



Short communication

Nanorod alumina-supported Ni–Zr–Fe/Al₂O₃ catalysts for hydrogen production in auto-thermal reforming of ethanolLihong Huang^a, Jian Xie^a, Rongrong Chen^a, Deryn Chu^b, Andrew T. Hsu^{a,*}^a Lugar Center for Renewable Energy, Indiana University-Purdue University Indianapolis, Indianapolis, IN 46202, USA^b U. S. Army Research Laboratory, Adelphi, MD 20783, USA

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ABSTRACT

Nanorod alumina-supported Ni–Zr–Fe/Al₂O₃ catalysts were prepared by co-impregnation, characterized by TEM, TPR, XRD, XPS, and TPD-pyridine, and tested in auto-thermal reforming of ethanol. The characterization results indicate that, with iron and zirconia promotion, the Ni_xFe_{1–x}Al₂O₄ mixture spinel forms, the valence of the surface Ni species is modified, and the acidity decreases. As a result, during a 30-h test over the Ni–Zr–Fe/Al₂O₃ catalyst, sintering is restrained, and the selectivity to hydrogen remains around 85.79% without obvious loss, while the un-promoted Ni/Al₂O₃ shows poor stability and selectivity.

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1. Introduction

Because of its self-sustainment for reaction heat, auto-thermal reforming (ATR) of bio-ethanol is a promising process for hydrogen production. Heterogeneous catalysts, such as supported Ni-based catalysts, have been extensively studied in ATR of ethanol; hydrogen selectivity, coke deposition, and carbon-containing product distribution are the main catalytic performance concerns to be addressed [1–3]. Within supported catalysts, the structures as well as morphology of supports are key factors for reactant adsorption and activation, and also play an important role in reaction pathway selection. On the other hand, the additives are effective promoters to modify the metal–support interaction and then improve the catalytic performance.

Gamma alumina is a typical support in Ni-based catalysts for steam reforming of ethanol because of its high surface area and the interactions between the metal and support. However, the dehydration of ethanol, which is the major source of coke formation in ethanol reforming, is promoted by the intrinsic strong acid sites on the surface of alumina [4]. Nanorod alumina, because of its high surface area and ordered morphology, provides specific structures for formation of possible active sites; these active sites provide potential improvements of the catalytic

performance [5]. Zirconia, with its relatively mild acid/basic properties and its high thermal stability, is often used as support or as a promoter to modify supports [6–8], while Fe shows positive trends on the improvement of ATR of ethanol in our previous work [9,10] because of its activity in water–gas shift reaction (WGS) [11] and the similarity of electronic properties with Ni.

In this work, the nanorod alumina as a support and the zirconia and iron as promoters, were introduced into Ni-based catalysts and tested in ATR of ethanol. Over the doped Ni-based catalysts, the structural and electronic modifications are observed, the acidity and sintering are restrained, and improved selectivity to hydrogen and improved stability are achieved.

2. Experimental

2.1. Catalyst preparation and characterization

The nanorod gamma alumina (1/8 in. pellets, 220 m²/g) was obtained from Alfa Aesar chemicals. As shown in Fig. 1, the nanorods are about 3–5 nm in diameter and 10–20 nm long. These Ni-based catalysts were prepared by co-impregnation of metal nitrate over sieved alumina particles of 20–40 mesh. After being dried at 110 °C for 12 h, samples were calcined in air at 650 °C for 6 h. Based on previous results [9,10], the catalyst compositions were chosen as follows: among the Ni/Al₂O₃, Ni–Zr/Al₂O₃, and Ni–Zr–Fe/Al₂O₃ samples, the amount of NiO was 15% (mass fraction) in all the catalysts, ZrO₂ was 8% in the last two, and Fe₂O₃ was 8% in the last one, while the remaining balance was Al₂O₃.

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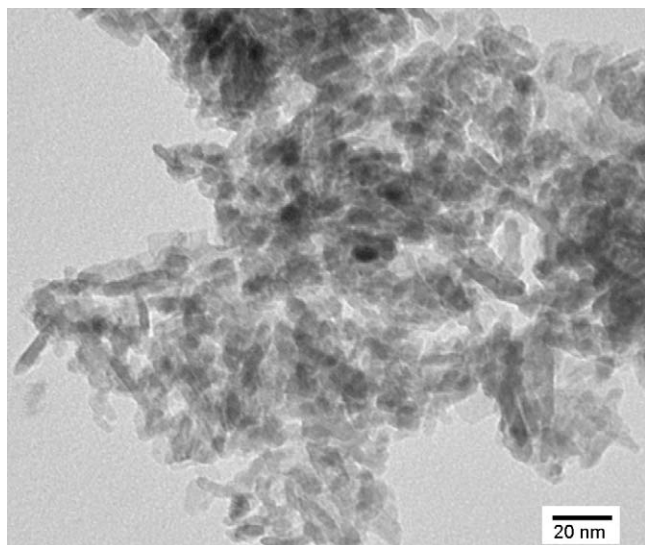


Fig. 1. TEM image of alumina nanorods.

Transmission electron microscopy (TEM) images were acquired on a Tecnai G2 12 Bio Twin TEM. The temperature-programmed reduction (TPR) was performed in a downstream fixed-bed quartz tube reactor at the atmospheric pressure. Calcined samples were stabilized to a stream of 5.0% H_2 in a H_2/N_2 mixture at 25 ml/min, and then the temperature was increased from room temperature to 800 °C at a linear heating rate of 10 °C/min. X-ray diffraction (XRD) analyses were conducted on a Siemens D5000 diffractometer with $Cu\ K\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was recorded by an Ultra DLD spectrometer (Kratos, UK) with $Al\ K\alpha$ radiation (1486.6 eV). The samples were reduced at 650 °C in a reaction cell, and then switched into the chamber for the XPS scan. The acidity of the catalysts was assessed by temperature-programmed desorption (TPD) of pyridine. The sample was first reduced in a stream of 5.0% H_2 in a H_2/N_2 mixture at 650 °C for 6 h, purged with nitrogen for 30 min at 650 °C, then cooled to 50 °C in nitrogen; and switched into a pyridine-saturated nitrogen flow for 30 min at 50 °C. After the sample was purged with nitrogen at 50 °C, the TPD of pyridine was performed at a heating rate of 15 °C/min.

2.2. Catalytic activity test

The ATR of ethanol was conducted in a fixed-bed reactor. Catalysts were loaded and reduced in 5% H_2 in a H_2/N_2 mixture at 650 °C for 6 h before the reaction. A feed of a water–ethanol mixture was vaporized at 160 °C, mixed with oxygen and nitrogen (nitrogen as an internal standard), and introduced into the catalyst bed for the ATR test at a molar ratio of $C_2H_5OH:O_2:H_2O = 1:0.5:3$. The definitions of ethanol conversion, carbon selectivity, and hydrogen selectivity are listed in Eqs. (1)–(3). Carbon selectivity (Eq. (2)) is based on carbon-containing products, while hydrogen selectivity (Eq. (3)) is defined on the basis of H_2 and hydrogen-containing hydrocarbons in product gases.

$$X_{\text{ethanol}} = \frac{F_{\text{ethanol in}} - F_{\text{ethanol out}}}{F_{\text{ethanol in}}} \quad (1)$$

$$S_{\text{carbon-containing product}} = \frac{F_{\text{carbon-containing product}}}{n_i(F_{\text{ethanol in}} - F_{\text{ethanol out}})} \quad (2)$$

$$S_{H_2} = \frac{2F(H_2)}{2F(H_2) + \sum y \cdot F(C_xH_yO_z)} \quad (3)$$

3. Results and discussion

3.1. Catalytic performance of Ni-based catalysts

In the process of ATR, ethanol can be transformed via two pathways: either by being transformed into ethylene thru the dehydration of ethanol, which always results in coke deposition via the polymerization of ethylene, or by being transferred into acetaldehyde via the dehydrogenation of ethanol. Acetaldehyde can be further transformed to CO, CH_4 , CO_2 , and hydrogen with water and oxygen via decomposition, reforming, water–gas shift reaction (WGSR), and partial oxidation (POX) [12–14]. Accordingly, the dehydrogenation pathway favors C_1 products and hydrogen production, while the activity for acetaldehyde transformation is also an important factor.

As shown in Fig. 2, the Ni-based catalysts were tested in ATR at 600 °C with a feed gas of $C_2H_5OH:O_2:H_2O = 1:0.5:3$ (molar ratio). The Ni/Al_2O_3 (Fig. 2(A)) shows relatively high initial activity. However, the selectivity to hydrogen shows poor performance, which declines from 75.82% to 26.07%. Meanwhile, the selectivity to ethylene increases from 36.34% to 76.97%.

Over the zirconia-promoted catalyst $Ni-Zr/Al_2O_3$ (Fig. 2(B)), the conversion of ethanol emerges near 100%, but decreases gradually to about 86%, while the selectivity to hydrogen still remains at 82.13% at the 30-h mark. Meanwhile, the selectivity to C_1 products – CO_2 , CO, and CH_4 – remains at a high level, accompanying the ethylene selectivity near 5.77%. Iron also promotes the activity of Ni-based catalysts [9,10]. As shown in Fig. 2 (C), for $Ni-Fe/Al_2O_3$, the conversion of ethanol remains at above 99% with little loss, and the selectivity of hydrogen remains around 86.22%, accompanying the increases of selectivity to CO_2 and CH_4 . But the selectivity to CO and C_2H_4 still stays at about 30% and 3.21%. At the same time, acetaldehyde (not shown in Fig. 2) emerges after 8 h and reaches about 1.5%, which suggests the loss of the activity of acetaldehyde conversion with time.

With the promotion of both zirconia and iron, the $Ni-Zr-Fe/Al_2O_3$ (Fig. 2(D)) shows both high activity and improved stability: the conversion of ethanol remains near 100%, and the selectivity to hydrogen remains at 85.79% without obvious loss. As to the carbon-containing products, as compared with that of the $Ni-Fe/Al_2O_3$, the selectivity over zirconia-promoted $Ni-Zr-Fe/Al_2O_3$ to carbon dioxide remains near 56%, which shows a high activity of the WGSR [15]. The disappearance of ethylene and acetaldehyde in product gas suggests the suppression of ethanol dehydration and the higher activity of acetaldehyde conversion due to the promotion effect of zirconia.

3.2. Reducibility of catalysts

TPR experiments were performed to test the reducibility of the Ni-based catalysts. Fig. 3(1) indicates that there are two reduction peaks. The peak γ near 795 °C can be attributed to the reduction of $NiAl_2O_4$ spinel, while the weak peak α suggests little exists as non-spinel Ni oxide [16–18]. With the promotion of zirconia, the slightly intensified peak α' in Fig. 3(2) indicates that reducible Ni oxide increases because zirconia is not easily reduced under these conditions. Over $Ni-Zr-Fe/Al_2O_3$, two obvious reduction peaks, α'' and β'' , emerge at the shoulder of peak γ'' . These two peaks can be attributed to the reduction of iron oxide and/or nickel oxide.

XPS spectra were recorded over the samples reduced at 650 °C to evaluate the reducibility. As shown in Fig. 4 of $Ni_{2p\ 3/2}$ spectra, two peaks emerge at the binding energies of 855.8 eV and 851.6 eV, which correspond to the characteristic peaks of Ni^{2+} and Ni^0 , respectively [19]. The area of the Ni^0 peaks near 851.6 eV increases by 84.9% in $Ni-Zr/Al_2O_3$ and by 263.5% in $Ni-Zr-Fe/Al_2O_3$, respectively, as compared with that of Ni/Al_2O_3 . These

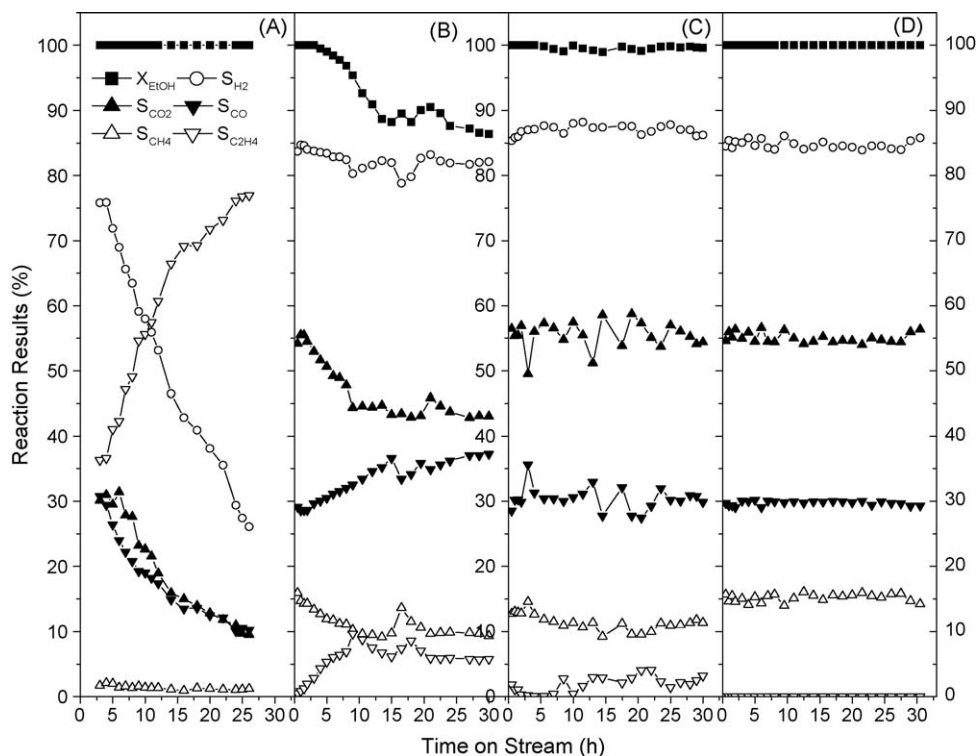


Fig. 2. Catalytic performance tests of (A) Ni/Al₂O₃, (B) Ni-Zr/Al₂O₃, (C) Ni-Fe/Al₂O₃, and (D) Ni-Zr-Fe/Al₂O₃ catalysts in auto-thermal reforming of ethanol at 10,000 h⁻¹ and 600 °C in the feed gas of CH₃OH:O₂:H₂O = 1:0.5:3 (molar ratio).

increases indicate that both zirconia and iron promote the reduction of nickel, but iron has a stronger effect.

3.3. Crystalline structure of catalysts

The cause of reducibility variation can be tracked to structural variation. Although the XRD patterns are similar to each other among these Ni-based catalysts, there are still some clues to identify the peaks. As shown in Fig. 5(1), the peaks near 45.1°, 37.0°, 66.5°, 31.4°, and 19.4° indicate that nickel aluminum spinel NiAl₂O₄ is formed via the surface reconstruction of the nickel and gamma alumina [16,20]. With zirconia in Ni-Zr/Al₂O₃ of Fig. 5(2), the peaks near 37.0° and 31.4° are broadened slightly, which suggests zirconia

can slightly promote the dispersion of NiAl₂O₄ and the ease of reduction, which can be confirmed by TPR and XPS results. As shown in Fig. 5(3) of Ni-Zr-Fe/Al₂O₃, the characteristic peaks of NiAl₂O₄ near 37.0° and 31.4° are broadened to lower angles, which are the positions of the NiFe₂O₄ spinel phase. The emerging peaks near 36.5° and 31.0° suggest that the spinel FeAl₂O₄ could be formed [21]. Because the ions of nickel and iron are similar in their ion radius (Fe²⁺ 0.074 nm, and Ni²⁺ 0.069 nm), and the spinel phases of NiAl₂O₄ and FeAl₂O₄ are categorized in the *Fd3m* space group, the mixed crystal phase Ni_xFe_{1-x}Al₂O₄ could be formed over iron-promoted nickel-based catalysts via part replacement of Ni by Fe in the NiAl₂O₄ spinel. No obvious zirconia peaks are observed in any of the samples, which suggest zirconia mainly exists in an amorphous state.

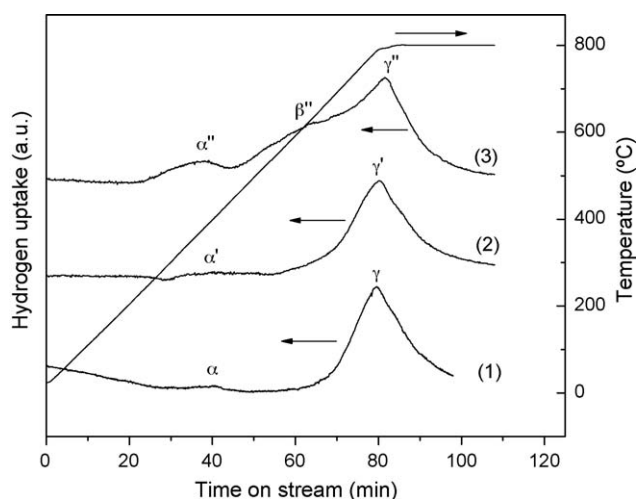


Fig. 3. TPR patterns of (1) Ni/Al₂O₃, (2) Ni-Zr/Al₂O₃, and (3) Ni-Zr-Fe/Al₂O₃ catalysts at 10 °C/min.

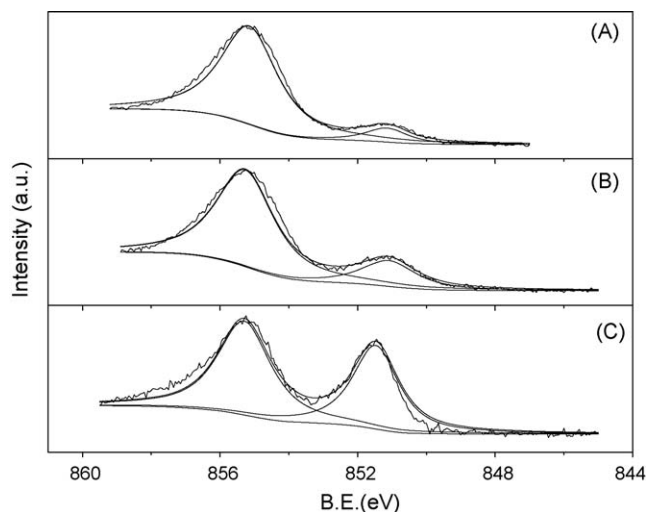


Fig. 4. XPS spectra of Ni_{2p 3/2} over reduced Ni-based catalysts: (A) Ni/Al₂O₃; (B) Ni-Zr/Al₂O₃; (C) Ni-Zr-Fe/Al₂O₃.

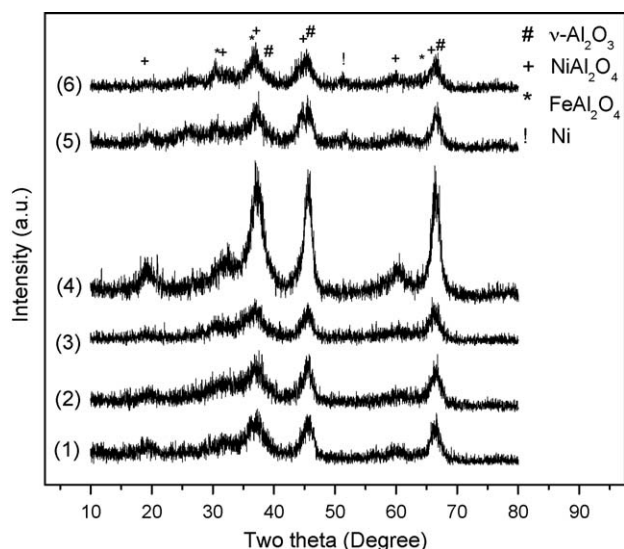


Fig. 5. XRD patterns of nickel-based catalysts: (1) Ni/Al₂O₃-as prepared; (2) Ni-Zr/Al₂O₃-as prepared; (3) Ni-Zr-Fe/Al₂O₃-as prepared; (4) Ni/Al₂O₃-spent; (5) Ni-Zr/Al₂O₃-spent; (6) Ni-Zr-Fe/Al₂O₃-spent.

As for the spent samples after ATR tests, Fig. 5(4) shows that all the peaks are intensified, which suggests the sintering of crystalline particles in Ni/Al₂O₃, while Fig. 5(5) and (6) indicate that zirconia and iron could constrain the sintering because there is no obvious change in either Ni-Zr/Al₂O₃ or Ni-Zr-Fe/Al₂O₃.

3.4. Acidity of catalysts

The acidity of alumina support plays an important role in the dehydration route. As shown in Fig. 6, the amount and the intensity of the acidity can be evaluated by the area and position in the patterns of TPD-pyridine [22]. The two peaks near 390 °C and 465 °C in Ni/Al₂O₃ (Fig. 6(1)) suggest that there are different acid sites with individual amounts and intensities. Over the Ni-Zr/Al₂O₃ (Fig. 6(2)), another peak emerging near 295 °C and the intensified peaks near 390 °C and 465 °C suggest the formation of new acid sites as well as an increase in the acid amount because of the introduction of zirconia. With introduction of iron, all peaks are significantly weakened within Ni-Zr-Fe/Al₂O₃; this change

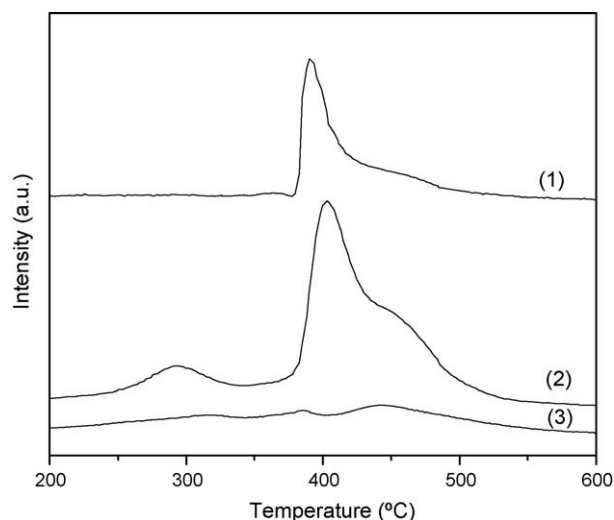


Fig. 6. TPD-pyridine over reduced Ni-based catalysts: (1) Ni/Al₂O₃; (2) Ni-Zr/Al₂O₃; (3) Ni-Zr-Fe/Al₂O₃.

indicates that the acidity is strongly suppressed and also explains the suppression of the dehydration reaction, which always occurs on acid sites in ATR tests.

Based on the characterizations, the main active component in Ni/Al₂O₃ is the partially reduced NiAl₂O₄ spinel, which promotes the dehydrogenation of ethanol and the transformation of acetaldehyde to C₁ products and hydrogen [2,23]. In ATR of ethanol, the sintering of the NiAl₂O₄ is observed over time; accordingly, the reaction pathway is shifted to the dehydration of ethanol, which results in the increase of ethylene accompanying the decrease of C₁ products and hydrogen selectivity.

With zirconia in Ni-Zr/Al₂O₃, on one hand, the acidity increases with the zirconia, which can promote ethanol dehydration; on the other hand, the zirconia promotes the reduction of the Ni oxide as an electronic promoter, where more nickel atoms exist as Ni⁰, and as a thermal stabilizer, where no obvious sintering is observed. The increased partially reduced Ni species promotes ethanol dehydrogenation and conversion of acetaldehyde, and the competitive dehydration pathway is suppressed in fact, despite the higher acidity. These effects result in the relative stability and preference to the ethanol dehydrogenation pathway in ATR of ethanol: a higher selectivity to hydrogen and C₁ products is observed. But with an increase in the acidity, the coke deposition via the ethanol dehydration results in an activity loss in ATR.

With both zirconia and iron in Ni-Zr-Fe/Al₂O₃, the spinel FeAl₂O₄ is formed. Because of the similarity of ion radii (Fe²⁺ 0.074 nm and Ni²⁺ 0.069 nm) and the coordination environment in the spinel phase, the mixture spinel Ni_xFe_{1-x}Al₂O₄ could be formed within Ni-Zr-Fe/Al₂O₃. Because of the heterogeneous atoms in this mixture spinel phase, more crystal defect sites are formed, which results in the increase in reducibility and activity and is proven by the results of TPR, XRD, and XPS. Furthermore, the acidity is significantly decreased via enveloping or damaging of the acid sites by the mixture spinel phase on the alumina surface. Consequently, high hydrogen selectivity and thermal stability are observed over the Ni-Zr-Fe/Al₂O₃ in ATR of ethanol.

4. Conclusions

Gamma alumina nanorods as support, and Zr and Fe as additives were introduced in Ni-based catalysts by co-impregnation. Within the Ni-Zr-Fe/Al₂O₃ sample, the mixture spinel Ni_xFe_{1-x}Al₂O₄ is formed, and the thermal stability and reducibility are improved, while the acidity is suppressed. During a 30-h test of ATR of ethanol, the sample shows an improved hydrogen selectivity, durability, and higher activity as compared with the un-promoted Ni/Al₂O₃: the conversion of ethanol remains near 100% and the selectivity to hydrogen remains around 85.79% without obvious loss.

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