BIMETALLIC CATALYSTS FOR SYNGAS PRODUCTION BY LOW TEMPERATURE ETHANOL STEAM REFORMING

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Summary

In this work we investigate the catalytic performances in terms of activity and stability of bimetallic Pt based catalysts in low temperature ethanol steam reforming. The influence of the metal loading as well as the temperature has been reported. Catalytic activity tests were carried out in a continuous flow fixed bed reactor (18 mm i.d.) with diluted reaction mixture ($C_2H_5OH/H_2O/N_2$ = 0.5/1.5/98 vol%), in the range 300-450°C at GHSV of 15,000 h^{-1}. Results proved that the most promising samples to study in the concentrated reaction system are the 3-Pt/10-Ni/CeO_2 and 3-Pt/10-Co/CeO_2, that showed the highest activity, H_2 selectivity and stability.

Keywords

Bio-ethanol, low temperature steam reforming, hydrogen, Pt-based catalysts

Introduction

In the last years H_2 attracts significant research interest because it is a clean fuel without co-production of greenhouse gases. Searching for a renewable H_2 source, ethanol seems to be the most effective since it is easy to store, safe to handle and transport. At low temperature ethanol steam reforming to H_2 or pre-reforming to CH_4 can increase the overall system efficiency, but the by-products formation leads to reduced selectivity and catalyst durability. Thus, the use of appropriate catalysts play a crucial role in hydrogen production through ethanol reforming. Base metals such as Ni, Co and noble metals such as Pt, Pd and Rh over appropriate supports show potential for ethanol SR, while the most investigated supports are Al_2O_3, MgO, SiO_2, ZnO, ZrO_2 and CeO_2[1,2]. In particular, studies carried out on Pt based catalysts supported on Al_2O_3 and CeO_2 showed that ceria supported ones are much more active and selective, since alumina is not able to promote the desorption of the secondary reaction products[3,4,5]. Furthermore, in order to improve the catalyst stability, the use of bimetallic catalysts, such as Ni-Cu and Pt-Ni based, has been proposed[6,7].

The aim of this work is to investigate the catalytic performances in terms of activity and stability of bimetallic Pt based catalysts in ethanol steam reforming at low temperature. The influence of the metal loading as well as the temperature has been reported. The catalytic activity tests were carried out in both diluted and concentrated reaction mixture.

Experimental

Commercially available CeO_2 (Aldrich) with a BET surface area of 80 m^2/g was used as support. Monometallic nickel, cobalt and silver based catalysts were prepared by impregnating the support respectively with $Ni(CH_3COO)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $AgNO_3$ aqueous solutions. Bimetallic Pt based catalysts were obtained by a successive impregnation with a platinum chloride ($PtCl_4$) aqueous solution. Powder samples were dried at 120°C overnight and calcined in air at 600°C for 3 h with an heating rate of 10°C/min. The catalysts were characterized by surface area measurements, X-ray diffraction, H_2-temperature programmed reduction.

Catalytic activity tests were performed on powder catalysts (180-355 μm) in the range 300-450°C in a continuous flow fixed bed reactor (18 mm i.d.) placed in a three zone electric oven, at atmospheric pressure. In diluted tests, ethanol and water were fed by saturating an N_2 flow at fixed temperature. The mixture was diluted with a N_2 stream, giving a typical feed gas composition of $C_2H_5OH/H_2O/N_2$ = 0.5/1.5/98 vol%. The GHSV was 15,000 h^{-1} and the reactor outlet concentrations of C_2H_5OH, H_2O, CH_4, CO, CO_2 and other by-products were monitored with an on line Nicolet Antaris IGS FT-IR multigas analyzer, equipped with an heated gas cell and a MCT-A N_2 liquid cooled detector. The H_2 and O_2 concentrations were measured respectively by CALDOS 27 and MAGNOS 206, ABB continuous analyzers.

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Results and discussion

The results of catalytic activity tests carried out on Pt-Ni based catalysts at different metal loading are reported in Table 1. The tests were performed at a fixed temperature of 300°C and the results were collected after 3 h of time on stream. In this abstract we reported only data relevant to the diluted tests, employed to realize the catalysts screening, in order to select the most promising samples to study in the concentrated reaction system.

Table 1. Catalytic activity performance of Ni and Pt-Ni based catalysts in EtOH steam reforming at 300°C

Catalyst	X_{EtOH}, %	X_{H2O}, %	Y_{H2}, %	S_{CH4}, %
10-Ni/CeO_2	89.1	26.1	25.2	16.6
20-Ni/CeO_2	80.3	21.1	22.6	18.8
1-Pt/10-Ni/CeO_2	100	50.5	43.5	34.8
1-Pt/20-Ni/CeO_2	100	47.6	42.1	34.3
3-Pt/10-Ni/CeO_2	100	48.5	44.6	49.8

The results showed improved catalytic performance of Ni-catalysts after platinum addition, with increased ethanol and water conversion (X). Among bimetallic samples, the catalyst 3-Pt/10-Ni/CeO_2 exhibited the highest H_2 yield (Y) and methane selectivity (S). Monometallic Ni-catalyst showed lower selectivity to methane and higher selectivity to acetaldehyde, suggesting that Ni favors the dehydrogenation reaction, whereas the presence of Pt induces the conversion of acetaldehyde into H_2 and carbon oxides. Catalysts characterization evidenced a high platinum metal dispersion onto the support surface, along with a Pt promoted nickel oxide reduction rate, suggesting a close contact of the both metals after calcination. Furthermore, the stability tests on these catalysts, performed at 300°C, showed any deactivation for 3-Pt/10-Ni/CeO_2 catalyst in 13 h of time on stream without CO formation (Figure 1), whereas the Ni/CeO_2 catalyst with the same metal content exhibits an evident deactivation, with a production of acetaldehyde and ethylene increased by increasing time on stream (not reported).

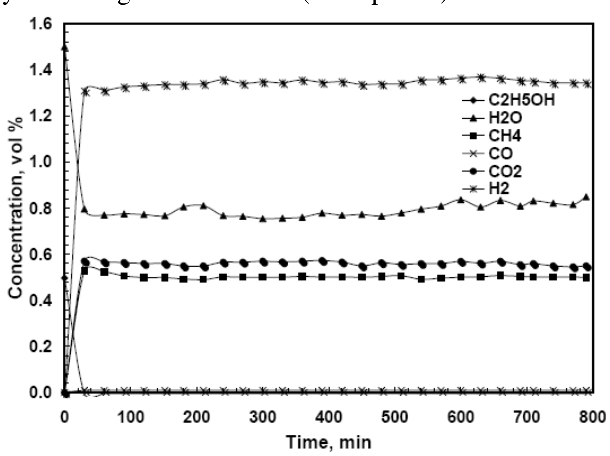

Figure 1. Stability tests of 3-Pt/10-Ni/CeO_2 catalyst

The results of catalytic activity carried out on Pt-Co and Pt-Ag catalysts are reported in Table 2.

Table 2. Catalytic performance of Pt-Co and Pt-Ag catalysts in EtOH steam reforming at 300°C

Catalyst	X_{EtOH}, %	X_{H2O}, %	Y_{H2}, %	S_{CH4}, %
3-Pt/10-Co/CeO_2	99.9	40.5	46.1	46.4
3-Pt/10-Ag/CeO_2	98.6	3.4	25.2	50.3

EtOH conversion is close to 100% on both catalysts. Silver is not able to convert water like cobalt, and hydrogen yield is higher in the presence of cobalt. Furthermore, on Pt-Co catalyst selectivity to CO (not reported) is lower, in contrast with silver based catalyst, suggesting that silver is not active in WGS reaction. No formation of secondary products is observed at this temperature. Furthermore, the Pt-Co catalyst did not suffer any deactivation in about 10 h of time on stream, while the Pt-Ag catalyst is a poor catalyst, and exhibited a marked deactivation after 2 h of time on stream at 300°C. The stability of these catalyst is negatively affected by an increase in temperature.

Conclusions

Results of catalytic activity tests performed in diluted reaction system showed that the most promising bi-metallic samples to study in the concentrated reaction are the 3-Pt/10-Ni/CeO_2 and 3-Pt/10-Co/CeO_2, that showed the highest activity, H_2 selectivity and stability. Ni/CeO_2 catalysts are not active in ethanol steam reforming reaction, but while platinum is added, acetaldehyde is converted into H_2 and carbon oxides, and despite the lower Pt amount, a sensible improvement on catalysts performances are obtained with respect to the monometallic 5%Pt/CeO_2 sample.

References

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