Hydrogen production by ethanol steam reforming over Cu and Ni catalysts supported on ZrO_2 and Al_2O_3 microspheres

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Abstract: Ethanol reforming process to produce hydrogen rich-gas stream is performed using Cu/Ni catalyst supported on zirconia and alumina microspheres prepared by hydrolysis method. Theses catalysts were tested in a fixed-bed reactor system employing steam reforming of ethanol. The operating temperature was 550°C and water/ethanol feed ratio 3/1. Although all catalysts were very active for ethanol conversion and very selective towards the desired products, but that one supported on zirconia microspheres was produced slightly better results. The data reveal high activity of the Cu/Ni/ZrO_2 catalyst for ethanol steam reforming and presented a good selectivity for H_2.

Introduction

In recent years, the hydrogen as fuel has attracted many attentions due to the potential application in electric vehicles and power station. There are four basic methods for hydrogen production at present: steam reforming reaction, partial oxidation, auto-thermal reforming and water electrolysis [1].

The use of oxygenated compounds like methanol and ethanol mainly, has been identified as a promising route for hydrogen production with high yields [2,3]. Ethanol as a source of hydrogen has several advantages compared to others “primary fuels” such as methanol and gasoline [4]. Ethanol can be easily storage and handling safety. It can be easily produced by renewable form from several biomass sources, including plants, waste materials from agro-industries or forest residue materials [5]. Besides, it does not contribute to the increase of the greenhouse effect since the steam reforming of ethanol releases the same amount of CO_2 as that absorbed by the biomass [6].

The reactions of ethanol over the surfaces of metal oxides and metals have been studied for many authors [7-10], and also the reactions of ethanol over M/CeO_2 catalysts [11].

In recent work, the authors have studied the reaction of ethanol over Ni/Cu and Co/Cu supported in zirconia [12].

It is known that the activity of a catalyst is greatly influenced by the method of catalyst preparation and the conditions of pretreatment [13].

Supported metal catalysts prepared by hydrolysis method should have catalytic activities and selectivity, which are comparable to catalysts prepared by more traditional method, as precipitation method. Potential applications of catalysts prepared by hydrolysis method are tied to their high thermal stability, their resistance to deactivation and the flexibility that such method has in the control of physical and chemical proprieties such as purity, homogeneity and controlled porosity combined with the ability to form large surface area materials at low temperature [14].

The aim of this work is the study of hydrogen production from steam reforming of ethanol, using a copper and nickel catalyst supported onto a zirconia and alumina microspheres prepared by the hydrolysis method. The aim reason to using different supports (ZrO_2 and Al_2O_3) to obtain a catalyst with high activity in steam reforming to maximize the ethanol conversion to hydrogen that is a high yield in hydrogen. The dependence of the catalytic activity and selectivity on the reaction temperature were studied. Long-term experiments in order to ensure catalysts stability was performed by carbon deposition process which resulting in catalyst deactivation was also investigated.

Experimental

The $Cu/Ni/ZrO_2$ and $Cu/Ni/Al_2O_3$ catalysts of different compositions were prepared by the hydrolysis method. Solutions of the $Cu(NO_3)_3.3H_2O$, $Ni(NO_3)_2.8H_2O$, $ZrO(NO_3)_2.xH_2O$, $Al(NO_3)_3.9H_2O$ were used as sources of Cu, Ni, Zr and Al, respectively. Urea and hexamethylenetetramine were used as gelation agent. The solution feed was sprayed directly into a column with warmed oil. The solids spheres obtained were washed with 2 mol L^{-1} ammonium hydroxide solutions. Then the catalyst was dried at 80ºC overnight and finally calcined at 450 ºC, to eliminate all organic compounds in the spheres.

The chemical composition of the calcined samples was determined by X-ray fluorescence was accomplished in a Rigaku-Denki RIX-3000. Characterization of catalysts was performed mainly by scanning electron microscopy, using a Philips XL-30 to image the size of the microspheres. Specific surface area was measured by the BET nitrogen adsorption technique with a micrometrics ASAP-2010 instrument. The quantification of the carbon deposited on the catalysts after the reaction was measured by elemental analysis of carbon, using a LECO CS-400 instrument.

Catalytic reactions were carried out in a fixed-bed glass reactor (i.d. = 10 mm), where 8.0 g of the catalyst was introduced. The operating temperature was controlled by a thermocouple placed inside the reactor. The reagents inlet flow was controlled by peristaltic pump, in order to operate at 1mL min^{-1} under atmospheric pressure. The catalytic reactions were carried out at different temperatures and molar ratio $H_2O/EtOH = 3/1$. The gases produced were analyzed on-line by a gas chromatograph (GC Varian CP-4900) equipped with a thermal conductivity detector and two columns (molecular sieve 5 A^o and porapak-Q). The molecular sieve column was used to determine H_2, CO and CH_4 using Ar as carrier gas and porapak-Q was used to analyzer the concentration of the C_2H_5OH and CO_2, using He as carrier gas.

Results and discussion

The active materials were Cu/Ni-based catalysts 2.0/5.0 and 4.0/8.0 wt% nominal composition all of them supported on ZrO_2 or Al_2O_3 microspheres. Table 1 shows the real chemical composition obtained by hydrolysis method of the different supported catalyst after calcinations at 450 ºC.

Table1: Real chemical composition of the Cu/Ni/ZrO_2 and Cu/Ni/Al_2O_3 catalysts after calcination at 450 ºC

Sample	Catalysts	Content (wt %)			
		Zr	Al	Cu	Ni
SZ1	2%Cu/5%Ni/ZrO_2	92	--	1.98	4.96
SZ2	4%Cu/8%Ni/ZrO_2	86	--	3.6	7.4
SA1	2%Cu/5%Ni/Al_2O_3	--	92	1.95	4.94
SA2	4%Cu/8%Ni/Al_2O_3	--	86	3.35	7.2

The sample SZ1 (2%Cu/5%Ni/ZrO_2) exhibit higher content of the copper and nickel metal, than the samples SZ2, SA1 and SA2.

The BET surface dates of the different catalyst were given in table 2. It is interesting to note that the heat treatment under the same conditions shows different results. The results of BET measurement indicated that the specific surface area of catalyst 2%Cu/5%Ni and 4%Cu/8%Ni supported on alumina microspheres were 185.7 and 192.6 m^2 g^{-1}, respectively. Larger than that of the catalyst 2%Cu/5%Ni and 4%Cu/8%Ni supported on zirconia microspheres (156.60 and 163.26 m^2 g^{-1}).

Table 2: Pore structure data of the Cu/Ni/ZrO_2 and Cu/Ni/Al_2O_3 catalysts after calcination at 450 ºC

Catalysts	S-BET (m^2 g^{-1})	V (cm^3 g^{-1})
2%Cu/5%Ni/ZrO_2	156.60	0.105
4%Cu/8%Ni/ZrO_2	163.26	0.102
2%Cu/5%Ni/Al_2O_3	185.7	0.108
4%Cu/8%Ni/Al_2O_3	192.6	0.239

Typical SEM photograph of microspheres prepared by hydrolytic method are showed in Fig. 1. Most of the microspheres are spherical and the mean diameter is about 0.85 mm.

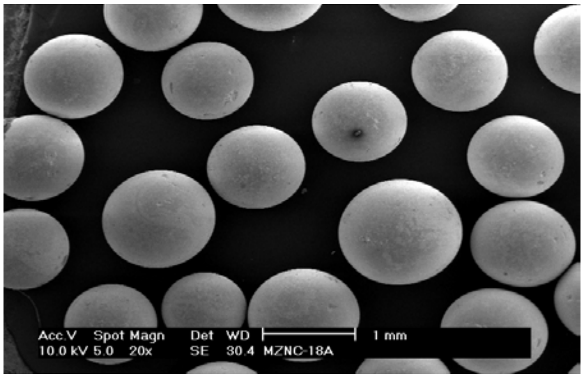


Fig. 1. SEM image of microspheres after calcining at 450 ºC.

Fig. 2 shows the temperature effect on catalytic activity and product distribution from ethanol steam reforming over $Cu/Ni/ZrO_2$ catalyst. According to the stoichiometry of the global steam reforming reaction, the molar ratio $H_2O/EtOH$ is fixed to 3.0. The ethanol conversion (X_{EtOH}) and selectivity to reaction products are plotted as functions of reaction temperature.

The catalyst was tested in the temperature range of 350 to 600 ºC, using the steam reforming process. It was observed that conversion of ethanol was 97% at temperature 350 °C. When temperature increasing to 500 ºC, the conversion increase to 100% increasing the water conversion, which permits to reduce the water concentration in feed without changing too much the performance during experiments carried out after long term reforming runs. The absence of water can be explained from the mechanism that involves copper and nickel sites, suggested by Marino et al. [15].

From the results, it was observed that the selectivity of H_2, CO and CO_2 kept increasing and reached a peak value of 60%, 7.0% and 18.0% at 550 °C respectively, while the selectivity of methane kept decreasing. The best selectivity to hydrogen was obtained at 550 ºC, so this temperature will be considered for testing other operating parameters.

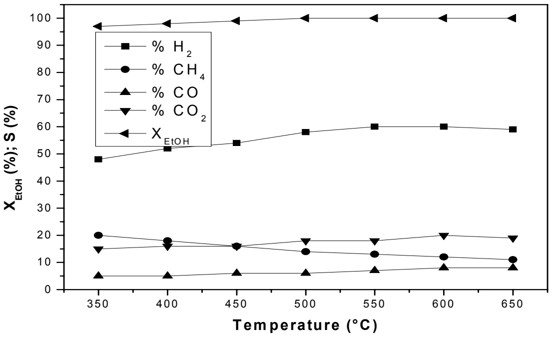
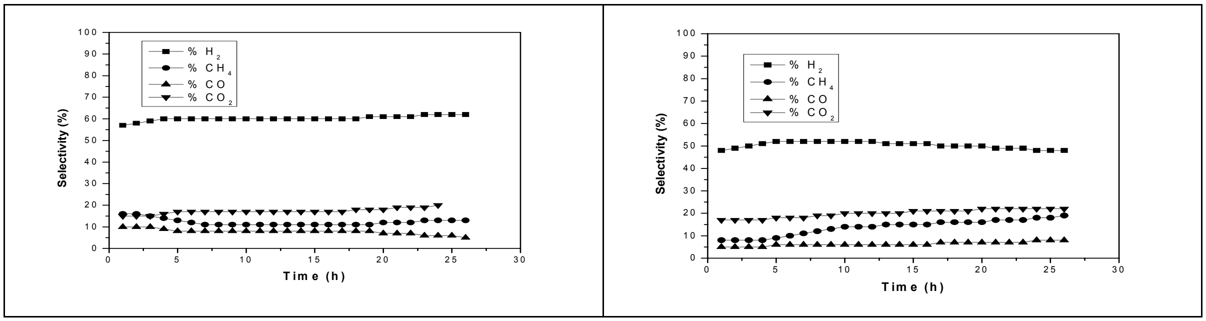


Fig. 2. Effect of reaction temperature range (350 to 650 °C) on conversion of ethanol (X_{EtOH}) and on selectivity of (H_2, CO, CO_2 and CH_4) obtained over the 2%Cu/5%Ni/ZrO_2 catalyst. Experimental condition: $H_2O/EtOH$ = 3/1

The stability and activity of the catalysts with time-on-stream were examined in the experimental conditions temperature at 550 °C and $H_2O/EtOH$ = 3/1 for 26h. The hydrogen yields for the $Cu/Ni/ZrO_2$ and $Cu/Ni/Al_2O_3$ catalysts were tested separately by steam reforming of ethanol. The behavior of each catalyst in terms of hydrogen concentration in a gaseous mixture is reported in Fig. 3. The selectivity of hydrogen for Cu/Ni catalyst supported on ZrO_2 microspheres increased from 57% to 60% and kept constant during 26 h and Cu/Ni catalyst supported on Al_2O_3 microspheres decreased during the last 9 h from 52% to 50%.



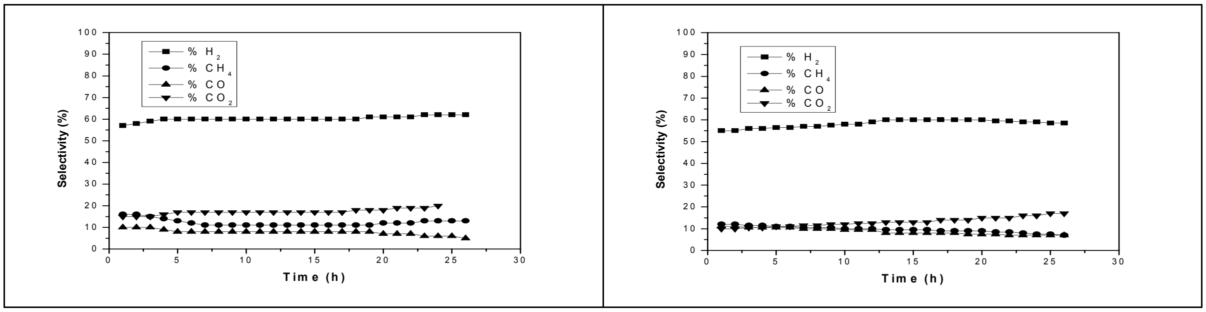
(a) (b)

Fig. 3. Selectivity of H_2, CO, CO_2 and CH_4 with time-on-stream over 2%Cu/5%Ni catalysts supported on: a) ZrO_2; b) Al_2O_3. Experimental conditions: T = 550 °C; $H_2O/EtOH = 3/1$; $X_{EtOH} = 100\%$.

Catalysts prepared by hydrolysis method show very good activity with very high ethanol conversion over the experimental conditions.

The comparative catalytic performance of the support material for ethanol steam reforming was also investigated. The result was compared with those obtained with the $Cu/Ni/ZrO_2$ and $Cu/Ni/Al_2O_3$ catalysts. It was observed that the results in terms of the performance are similar, but the zirconia-supported Cu/Ni catalysts showed higher activity than the alumina-supported catalysts.

Ethanol reforming over both 2%Cu/5%Ni and 4%Cu/8%Ni catalysts supported on ZrO_2 was studied on-board in optimized conditions. Results in terms of product selectivities for the two catalysts are shown in Fig. 4. It is observed that increasing Cu/Ni content from 2%Cu/5%Ni to 4%Cu/8%Ni results in higher selectivities to H_2.



(a) (b)

Fig. 4. Selectivity of H_2, CO, CO_2 and CH_4 with time-on-stream over: a) $2\%Cu/5\%Ni/ZrO_2$; b) $4\%Cu/8\%Ni/ZrO_2$. Experimental conditions: T = 550 °C; $H_2O/EtOH = 3/1$; $X_{EtOH} = 100\%$.

It is known that deactivation of supported catalysts during ethanol steam reforming is mainly due to carbon deposition. It was investigate the coking deposit during the reaction of ethanol steam reforming at 550°C and molar ratio $H_2O/EtOH = 3/1$ over $Cu/Ni/ZrO_2$ and

$Cu/Ni/Al_2O_3$ catalyst. Alumina produces ethylene in the dehydration of ethanol that acts as very strong promoter of carbon formation. This lead the system to a rapid collapse, according Nakano et al. [16].

Table 3 shows carbon deposits accumulated on the catalysts during ethanol steam reforming. Independent of the carbon amount, the present experiments had shown that carbon formation is the main reason for the catalyst performance decrease for support Al_2O_3. For this reason the catalytic performance of the Cu/Ni supported on zirconia prepared using the hydrolysis method give higher selectivies in H_2. Oxides having basic character such as ZrO_2 has been found to inhibit ethylene formation. This catalyst is promising to use in the process of steam reforming of ethanol.

Table 3: Percentage of carbon deposits on $Cu/Ni/ZrO_2$ and $Cu/Ni/Al_2O_3$ catalysts

Catalysts	Carbon (%) before reaction	Carbon (%) after reaction
$2\%Cu/5\%Ni/ZrO_2$	0.53	3.60
$2\%Cu/5\%Ni/Al_2O_3$	0.59	4.42

Conclusions

In this work, it is demonstrated that bimetallic catalysts on different supports (Cu/Ni supported on ZrO_2 or Al_2O_3), with varying surface areas and pores volume can lead to major difference in the catalytic properties for the oxidative steam reforming of ethanol.

The results also show that Cu/Ni is the active for the catalytic process. Hydrogen is the main constituent of the reaction steam reforming of ethanol, which also produces CO, CO_2 and CH_4. A significant performance of Cu/Ni catalyst supported on ZrO_2 in a production of hydrogen by steam reforming of ethanol exhibits very good activity, selectivity and long-term stability. A considerate amount of carbon is deposited in all catalysts after 26 h of reaction, however, did not appear to influence its activity or selectivity characteristics and the catalyst can be regenerated.

In conclusion, the choice of support is very important in steam reforming of ethanol. The catalysts supported on the ZrO_2 are significantly more active and selective for ethanol steam reforming for the production of a hydrogen-rich gas, compared to catalysts supported on the Al_2O_3. Long-term tests conducted under experimental conditions showed that the catalyst of $Cu/Ni/Al_2O_3$ is very active, but the Cu/Ni catalysts supported on zirconia are generally more active and modify the selectivity of the catalysts. The different result obtained over catalysts supported on ZrO_2 and Al_2O_3 with an equal Cu/Ni content shows that Cu/Ni interaction with the support plays an important role in the reaction. This observation suggests that a support is an important parameter to control the activity and selectivity of the catalysts. The catalyst $Cu/Ni/ZrO_2$ is acceptably stable and could be a good choice to be used in ethanol steam reforming.

Acknowledgements

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