ABSTRACT: The suppression of methane and coke formation over Ni-based catalysts for low temperature ethanol steam reforming remains challenging. This paper describes the structural evolution of Fe-modified Ni/MgAl2O4 catalysts and the influence of iron species on methane and coke suppression for low temperature ethanol steam reforming. Ni–Fe alloy catalysts are gradually oxidized by water to generate Ni-rich alloy and γ-Fe2O3 species at steam-to-carbon ratio of 4. The electron transfer from iron to nickel within Ni–Fe alloy weakens the CO adsorption and effectively alleviates the CO/CO2 methanation. The oxidation capacity of γ-Fe2O3 species promotes the transformation of ethoxy to acetate groups to avoid methane formation and the elimination of carbon deposits for anticoking. Ni10Fe10/MgAl2O4 shows a superior performance with a highest H2 yield of 4.6 mol/mol ethanol at 400 °C for 15 h. This research could potentially provide instructions for the design of Ni-based catalysts for low-temperature ethanol steam reforming.

KEYWORDS: ethanol steam reforming, Ni-based catalysts, hydrogen production, methane suppression, anticoking catalysts
CO + H₂O = H₂ + 2CO₂ \[\Delta H_{298K}^{\theta} = -41.2 \text{ kJ/mol}\] (2)

Acetaldehyde decomposition:
CH₃CHO = CH₄ + CO \[\Delta H_{298K}^{\theta} = -18.8 \text{ kJ/mol}\] (3)

Methanation:
CO + 3H₂ = CH₄ + H₂O \[\Delta H_{298K}^{\theta} = -205.8 \text{ kJ/mol}\] (4)

CO₂ + 4H₂ = CH₄ + 2H₂O \[\Delta H_{298K}^{\theta} = -164.9 \text{ kJ/mol}\] (5)

Hydrogenation:
C + 2H₂ = CH₄ \[\Delta H_{298K}^{\theta} = -73.8 \text{ kJ/mol}\] (6)

Methane steam reforming:
CH₄ + H₂O = 3H₂ + CO \[\Delta H_{298K}^{\theta} = 205.5 \text{ kJ/mol}\] (7)

Several nickel-based catalysts have been proposed for methane suppression during low-temperature hydrogen production processes.\textsuperscript{33–38} The suppression of methane in this research can be classified into two strategies. The first is the modification of active Ni sites through geometric and/or electronic aspects. In terms of geometry, the methanation active sites of nickel-based catalysts can be selectively occupied by doping with alkali metals, thereby reducing methane selectivity. Ang et al. found that Na-doped nickel-based catalysts could suppress the formation of methane. They postulated that the doped Na⁺ ions could preferentially occupy highly uncoordinated Ni sites at step defect sites which are responsible for catalyzing the methanation process.\textsuperscript{30,33} Lu and co-workers reached a similar conclusion by investigating nickel-based catalysts with K doping in steam-reforming reactions.\textsuperscript{32} As for electronic regulation, the modification of the electronic state of nickel can be achieved by forming alloys with transition metals. Therefore, the adsorption strength of intermediate species such as CO could be altered to suppress the formation of methane. Watanabe et al. reported that the hollow Ni–Fe–Al oxide nanocomposite catalysts could weaken the strength of CO adsorption on Ni metal and suppress hydrogen adsorption due to the formation of an Ni–Fe alloy, which inhibited CO dissociation and subsequent hydrogenation to form methane.\textsuperscript{36} David et al. investigated the copper-plated Raney nickel catalyst and also found that the methanation reaction was well suppressed due to the disruption of Ni ensembles by copper.\textsuperscript{18}

In addition to the modification of active Ni sites, the formation of methane can also be suppressed by changing the oxidation capacity of the catalysts to affect the intermediate reaction path. The catalyst with strong oxidation capacity can promote the formation of surface oxygen species such as hydroxyl groups during the reaction. Rodriguez and co-workers explored the Ni–CeO₂ catalyst and observed that the reducible ceria promotes the dissociation of water to form the surface hydroxyl groups, which react with the methyl groups to produce CO₂ and suppress the formation of CH₄.\textsuperscript{43,47,58} Watanabe et al. reported Ni–Fe catalyst supported on mesoporous CeO₂–ZrO₂ and found that the addition of zirconia to ceria enhanced the mobility of lattice oxygen in the mixed oxide, thereby accelerating the conversion of CO to CO₂ and inhibiting the formation of methane.\textsuperscript{41} Fe is a widely used promoter in Ni-based catalysts due to its low price and has been extensively studied in catalytic reforming reactions.\textsuperscript{42–47} In addition to forming alloys with nickel, iron also has strong oxygen storage and supply capability. Muller et al. found that Ni–Fe catalysts tend to form alloy after H₂ reduction and can segregate into FeO and Ni-rich alloy during methane dry reforming reaction, and the iron oxide can participate in the elimination of carbon deposits.\textsuperscript{46} Marin and his co-workers reached the similar conclusion and they observed the formation of FeOₓ in the presence of CoO.\textsuperscript{47} Kawi and his co-workers explored the nickel–iron alloy supported over iron-alumina catalysts for steam reforming of biomass tar. They found that the synergy between Ni and Fe atoms in Fe-rich Ni–Fe alloy particles was crucial for the high activity.\textsuperscript{42} Furthermore, during the reforming process, Fe⁹ species in reduced catalysts can be partially oxidized, which could enhance the reforming process by providing necessary oxygen species. Tomishige et al. conducted the study on steam reforming of model aromatic compounds of biomass tar (benzene, toluene, and phenol) over Ni–Fe catalysts and drawn the similar conclusion.\textsuperscript{38} They found that Ni–Fe alloy could be oxidized by steam due to the high oxygen affinity of Fe. However, the phase state of Fe and the structure evolution of Ni–Fe catalysts under the presence of water has not been clarified clearly yet. Therefore, to explore the structure evolution of Ni–Fe catalysts under steam reforming conditions, Fe, as an active component of high-temperature water gas shift reaction, is added into the Ni-based catalyst for ESR. The presence of Fe species can not only regulate the nickel sites through the formation of Ni–Fe alloy after reduction but also utilize the oxygen supply capacity of Fe in the weak oxidation reaction atmosphere to effectively suppress the formation of methane.\textsuperscript{44,46–49} For ESR, the study of the role of Fe species within Ni–Fe catalysts is of fundamental and practical importance for the suppression of methane formation.

This paper describes the effect of different iron species on methane suppression in low temperature ethanol steam reforming, and a group of Ni–Fe catalysts supported on Mg₃Al₂O₄ were designed and synthesized. Mg₃Al₂O₄ is selected as the support owing to its excellent mechanical strength, good chemical stability, low acidity, and high sintering resistance due to strong interaction with active components.\textsuperscript{50–52} Various techniques including X-ray powder diffraction (XRD), transmission electron microscopy (TEM), H₂ temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO) and X-ray photoelectron spectroscopy (XPS) were carried out to characterize the structure of fresh and spent catalysts. Moreover, the dynamic changes of the catalysts during the reaction process are determined with in situ Raman spectroscopy and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The influence of Fe species on the inhibition of methane and carbon deposition is further discussed.

2. RESULTS AND DISCUSSION

2.1. Characterization of Calcined and Reduced Catalysts

Nitrogen physisorption tests were carried out to reveal the specific surface area, pore volume, and average pore size of different catalysts with various Fe loadings, which are summarized in Table 1. For NiFe/Mg₃Al₂O₄ catalysts, the specific surface area and pore volume slightly decrease with the
The results suggest that a small part of Ni and Fe could block the pores of the support during the preparation of the catalysts.

The reducibility of the catalysts was investigated by H2-TPR, and the results are shown in Figure 1A. For the MgAl2O4 sample, no reduction peak is observed, which further suggests the inertness of the support. As for the Fe10/MgAl2O4 sample, the reduction peaks located at 392, 550, and 676 °C are related to the three reduction stages of Fe2O3 to metallic Fe. According to the previous research, the reduction of pure NiO to metallic Ni generally occurred at 400 °C or lower temperature.50 However, when nickel species are in a highly dispersed state or in strong interaction with the support, the reduction temperature will increase significantly compared with that of pure NiO.53−55 As for the prepared Ni10/MgAl2O4 catalyst, a broad peak attributed to the reduction of NiO is observed at around 630 °C, which is much higher than the reduction temperature of pure NiO. It proves that nickel species exhibit a good dispersion state and strong interaction with MgAl2O4 support, which is consistent with the previous research results.50,52 When Fe was introduced, the main reduction peak is found to shift to a lower temperature at around 570 °C, indicating that the introduction of Fe can greatly promote the reduction of nickel. The reduction degree of different NiFe/MgAl2O4 catalysts upon reduction at 700 °C for 1 h was calculated from H2-TPR, which is listed in Table S1. The result reveals that almost all the Fe and Ni species are reduced for NiFe/MgAl2O4 samples, while Ni species are partially reduced for Ni10/MgAl2O4.

XRD patterns of calcined and reduced NiFe/MgAl2O4 catalysts with different Fe contents are presented in Figure 1B,C to examine the structure of catalysts. For all calcined samples, the diffraction peaks of MgAl2O4 (31.3, 36.9, 44.8, 55.7, 59.4, and 65.2, 77.3°, Powder Diffraction File (PDF) card no. 21-1152) can be clearly observed, which suggests the successful synthesis of the support. The peaks of NiO (43.3 and 62.9°, PDF 44-1159) are detected in Ni10/MgAl2O4 catalyst but not in Fe-contained catalysts, indicating that the introduction of Fe can promote the dispersion of Ni species. In addition, the diffraction peaks related to various iron oxides are not observed in all Fe-contained catalysts, which further proves the good dispersion state of the catalysts. Upon reduction at 700 °C for 1 h in 10% H2/N2, metallic Ni species (44.5 and 51.8°, PDF 04-0850) are distinguished in Ni10/MgAl2O4 catalyst, while a new peak attributed to Ni−Fe

| sample          | BET surface area (m²/g) | pore volume (cm³/g) | pore size (nm) | particle size (nm) | particle size (nm) |
|-----------------|-------------------------|---------------------|----------------|-------------------|-------------------|
| MgAl2O4         | 35                      | 0.05                | 5.02           | 8.3/10.6          |
| Ni10/MgAl2O4    | 32                      | 0.05                | 5.36           | 7.6               | 8.4/9.1           |
| Ni10Fe5/MgAl2O4 | 28                      | 0.05                | 5.65           | 8.0               | 8.4/9.1           |
| Ni10Fe10/MgAl2O4| 27                      | 0.04                | 5.47           | 7.2               | 7.8/8.5           |
| Ni10Fe15/MgAl2O4| 24                      | 0.04                | 5.56           | 7.9               | 8.2/9.2           |
| Ni10Fe20/MgAl2O4| 26                      | 0.04                | 6.58           | 8.2               | 9.4/10.8          |

a Determined by nitrogen adsorption−desorption tests. b Particle size of Ni or Ni−Fe alloy in reduced catalysts, determined by TEM results. c Particle size of Ni or Ni−Fe alloy in reduced and spent catalysts, determined by XRD patterns.

Figure 1. Structure of the Ni10/MgAl2O4 and NiFe/MgAl2O4 catalysts. (A) TPR profile of NiFe/MgAl2O4 with various Fe loadings. XRD patterns of (B) calcined and (C) reduced NiFe/MgAl2O4 catalysts with various Fe loadings. (D−F) DRIFTS spectra of NiFe/MgAl2O4 with different Fe loadings in 1900−2300 cm−1 after CO chemisorption at 25 °C for 30 min. (G) Fe/Ni atomic ratios of surface and bulk of NiFe/MgAl2O4 with various Fe loadings.

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alloy at around 50.7° is detected for Fe-contained catalysts which is consistent with the phase diagram of bimetallic Ni−Fe system. The particle size of Ni or Ni−Fe alloy in reduced catalysts calculated from XRD and TEM results are summarized in Table 1 and Figure S2. From the results, it can be known that all catalysts have similar particle sizes (7−9 nm) after reduction. It is worth noting that the diffraction peaks of Ni−Fe alloy are shifted to lower 2θ values with the increase of Fe content due to the fact that more Fe is involved in the formation of the alloy. However, when the Fe content is more than 10%, the diffraction peaks of the Ni−Fe alloy do not change significantly with the increase of Fe content. This suggests that the excessive iron cannot participate in the formation of the alloy, but may exist on the surface of the catalysts in the form of metal or an oxide. The catalyst structure will be further explained through experimental data in the following sections.

Based on the above results of XRD and TPR, it is obvious that the addition of Fe can greatly improve the dispersion and reduction properties of nickel. Furthermore, the introduction of Fe can form Ni−Fe bimetallic alloy after reduction, thereby effectively regulating the state of the active component nickel in terms of the electronic and/or geometric structures.

2.2. ESR Catalytic Activity and Stability

The ESR catalytic activity of different samples has been tested at 400 °C with a specific steam-to-carbon molar ratio (S/C) of 4. Ethanol conversion and product distribution on the NiFe/MgAl2O4 catalysts are illustrated in Figure 2A,B. It is clearly found that Fe-contained catalysts exhibit better methane inhibition effect compared with Ni10/MgAl2O4 catalysts. Methane selectivity decreases significantly as the Fe content increases in bimetallic catalysts, accompanied by the increased selectivity of H2. As shown in Figure 2C, Ni10/Fe10/MgAl2O4 catalyst exhibits the best hydrogen production performance with the H2 yield increasing from 2.7 to 4.6 mol/mol ethanol compared with the sample without Fe. As shown in Table S2, the Ni10Fe10/MgAl2O4 sample shows relatively high ethanol reforming performance compared with other previously reported Ni-based catalysts. To further investigate the effect of iron introduction on catalyst deactivation, ESR stability tests of Ni10/MgAl2O4 and Ni10Fe10/MgAl2O4 samples were carried out at 400 °C, and the results are shown in Figure 2D and Figure S3. It is noteworthy that the pure nickel catalyst quickly deactivates over time, and the ethanol conversion drops to 50% after 15 h. However, Ni10Fe10/MgAl2O4 sample maintains an ethanol conversion of approximately 90% with relatively high hydrogen production efficiency in a 3 h stability test, indicating that the enhanced catalytic stability derived from Fe addition can be achieved.

Although the introduction of Fe can effectively suppress the formation of methane, excessive Fe exerts an adverse effect on the reaction, which is manifested in the decrease of ethanol conversion and the formation of C2+ byproducts as shown in Figure 2B. This is potentially because excessive iron species would partially cover nickel active sites on the surface of the catalyst as mentioned above and alleviate the capability of C=C bond cleavage, which is confirmed through DRIFTS spectra of CO chemisorption over catalysts as illustrated in Figure 1D–F. For the Ni10/MgAl2O4 and Ni10Fe10/MgAl2O4 samples, one single peak centered at around 2055 cm⁻¹ is detected distinctly after purging CO for 10 min, corresponding to the linearly adsorbed CO on the surface of metallic Ni. In order to prove that Ni-Co adsorption peak can also exist on the alloy surface, Ni10,Fe alloy phase was prepared and the same CO adsorption experiment was performed. As shown in Figure S4, it can be clearly found that the adsorption peak of Ni-Co is observed around 2055 cm⁻¹ on the surface of Ni10Fe alloy. However, for Ni10Fe20/MgAl2O4 catalyst with excessive iron content, the CO linear adsorption peak is not observed even after 30 min. Additionally, the calculated surface and bulk Fe/Ni ratios of the samples with different Fe contents after reduction could also confirm this, as shown in Figure 1G. The bulk content of nickel and iron in the alloy could be calculated based on Vegard’s law according to the Ni−Fe alloy peak position, and the surface Fe/Ni ratios are obtained from XPS test results. As for Ni10Fe10/MgAl2O4 catalyst, the overall, surface and bulk Fe/Ni atomic ratio are 1.1, 1.3 and 1.0, respectively. It can be obviously found that with the increase of Fe content, more iron species exist on the catalyst surface after reduction, instead of participating in the formation of bulk alloy. It can be demonstrated that although the addition of iron can largely inhibit the production of methane, the excessive iron will exert a negative impact on the catalytic performance of the reaction because nickel sites will be covered by Fe species after the reduction.

2.3. Characterization of Spent Catalysts

In order to explore the structural changes of the reduced nickel−iron catalyst during the reaction, the spent catalysts were characterized by XRD, as shown in the Figure 3A. It is clearly found that the diffraction peaks of Ni−Fe alloy are shifted to higher 2θ values after the reaction, implying the change of Fe and Ni content in bulk alloy. According to Vegard’s law, it can be calculated that the iron content in the alloy decreases and the Ni−Fe alloy is transformed to Ni-rich alloy during the reaction as shown in Figure 3B. Moreover, the new diffraction peaks around 53.7° and 57.3° assigned to γ-Fe2O3 are detected after the reaction. The content and particle size of γ-Fe2O3 could also be calculated on the basis of Vegard’s law (Table S3). These results indicate that the iron in
the reduced nickel−iron alloy could be oxidized by the water and segregate from the alloy during the reaction, leading to the formation of iron oxides. In order to analyze the valence state of Fe on the catalyst surface before and after the reaction, XPS tests were performed on the reduced and spent Ni10Fe10/MgAl2O4 catalyst, and the Fe 2p XPS results are shown in Figure S5. The peak located at 706.8, 709.8, and 712.2 eV could be attributed to Fe0 2p3/2, Fe2+ 2p3/2, and Fe3+ 2p3/2, respectively.58 It is obviously found that the Fe0 content greatly decreased after the reaction, which also proves that the iron can be oxidized during the reaction. These results are consistent with the previous research and related thermodynamic calculation results as illustrated in Figure S6.46−49,59,60 In order to further prove the oxidation effect of water in the steam reforming reaction, the reaction orders of water and ethanol was measured over Ni10Fe10/MgAl2O4 catalyst as illustrated in Figure S7. The higher reaction order with respect to ethanol and lower reaction order with respect to H2O also indicates that water could participate in the oxidation process of the catalysts. Additionally, to further prove the existence of the segregation process, the elemental distribution of Ni10Fe10/MgAl2O4 was tested using energy-dispersive X-ray spectroscopy (EDX)-STEM mapping as illustrated in Figure 3C. Both Fe and Ni elements are distributed uniformly after reduction, indicating the formation of Ni−Fe alloy. After the reaction, Fe was oxidized by H2O and the Fe−Ni alloy was decomposed partially, which led Fe to segregate from the bulk to the surface of the catalyst particle.

To further clarify the phase transition process and the existence form of the iron species in the reaction process, in situ Raman test was conducted and the results are shown in Figure 3D. Before reduction, the peak of α-Fe2O3 at 490 cm−1 and the peak of NiO at 710 cm−1 can be clearly observed which is consistent with the previous study.61,62 Upon reduction, these peaks related to oxides gradually disappear, indicating the reduction of the catalyst and formation of nickel−iron alloy. When the ethanol−water mixture was delivered into the system for a period of time, the peak of γ-Fe2O3 located at 330, 376, 472, and 620 cm−1 can be clearly observed.63 This in situ characterization directly observes the oxidation process of the Fe species from alloy to γ-Fe2O3 in the reaction atmosphere under the presence of water. This is consistent with the XRD results after the reaction. The change
of catalyst structure inevitably affects the catalytic performance, which will be explored in the following content.

### 2.4. Structure and Performance Relationship

As mentioned above, in order to further explore the effect of the iron segregation process on the reaction performance, a 5 h activity test was conducted on different catalysts, and the result is presented in Figure S8A,B. It can be found that samples of Ni10/MgAl2O4 and Ni10Fe10/MgAl2O4 exhibit completely different product distribution. For the Ni10/MgAl2O4 sample, the selectivity of each product remains basically stable during the reaction. However, for Ni10Fe10/MgAl2O4 catalyst, the whole process can be divided into iron-steam stage and steam reforming stage, respectively. In the first stage, it can be clearly found that the selectivity of hydrogen gradually decreases, accompanied by the increase in methane and carbon dioxide selectivity. It can be explained that at the initial stage of the reaction water is also capable of oxidizing the Fe in the Ni–Fe alloy to generate additional hydrogen, resulting in high selectivity for hydrogen and relatively low selectivity for carbon dioxide. The amount of the additional hydrogen calculated from the amount of generated CO2 is a lower methane selectivity than the Ni10/MgAl2O4 sample, indicating the effective suppression of methane selectivity. This is because the γ-Fe2O3 species generated by water oxidation in the first stage can participate in the methane suppression process, resulting in a decrease in methane selectivity. This is consistent with previous research that increasing the oxygen supply capacity of the catalyst can effectively suppress the formation of methane. It shows that the oxidation segregation process of the Ni–Fe alloy has a positive effect on methane suppression and can effectively increase the yield of hydrogen. The results of the hydrogen and methane yields of these two catalysts over time are illustrated in Figure 4A. It can be clearly observed that methane production gradually decreases over time due to the formation of γ-Fe2O3 species.

It is worth noting that at the beginning of the reaction, even before the Fe oxidation, the Ni10Fe10/MgAl2O4 catalyst also achieves a lower methane selectivity than the Ni10/MgAl2O4 sample, indicating the effective suppression of methane formation for the Ni–Fe alloy. The results are consistent with previous literature reports, which found that the formation of alloy could weaken the strength of CO adsorption on Ni sites and suppress CO dissociation and subsequent hydrogenation in forming methane. For verification, the methanation activity tests at 400 °C were carried out on the two reduced catalysts as shown in Figure S9A,B. The methanation reaction (eqs 4 and 5) is a major route for methane production in low-temperature ESR, especially for Ni-based catalysts. After reduction, the catalyst exists in the form of metallic nickel and nickel–iron alloy based on the XRD results, respectively. In addition, in the hydrogen-rich atmosphere of the methanation reaction, the catalysts can maintain the metallic state or alloy phase. Therefore, we can focus on exploring the influence of the nickel–iron alloy during the entire reaction. The methanation activity test demonstrates that the NiFe catalyst exhibits a lower conversion of CO/CO2 and decreased yield of CH4 compared to the Ni10/MgAl2O4 sample. Thus, it could be concluded that the formation of nickel–iron alloy can effectively inhibit the methanation reaction, especially for CO methanation. Then the CO-TPD test was conducted to explore the CO adsorption capacity of different catalysts, and the results are shown in Figure 4B. Two CO desorption peaks can be observed for both catalysts. The low-temperature peak below 100 °C is related to CO molecular adsorption on the sample, which is useless for methanation. However, the high-temperature peak between 300 and 450 °C is associated with CO dissociative adsorption on the surface of catalysts, which mainly contributed to methanation. As for the Ni10/MgAl2O4 sample, the CO dissociative adsorption peak is observed at around 420 °C. However, the temperature decreases to about 320 °C for the Ni10Fe10/MgAl2O4 catalyst, which suggests that the adsorption strength of CO is weaker. CO2-TPD presents similar results as shown in Figure S9C. Additionally, the results of the CO chemical desorption test illustrated in Figure S9D can also prove that CO on nickel–iron catalyst is easier to desorb. The adsorption strength of CO on the surface of the catalyst is closely related to the electron density on the surface, and it is generally believed that high electron density is beneficial for desorption. Thus, in order to explore whether the introduction of iron will affect the electronic state of nickel, XPS tests were performed on the two reduced catalysts as shown in Figure 4C. For the Ni10/MgAl2O4 sample, three peaks are observed located at 852.6, 855.5, and 861.2 eV corresponding to Ni0, Ni2+, and satellite peaks, respectively. When iron is introduced, the peak of the metallic nickel shifts significantly in the direction of low binding energy and is located at 851.8 eV. These results prove that the electron-transfer process from iron to nickel weakens the CO adsorption and inhibits its subsequent hydrogenation to form methane, which is in broad agreement with previous research.

In addition to nickel–iron alloy, it has been mentioned that the generation of γ-Fe2O3 during the reaction can also inhibit methane production. To further explore the inhibitory effect of γ-Fe2O3 on methane, a preoxidation reaction test was performed. After the different degrees of water preoxidation, the shift of the Ni–Fe alloy peak and the appearance of the γ-Fe2O3 phase located at 57.3° can be clearly observed in the XRD results shown in Figure S10. The ESR reaction results of the preoxidized catalyst are shown in Figure 4D. It is found that the selectivity of methane further decreases after preoxidation, which indicates that the γ-Fe2O3 phase can effectively suppress the formation of methane. However, it is worth noting that the ethanol conversion of the preoxidized catalyst decreases slightly, which may be caused by the partial coverage of nickel sites by γ-Fe2O3 formed after oxidation.

In situ DRIFTS experiments of Ni10/MgAl2O4 and Ni10Fe10/MgAl2O4 catalysts under the reaction conditions (S/C = 4) at different temperatures were carried out to further explore the inhibition mechanism of γ-Fe2O3 on methanation as presented in Figure 4E,F. The assignments of adsorption bands over both catalysts during the steam reformation of ethanol are listed in Table S5. For both catalysts, the peaks which belong to an ethoxy group at 1055 and 1105 cm−1 are observed at 100 °C. Moreover, the intensity of these two peaks at
decreases as the temperature increases to 400 °C accompanied by the appearance and enhancement of COO bands of acetate species. These changes reveal the conversion process of ethoxy to acetate, which is consistent with the literature. Compared with the pure nickel catalyst, the Ni10Fe10/MgAl2O4 sample presents more obvious signal peaks of acetate at a lower temperature (200 °C). Moreover, the intensity of the COO signal peak of Ni10Fe10/MgAl2O4 is much higher than that of pure nickel catalyst, indicating that the introduction of Fe species greatly promotes the oxidation process of ethoxy groups due to the formation of iron oxides during the reaction. Besides, for pure nickel catalyst, the characteristic peak of acetaldehyde can be observed at 1740 cm⁻¹ at above 300 °C, and the signal of gas-phase methane can also be seen at 400 °C, but these peaks are not detected for iron-containing catalyst. These results indicate that the addition of iron can exert an influence on the reaction path, promoting the oxidation process of ethoxy to the acetate group, thereby inhibiting the formation of acetaldehyde intermediate and its subsequent decomposition to generate methane. The strong oxidation ability of the Ni10Fe10/MgAl2O4 catalyst is attributed to the γ-Fe2O3 species produced by water oxidation during the reaction.

2.5. Carbon Deposition Analysis

Various characterization techniques were conducted in order to understand the origin of catalyst deactivation and their difference in deactivation behavior. The carbon deposition degree of spent catalysts with various Fe loadings after 15 h reaction was identified by TPO as illustrated in Figure 5A. It was obvious that, with the introduction of Fe, the amount of carbon deposition decreases significantly, which indicates the superior capability of NiFe/MgAl2O4 catalysts for anticoking. Additionally, two different peaks of CO2 production in the TPO spectra are observed located around 405 and 520 °C, respectively. The existence of these two different kinds of coke species has been widely reported. It is generally accepted that the first peak at lower temperatures is related to the oxidation of amorphous carbon species, while the second peak at higher temperatures can be attributed to the combustion of graphitic carbon. Raman spectra of spent NiFe/MgAl2O4 catalysts with various Fe loadings are shown in Figure 5B. Characteristic D and G bands of carbon located at 1250−1350 and 1500−1700 cm⁻¹ are observed obviously. The D band is attributed to the disordered carbon species (e.g., amorphous or defective filamentous carbon), whereas the G band is related to the stretching mode of the sp² band in ordered graphite and the ratio of I_D/I_G is shown in Figure 5C. The results of the Raman test also prove that two different types of carbon deposits coexist on both spent catalysts, which is consistent with the trends observed in the TPO experiments presented in Figure 5A.

As mentioned before, γ-Fe2O3 species are generated continuously during the reaction. In order to find out whether this is the reason for the better carbon deposition resistance of the nickel−iron catalyst, a carbon deposition gasification test was performed. After the ethanol steam reforming reaction activity test, N2 was introduced into the reactor under in situ conditions, and the CO/CO2 in the product was detected to determine whether the formed iron oxide species could react with the carbon deposition. The results of the carbon deposition gasification test for the Ni10Fe10/MgAl2O4 sample are shown in Figure 5D. It can be clearly seen from the figure that the signal of carbon dioxide begins to appear at 330 °C. As the temperature rose, the production of carbon dioxide gradually increases. This indicates that the γ-Fe2O3 species produced during the reaction can indeed react with the carbon deposition on the surface of the catalyst, which is also consistent with previous research and thermodynamic calculation presented in Figures S11 and S12. Moreover, this also explains why fewer carbon deposits are formed during the reaction of the iron-contained catalysts. O2-TPO and Raman tests were also conducted on the two samples before and after the gasification test as presented in Figure S13. Both the Raman and O2-TPO tests can reach the same conclusion that the carbon deposition is greatly reduced after the gasification test of the Ni10Fe10/MgAl2O4 catalyst. However, for the pure nickel sample, the content of carbon deposition remains unchanged before and after the gasification test. The above results indicate that the existence of iron oxide species is the main cause of carbon gasification process. The iron oxide species produced by the segregation during the reaction can react with the carbon deposits, thereby greatly reducing the coke content of the nickel−iron catalysts.

2.6. Scheme and Mechanism

Overall, the proposed reaction pathways based on the results of in situ DRIFTS and methanation tests for both catalysts are illustrated in Figure 6. For the Ni10/MgAl2O4 sample, NiO is reduced to the metallic state before the reaction. On one hand, the presence of metallic nickel converts ethoxy groups into acetaldehyde intermediates and then decomposes to generate methane. On the other hand, nickel itself possesses a higher CO/CO2 methanation activity, which ultimately leads to a higher selectivity of the methane byproduct. Moreover, large amounts of carbon deposits are produced as the reaction proceeded due to the poor anticoking ability of pure nickel catalyst. As for the Ni10Fe10/MgAl2O4 sample, the catalyst exists in the form of nickel−iron alloy after reduction. Then the iron in the alloy was gradually oxidized by water to form nickel-rich alloy and γ-Fe2O3 species during the reaction. On one hand, the presence of the nickel−iron alloy effectively inhibits the activity of the methanation reaction. On the other
hand, the γ-Fe2O3 species formed during the reaction promotes the oxidation of ethoxy groups to the acetate species, thereby effectively avoiding the production of the methane precursor, acetaldehyde. These two different iron species work together to suppress the formation of methane. In addition, the produced iron oxide species can also react with carbon deposits, resulting in nickel–iron catalysts with better resistance to carbon deposits.

3. CONCLUSIONS

In summary, we have demonstrated the design and application of NiFe/MgAl2O4 catalysts for hydrogen production in low-temperature ethanol steam reforming. The Fe species have a profound influence on the structure and catalytic performance of this bimetallic catalyst. The catalysts exist in the form of Ni–Fe alloy after reduction, and then the alloy is gradually oxidized by water to generate Ni-rich alloy and γ-Fe2O3 species during the reaction. The introduction of Fe species largely suppresses the production of methane and greatly improves the hydrogen yield under low temperature. On one hand, nickel–iron alloy can effectively suppress the CO/CO2 methanation reaction activity due to electron transfer from Fe to Ni. On the other hand, γ-Fe2O3 species formed during the reaction can inhibit the formation of methane, since γ-Fe2O3 species promote the conversion of ethoxy to acetate groups, thereby inhibiting the production and subsequent decomposition of acetaldehyde, the precursor of methane. In addition, γ-Fe2O3 species can also react with carbon deposits, resulting in better anticoke ability and excellent stability. The Ni10Fe10/MgAl2O4 sample shows the best reaction performance with more than 90% ethanol conversion for 15 h and an increase in the hydrogen yield from 2.7 to 4.6 mol/mol ethanol compared with Ni10/MgAl2O4 catalyst. This study provides insight to the structure–performance relationship of the Ni–Fe system, which is a promising catalyst candidate for further study in reforming reactions.

4. EXPERIMENTAL DETAILS

4.1. Catalyst Preparation

MgAl2O4 supports were prepared by hydrolysis of aluminum isopropoxide (Alfa Aesar (China) Chemical Co., Ltd., 98.0%) with Mg(NO3)2·6H2O (Alfa Aesar (China) Chemical Co., Ltd., 98.0%) in ethanol according to the literature. Stoichiometric quantities of aluminum isopropoxide (0.1 mol) and magnesium nitrate hexahydrate (0.05 mol) were mixed in 300 mL of denatured ethanol. The mixture solution was sealed and then stirred continuously for 1 h. Then the solution was heated to 80 °C and held there for several hours until the ethanol was evaporated and the resultant gel was dried at 90 °C overnight. Finally, the dried powders were calcined in ambient air at 900 °C for 12 h with a heating rate of 5 °C/min, resulting in the formation of MgAl2O4 supports with pure spinel crystal phase.

A series of NiFe/MgAl2O4 catalysts with different Fe loadings were prepared by an incipient impregnation method. Ni(NO3)2·6H2O (Aladdin (China) Chemical Co., Ltd., 98.0%) and Fe(NO3)3·9H2O (Chemart (Tianjin) Chemical Technology Co., Ltd., 98.5%) were used as precursors. The as-synthesized MgAl2O4 was used as the support. The loading of nickel was fixed at 10 wt %, and the loadings of Fe were 5, 10, 15, and 20 wt %, respectively. NiFe/MgAl2O4 catalysts were denoted as Ni10Fe5/MgAl2O4, Ni10Fe10/MgAl2O4, Ni10Fe15/MgAl2O4, and Ni10Fe20/MgAl2O4 according to the various Fe loadings. Ni10/MgAl2O4 catalyst was also prepared by the incipient impregnation method for comparison. Upon impregnation, the solids were dried at 90 °C overnight and calcined at 500 °C for 4 h with a heating rate of 5 °C/min.

4.2. Methods for Characterization

X-ray diffraction patterns (XRD) were obtained with a Bruker D8 Focus operated at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation (λ = 1.54056 Å). The XRD sample was exposed to Ar stream (30 mL/min) for removal of residual CO/CO2 in the stream. Once the signal of TCD reached a steady state, the system was exposed to Ar stream (30 mL/min) for 1 h before adsorption. After being cooled to 50 °C, the system was exposed to a stream of CO/CO2 gas (30 mL/min) to carry out CO/CO2 adsorption for 30 min. Next, the system was exposed to Ar stream (30 mL/min) for removal of residual CO/CO2 in the stream. The binding energies were calibrated to 285 eV to pass through a bubbler containing a mixture of ethanol and water to purge the mixture into the sample cell at 50 °C and holding for 30 min, (2) feeding He without passing through the bubbler to sweep ethanol in gas phase for spectra collection, and (3) increasing the temperature from 50 to 400 °C and collecting the sample spectra at desired temperatures.

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A CO chemisorption test was performed using the same Nicolet 1SS00 spectrometer apparatus. All samples were pretreated at 600 °C under a 10 vol % H2–Ar flow for 1 h and cooled down to 25 °C to obtain a background spectrum. This collected spectrum was then subtracted from the sample spectra for each measurement. Then a flow of 20% CO–Ar was fed into the pipeline to explore CO chemisorption and subsequently flushed with Ar for 30 min.

Morphologies of catalysts were characterized using a JEM-F200 transmission electron microscope (TEM) under a working voltage of 200 kV, which was equipped with a liquid nitrogen cooled energy-dispersive X-ray spectroscopy (EDS) detector for elemental analysis. The powder was first dispersed in ethanol by ultrasonication and then supported on a copper grid-supported transparent carbon foil.

Elemental composition of the prepared catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (VISTA-MPX, Varian). Prior to the measurements, the samples were first dissolved in nitric acid solution and the concentrations of elements were estimated to be close to the standard solutions for a better accuracy.

Raman spectroscopy was used to detect the type of carbon deposits. The spectra were obtained from a Renishaw inVia Raman spectrometer. The wavelength of laser source is 532 nm.

**In situ** Raman test was performed using the same spectrometer apparatus. The details of experimental method are illustrated in Figure S1A. After a reduction process at 700 °C for 1 h in a flow of 10 vol % H2/Ar, the ethanol–water mixture was purged into the system for ESR reaction. The spectra were obtained from the same Raman spectrometer.

### 4.3. Catalytic Reaction Test

Ethanol steam reforming was conducted at atmospheric pressure in a quartz fixed-bed reactor (Φ 10 × 30 mm) packed with 50 mg of 20–40 mesh catalysts diluted with 1.5 mL quartz particles (20–40 mesh). Prior to the test, the catalysts were reduced at 700 °C for 1 h in a flow of 10 vol % H2/N2 (60 mL/min). Before the introduction of the feed gas, the reactor was cooled to 400 °C and the catalyst bed was purged with N2 (50 mL/min) for 0.5 h. After that, the liquid solution with a specific steam-to-carbon molar ratio (S/C) of 4 and a flow rate of 0.05 mL/min was fed through an HPLC pump (P230, Elite, China) into a heated chamber (200 °C) to evaporate the mixture completely in the steam of N2 (50 mL/min). The products were analyzed online by an Agilent 7890A gas chromatograph (GC) equipped with a TCD and a flame ionization detector (FID). The GC was equipped with a Porapack-Q column for analyzing possible organic species (e.g., CH4, C2H6, CH3CHO, CH3CH2OH, and CH3COCH3) and a TDX-01 column to analyze the incondensable gas like H2, CO2, and CO.

Ethanol conversion and selectivity of different products were calculated as follows

\[
X_{\text{Ethanol}}(\%) = \frac{F_{\text{Ethanol, in}} - F_{\text{Ethanol, out}}}{F_{\text{Ethanol, in}}} \times 100
\]

(8)

\[
S_i(\%) = \sum \frac{F_i}{(F_{\text{out}})} \times 100
\]

(9)

where \( F \) represents the molar flow rate of CH\(_2\)\(_x\)OH or each product (mol/min) and \( i \) represents the species in the products, including H\(_2\), CH\(_4\), CO, CO\(_2\), CH\(_3\)CH\(_2\)OH, and CH\(_3\)COCH\(_3\). N\(_2\) was used as an internal reference to evaluate the carbon balance.

### 4.4. Methanation Reaction Test

The methanation reaction (eqs 6 and 7) is a major route for methane production in low-temperature ethanol steam reforming, especially for Ni-based catalysts. A methanation reaction test was conducted at atmospheric pressure in the same fixed-bed reactor. As the reaction activity test operation, the catalysts were prereduced before the reaction. Then, a mixture of gas with a flow rate of 100 mL/min (10% CO, 30% H\(_2\), and 60% N\(_2\)) was purged into the reactor CO methanation test at 400 °C. The CO\(_2\) methanation test was conducted under the same conditions as CO except for the gas feed flow (10% CO, 40% H\(_2\), and 50% N\(_2\)). The products were analyzed online by an Agilent 7890A gas chromatograph (GC). CO/CO\(_2\) conversion and selectivity of different products were calculated as the following equations:

\[
X_{\text{CO}}(\%) = \frac{F_{\text{CO, in}} - F_{\text{CO, out}}}{F_{\text{CO, in}}} \times 100
\]

(10)

\[
X_{\text{CO2}}(\%) = \frac{F_{\text{CO2, in}} - F_{\text{CO2, out}}}{F_{\text{CO2, in}}} \times 100
\]

(11)

\[
S_{\text{CH4, produced}}(\%) = \frac{F_{\text{CH4, produced}}}{F_{\text{CO, in}} \times X_{\text{CO}}} \times 100
\]

(12)

\[
S_{\text{CH4, produced}}(\%) = \frac{F_{\text{CO2, out}}}{F_{\text{CO2, in}} \times X_{\text{CO2}}} \times 100
\]

(13)

### 4.5. Preoxidation Reaction Test

In order to explore the effect of water on the catalyst structure and reaction performance, preoxidation reaction test was conducted at atmospheric pressure in the same quartz fixed-bed reactor. Prior to the test, the catalysts were reduced at 700 °C for 1 h in a flow of 10 vol % H\(_2\)/N\(_2\) (60 mL/min). Then the reactor was cooled to 400 °C, and the water was purged into the reactor for oxidation of the catalysts. After that, the ethanol–water mixture was fed into the system, and the ESR reaction test was conducted.

### 4.6. Carbon Gasification Test

In order to explore the mechanism of carbon deposition inhibition and elimination in the reaction process, a carbon deposition gasification test was carried out. After the ESR activity test, a N\(_2\) flow was purged into the reactor for 30 min to eliminate the influence of the residue of the reaction product. After the reactor was cooled to 30 °C, the temperature was programmed to rise to 400 °C at a ramping rate of 10 °C/min under N\(_2\) atmosphere to observe whether there are CO and CO\(_2\) signals in the product.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00217.

Experimental details and supporting data (PDF)

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Author Contributions

J.G. conceived and coordinated the research. Y.W. contributed to catalyst synthesis and catalytic experiments. Y.W. and Q.X. analyzed the XPS data. Y.W., C.P., H.T., X.Z., and J.G. wrote the manuscript. All authors participated in discussion of the research.

Notes

The authors declare no competing financial interest.

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