The structure and performance of \((\text{Ni}_4\text{Fe})_m\text{Ag(PrZr)_nO}_x\) catalyst for ethanol steam reforming

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Abstract. Co-precipitation method is used to synthesize \(\text{Pr}_p\text{Zr}_q\text{O}_x\) composite oxide support and impregnation method is adopted in preparing \((\text{Ni}_4\text{Fe})_m\text{Ag(PrZr)_nO}_x\) catalysts. X-ray power diffraction (XRD), Temperature programmed reduction (TPR) and Temperature programmed oxidation (TPO) are used to characterize the catalysts. The results indicate that not only the improvement of catalytic activity is remarkable, but also an excellent capacity of resistance to carbon deposition when Ag dropped into the Ni-Fe bimetallic catalysts. XRD spectrum of the fresh \((\text{Ni}_4\text{Fe})_m\text{Ag(PrZr)_nO}_x\) catalysts present characteristic diffraction peak of tetragonal crystal phase ZrO\(_2\), rhombohedral Fe\(_2\)O\(_3\), hexagonal NiO and cubic Ag\(_2\)O while no diffraction peak of praseodymium oxide appears because the doped praseodymium ions can enter the ZrO\(_2\) lattice. After 823K's pretreatment by H\(_2\), the main active components are cubic Ni\(_0\) and cubic Ag\(_0\). TPR shows that the presence of Ag is of great benefit to the reduction of Fe\(_2\)O\(_3\) and NiO: the peaks maximum due to the Fe\(_2\)O\(_3\)→Fe\(_3\)O\(_4\) and NiO→Ni\(_0\) reduction of the Ag-containing sample are shifted by more than 150K to lower temperatures in comparison with Ni-Fe bimetallic metallic catalysts. \((\text{Ni}_4\text{Fe})_16\text{Ag(PrZr)_64.8O}_x\) catalyst shows its best catalytic activity in ethanol steam reforming. Under the following conditions, reaction temperature 773K, ethanol/water with molar ratio of 1:6, weight hourly space velocity (WHSV) of 11.8 h\(^{-1}\), the ethanol conversion rates are nearly 100% and the molar percentage of H\(_2\), CO, CH\(_4\), CO\(_2\) are 70.5%, 1.8%, 7.9%, and 19.6% respectively.

1. Introduction

Ni-based catalyst such as Ni/ZrO\(_2\) has been widely used in the steam reforming of ethanol, because of the advantages of high C-C bond-breaking activity and it is relatively cheap [1-5]. But there are also some problems of Ni-based catalyst such as low activity of water gas shift, serious methanation, easy carbon deposition and sintering in ethanol steam reforming[6-8]. Some catalysts with Ag, Cu as main active components have been adopted in steam reforming reaction of ethanol, and it is found that these catalysts can inhibit the process of ethanol dehydration into alkene. However, they also have the defect of low activity at low temperature[9]. Fe-based catalyst, with good water gas shift capacity, is also easy to sinter to inactive. Based on the above study, some researchers introduce components such as Mn, Cr, Fe, Co and Cu into Ni-based catalysts, so that the activity and selectivity of catalytic reaction are improved due to the synergistic catalytic effect of a variety of active components.

The influences of catalyst supports on the reaction of ethanol steam reforming have been extensively studied, and ZrO\(_2\) becomes a common catalyst support because of its proper acid-base property, good thermal and chemical stability[10]. Taking into account the two valence states of Pr (+3 and +4), oxides composed of Pr and Zr may have good properties of oxygen storage and release,
thus catalyst prepared by Pr-Zr composite oxide supported transition metal equipped with better
catalytic activity and selectivity in ethanol steam reforming, especially beneficial to lowering the
selectivity of CO.

In this paper, (Ni$_4$Fe)$_m$Ag(PrZr)$_n$O$_x$ catalysts are prepared, and that structure and properties of the
catalysts are studied by using XRD, TPR and TPO technology, and the catalytic activity and
selectivity in ethanol steam reforming are evaluated at last.

2. Experimental section
The mixed metal nitrates solution is dropped into ammonium carbonate solution with vigorous stirring,
and then go through a process of aging and filtration. The obtained precipitation is washed by ethanol,
and dried. Support can be collected after a calcination under the temperature of 923 K. Nitrates of Ni,
Fe and Ag are loaded on the support with impregnation and at last, (Ni$_4$Fe)$_m$Ag(PrZr)$_n$O$_x$ catalysts are
achieved after drying and roasting under temperature of 923 K.

Ethanol steam reforming was conducted on a WFS-3015 catalyst evaluation device under the
pressure of 0.5 MPa. Before the reaction, H$_2$-Ar mixed gas with a ratio of 1:1 is passed into catalyst
which will be reduced under the temperature of 823 K for 2 h. Pumping into ethanol aqueous solution
with micro pump continuously with rate of 0.1 ml·min$^{-1}$ and the ethanol-water molar ratio is 1:6.
Having been vaporized under 473 K, the gas is mixed with the carrier of Ar and led into a micro fixed-
bed reactor with a flow rate of 30 ml·min$^{-1}$. The generated gas is then led into an SP-6800A gas
chromatograph (TDX-02 carbon molecular sieve column, thermal conductivity detector) and goes
through an online analysis, while the liquid product is studied via an SP-6800A gas chromatograph
(AE.FFAP capillary column, flame ionization detector) and Qianpu chromatographic workstation is
used in order to take data processing.

2.1. The structure of catalyst
Figure 1 is the XRD spectrum of (Ni$_4$Fe)$_m$Ag(PrZr)$_n$O$_x$ catalysts. As indicated, the XRD spectrum of
(Ni$_4$Fe)$_m$Ag(PrZr)$_n$O$_x$ catalysts present characteristic diffraction peak of tetragonal crystal phase ZrO$_2$
(2θ=29.86°,34.51°,49.72°,58.52°;PDF#42-1164), these diffraction peak of tetragonal crystal phase
ZrO$_2$ shift to low angle compared with the pure ZrO$_2$, and no diffraction peak of praseodymium oxide
appears, which means the doped praseodymium ions can enter the ZrO$_2$ lattice to replace the
zirconium ions to form the tetragonal crystal phase framework. The fresh catalysts also appear to
be a weak diffraction peaks of rhombohedral phase Fe$_2$O$_3$ (2θ=72.3°,80.7°,83.0°;PDF#33-0664) and
hexagonal crystal phase NiO (2θ=37.3°,43.3°,62.9°;PDF#44-1159). Besides, a weak diffraction peak
(2θ=32.8°,38.1°;PDF#65-6811) of cubic crystal phase Ag$_2$O appears with the increase of Ag
component. After a hydrogen reduction under 823 K, diffraction peaks of NiO can no longer be found
on XRD spectrum of the catalysts, a diffraction peak of cubic crystal phase Ni appears instead
(2θ=44.3°,51.9°,76.3°;PDF#04-0850). Moreover, diffraction peaks of Ag of cubic crystal phase
(2θ=38.1°,77.4°;PDF#04-0783) appear on catalysts with large amount of Ag component, and it
indicates that both Ni and Ag components exist as elementary substances after the fresh catalysts
being reduced by hydrogen under 823 K for 2 h. According to the XRD spectrums of these reduced
catalysts, no diffraction peaks of pure Fe nor Fe$_3$O$_4$ but rhombohedral crystal phase Fe$_2$O$_3$ are found.
However, the TPR analysis indicates that, under the temperature of 773 K, Fe$_2$O$_3$ has already been
reduced to Fe$_3$O$_4$ by hydrogen which can therefore confirm the existence of Fe$_2$O$_3$ and Fe$_3$O$_4$ in
catalyst as Fe component. After being used in ethanol steam reforming, XRD diffraction peaks of all
components of catalyst do not have any further changes, which suggest a good stability.
2.2. The TPR characterization of catalyst

Figure 2 presents the TPR results of \((\text{Ni}_4\text{Fe})_m\text{Ag(PrZr)}_n\text{O}_x\). It is evident that there is a small reduction peak of \(\text{Ni}_4\text{Fe}(\text{PrZr})_4\text{O}_x\) catalysts around 673 K and it can be attributed to \(\text{Ni}^{2+}\rightarrow\text{Ni}^0\) reduction process which is consistent with [11]. A big reduction peak appears before the temperature reaches 873 K, and it is a result of overlapping reduction peaks of \(\text{Ni}\) oxides and \(\text{Fe}\) oxides according to literature [11,12] and the molar ratio of \(\text{Ni}\) and \(\text{Fe}\) components used in preparing catalysts, which indicates strong interactions between \(\text{Ni}\), \(\text{Fe}\) and support of catalysts.

Big reduction peaks of \((\text{Ni}_4\text{Fe})_m\text{Ag(PrZr)}_n\text{O}_x\) catalysts appear around 673 K due to the reduction reaction of \(\text{Ni}^{2+}\rightarrow\text{Ni}^0\) and have confirmed the conclusion in literature [11]. A small reduction peak shows up again because of \(\text{Fe}_2\text{O}_3\) being reduced to \(\text{Fe}_3\text{O}_4\) just as the discovery of literature [12], while the reduction process of \(\text{Fe}_3\text{O}_4\rightarrow\text{Fe}\) contributes to the reduction peak around 973 K as indicated in literature [13]. Compared with catalysts that haven’t been added in \(\text{Ag}\), reduction peaks of \(\text{Ni}\) oxides in \((\text{Ni}_4\text{Fe})_m\text{Ag(PrZr)}_n\text{O}_x\) catalysts appear in lower temperature areas, and they are separated from the ones of \(\text{Fe}\) oxides which means \(\text{Ag}\) can reduce the interaction between \(\text{Ni}\) and \(\text{Fe}\), as well as \(\text{Ni}\) and supports, thus increase the reduction activity of \(\text{Ni}\) component. However, when the amount of \(\text{Ag}\) component increases to a certain value (i.e., the molar ratio of \(\text{Ag}: (\text{Ni} + \text{Fe})\) is larger than 1:10), the reduction peaks of \(\text{Ni}\) oxides will move to the lower temperature areas. Taking XRD and TPO spectrums into consideration, a conclusion can be drawn that in catalyst with large amount of \(\text{Ag}\).
component, the reduction peaks appear around 673 K can be attributed to not only the reduction process of Ni$^{2+}$→Ni$^0$, but also Ag$_2$O→Ag$^0$, and relevant evidences can be found in literature [14].

2.3. The carbon deposition resistance of catalyst

According to previous study[15-17], serious carbon deposition always appears in ethanol steam reforming taken on Ni-based catalysts. To have further study, (Ni$_4$Fe)$_m$Ag(PrZr$_4$)$_n$ Ox catalysts having been used in ethanol steam reforming are analyzed in TPO tests. As shown in Figure 3, the oxygen consumption peak around 673 K is related to the oxidation of Ni→NiO, and with the increase of Ag component, a left shoulder peak appears at about 573 K which is believe to be a oxidation process of Ag overlaying the oxidation process of Ni. Figure 3 (e) (f) show that there is an apparent inverted peak at the temperature of 873 K. To identify of which gas species the inverted peak is, a speculation is made that this peak is caused by generated gases of oxidized carbon deposition on catalysts, such as CO and CO$_2$. In order to confirm this conjecture, TPO test gas (3% O$_2$-97% Ar) is used as reference gas with a consistent temperature of 873 K and the results of quantitative input of 0.45 ml CO and CO$_2$ are shown in Figure 4. Figure 4 has proven the speculation made before. Then, fresh catalyst and catalyst having been used in ethanol steam reforming are going through TPR-TPO cycle test separately and the results suggest that no inverted peak appear in TPO curve of hydrogen-reduced fresh catalyst. At around 873K, an invert peak appears on the first TPO test curve of the latter catalyst but not the second TPO test curve, because the carbon deposition on catalyst having been used in ethanol steam reforming has been completely oxidized in the first TPO test. Another conclusion drawn through Figure 3 is that among (Ni$_4$Fe)$_m$Ag(PrZr$_4$)$_n$ Ox catalysts, only the ones with few amount of Ag show inverted peaks in their TPO curves which can be found in (e) and (f) of Figure 3. However with the increase of Ag component, inverted peaks on TPO curve keep on decreasing or even disappear, which indicates that the Ag component in catalyst can inhibit carbon deposition generated in ethanol steam reforming.
2.4. Evaluation of catalytic activity

(Ni₄Fe)ₙAg(Pr₃Zr₄)ₙOₓ catalysts with Pr/Zr ratio of 1:9, 2:8, 3:7, 4:6 and 5:5 are prepared separately. Their catalytic activity in ethanol steam reforming are studied in the temperature range of 623K – 873K and shown in Figure 5. It can be observed in Figure 5 that the ethanol conversion rate increases with temperature rising indicating catalytic activity has positive relationship with temperature. When implementing ethanol steam reforming in high temperature area (≥773 K), the catalysts Ni₄Fe(PrZr₄)₂Oₓ show the highest ethanol conversion activity.

In Figure 6, compared with the Ni₄Fe(PrZr₄)₂Oₓ catalysts (see figure 6 g), (Ni₄Fe)ₙAg(Pr₃Zr₄)ₙOₓ catalysts doped Ag component present higher catalytic activity in ethanol steam reforming and if the temperature grows higher than 773 K then ethanol conversion rate is higher than 99%. Among several evaluated catalysts, (Ni₄Fe)₁₆Ag(PrZr₄)₆₄.₈Oₓ catalyst shows the highest activity especially in lower temperature, and the ethanol conversion rate can reach 98.6% on this catalyst at 623 K while which is only 87.1% on Ni₄Fe(PrZr₄)₂Oₓ catalyst without Ag component. However the ethanol conversion rate is close to 100% on (Ni₄Fe)ₙAg(PrZr₄)₆₄.₈Oₓ at 773 K, the gas-phase products consist of 70.5% H₂, 19.6% CO₂, 1.8% CO and 8% CH₄ accordingly.
3. Conclusion
The (Ni₄Fe)₄Ag(PrZr₄)₄Oₓ catalysts have the framework of tetragonal crystal phase ZrO₂, and that the doped praseodymium ions can enter the ZrO₂ lattice. The active components of fresh catalysts, as rhombohedral Fe₂O₃, hexagonal NiO and cubic Ag₂O, dispersed uniformly on its surface. After 823K’s pretreatment by H₂ or undergo ethanol steam reforming, the main active components are cubic Ni⁰ and cubic Ag⁰, and Fe₂O₃ is partly reduced to Fe₃O₄. The presence of Ag make for the reduction of Fe₂O₃ and NiO, meanwhile the catalysts doped Ag component present higher catalytic activity in ethanol steam reforming.

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