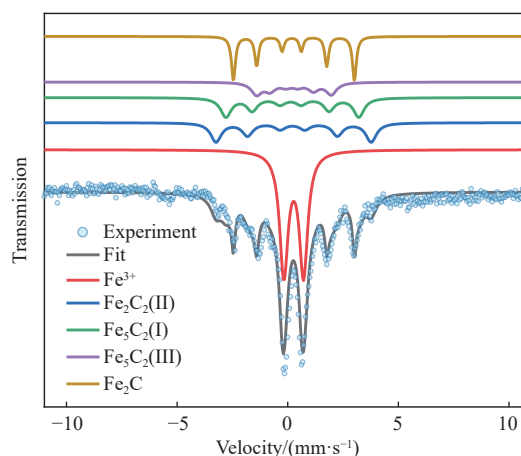


Fig. 10 Mössbauer spectra of spent Co1Fe1Na1 catalyst

Table 3 The Mössbauer fitting results of spent Co1Fe1Na1 catalyst

Phase	Hhf/T	IS/(mm·s ⁻¹)	QS/(mm·s ⁻¹)	Area/%	Content/%
χ -Fe ₅ C ₂	21.80	0.24	0.05	16.61	43.67
	18.67	0.17	0.08	16.63	
	10.50	0.23	0.10	10.42	
Fe ₂ C	17.00	0.23	0.10	14.06	14.06
Fe ³⁺	—	0.27	0.89	42.27	42.27

3 Conclusion

A series of CoFeNa/Al₂O₃ catalysts were prepared *via* an incipient wetness impregnation method. Notably, the Co1Fe1Na1 catalyst ($n(\text{Co}):n(\text{Fe}):n(\text{Na}) = 1:1:1$)

exhibited superior catalytic performance in syngas-to-alcohol reactions at 260 °C and 2.0 MPa, with distinct selectivity toward ethanol and propanol. The total alcohol selectivity reached 45%, with C₂₊ alcohols accounted for as high as 94.1% of the total alcohol products. Structural characterizations revealed that Fe incorporation efficiently

modulated the electronic structure of Co species, improved the reducibility of the catalyst, and promoted the transformation of surface lattice oxygen into adsorbed oxygen species, thereby boosting the reactivity of oxygen-containing intermediates. Meanwhile, the Na promoter facilitated the formation of Co-Fe alloy active sites during reaction and further induced the generation of carbide phases (e.g., Co_2C , FeC_x) under syngas atmospheres. Combined *in situ* spectroscopic investigations and post-reaction catalyst analyses confirmed that the synergistic interplay between alloy and carbide sites efficiently regulated the balance between CO dissociation and non-dissociative adsorption/insertion, promoted CO insertion into olefinic intermediates, and suppressed excessive hydrogenation and chain overgrowth, ultimately enabling the highly selective formation of ethanol and propanol. This study offers valuable theoretical insights and experimental guidance for the precision engineering of dual active-site architectures in Co-based catalysts *via* multi-promoter synergy, providing an effective strategy for the selective and efficient conversion of syngas to higher alcohols.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Na 助剂协同调控 Co-Fe 合金-碳化物双位点： 合成气定向转化制 C₂₊醇

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摘 要: 设计高效的合成气制醇催化剂对于实现煤基资源高值化利用和保障国家能源安全具有重要意义。本研究采用浸渍法制备了一系列 Na 改性的 CoFe/Al₂O₃ 催化剂, 并系统评价了其在合成气制 C₂₊醇反应中的催化性能。通过 XRD、N₂ 吸附-脱附、H₂-TPR、XPS、原位红外、原位拉曼和穆斯堡尔谱等多种表征手段, 揭示了 Na 助剂协同调控了 Co-Fe 合金位点的生成, Fe 助剂调节了 Co 物种的电子状态并促进晶格氧向吸附氧的转化, 合金位点与金属碳化物位点的协同作用增强了烯烃中间体的 CO 插入能力, 显著提高了醇选择性。在 260 °C、2 MPa 条件下, Co1Fe1Na1 催化剂表现出最佳性能, 总醇选择性达 45%, 其中, C₂₊醇占比达 94.1%。本研究为 Co 基催化剂的结构设计及其在合成气制 C₂₊醇中的高效转化提供了新思路。

关键词: CO 加氢; 乙醇; C₂₊碳醇; 钴基催化剂

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