

Experimental study of hydrogen production from ethanol reforming in a fluidized bed reactor.

Vincenzo Palma, Concetta Ruocco*, Antonio Ricca

Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 83040 Fisciano, SA, Italy

*Corresponding author: cruocco@unisa.it

Highlights

- The Pt-Ni/CeO₂-SiO₂ sample displayed promising behavior for ethanol oxidative reforming.
- Fluidized bed reduced carbon formation of 4 times with respect to the fixed bed reactor.
- A plateau condition was reached after 400 h of test in the fluidized bed reactor.
- The net coke formation was equal to zero at plateau condition with no more deactivation.

1. Introduction

Hydrocarbons reforming is a mature technology and the employment of alternative H₂ sources (i.e. bioethanol) for this process is a very promising route in the search for sustainable energy solutions. At that end, oxidative steam reforming (OESR) is preferred [1]: O₂ co-feeding and partial ethanol oxidation allows providing the required reaction heat directly within the catalytic bed; moreover, O₂ strongly helps to reduce coke deposition, a serious concern for catalyst lifetime. This process is commonly studied in fixed bed reactors (PBR); however, in a process intensification view, fluidized bed reactors (FBR) attract increasing interest, due to the improved heat and mass transfer, limited cold spots and reactor plugging due to coke [2]. This study is focused on OESR over a bimetallic Pt-Ni catalyst supported on CeO₂-SiO₂. The research is devoted to highlight the role of reactor configuration (fixed and fluidized bed) on catalyst activity and stability. The evolution of coke during the reaction in FBR was also investigated.

2. Methods

Pt-Ni/CeO₂-SiO₂ catalysts were prepared using a wet impregnation method. First, an aqueous solution of Ce(NO₃)₃·6H₂O (Strem Chemicals) was prepared with a total metal concentration of 1.5 M, in order to reach a support composition of 30wt% in ceria. The calcined support (mesoporous silica gel, 90-115 μm, Sigma-Aldrich), was added to the solution and impregnation was carried out for 2 h at 80°C. The resulting solid was dried overnight and calcined at 600°C for 3h. For Ni and Pt impregnation, performed sequentially, a known amount of nickel nitrate hexahydrate and platinum chloride (Strem Chemicals) was dissolved in deionized water. Ni and Pt content was fixed to 10wt% and 3wt%, respectively, on the basis of ceria mass.

The catalyst performances for OESR were evaluated at 500°C, 1 atm and ethanol partial pressure of 0.1 (H₂O/C₂H₅OH of 4 and O₂/C₂H₅OH of 0.5). Prior to the reaction, the catalyst (7 g), diluted with the bare CeO₂-SiO₂ (22.6 g), was reduced at 600°C for 1 h using 5 %H₂/N₂ mixture; afterwards, the reacting mixture was fed to the reactor with a total flow-rate of 770 Ncm³·min⁻¹ (corresponding to a weighty hour space velocity WHSV of 4.1 h⁻¹). Further tests were performed at WHSV of 12.3 h⁻¹ and catalytic mass as well as total flow rates were changed accordingly. The reactor exit was monitored with an FT-IR Spectrophotometer (Thermo-Scientific) and two analyzer modules (ABB), capable of detecting H₂ and O₂ concentrations.

3. Results and discussion

A comparative study on the effect of fluidized bed and fixed bed reactor in OESR was preliminary carried out at WHSV=4.1 h⁻¹. In both the operative modes, a stable behavior was initially observed: ethanol was completely converted for almost 130 h of TOS and hydrogen yield fairly agreed with the value predicted by thermodynamics. However, hydrogen profile in the fluidized bed reactor was always higher than that of the fixed bed while a faster deactivation was recorded in the PBR. This clearly indicates that fluidization favors methane steam reforming reaction. In fact, methane concentration slightly decreased in comparison to the PBR, thus resulting in a higher hydrogen production. In addition, the synthesis gas ratio (mol_{H₂}/mol_{CO}) increased of almost 40% in the FBR. Moreover, thermo-gravimetric analysis (TGA) performed on the spent

catalysts proves that FBR allows coke selectivity reduction of almost 4 times: due to the constant catalyst recirculation, particles were continuously exposed to steam and oxygen. As a result, carbon formed would be readily removed via gasification reactions. The stability test over the Pt-Ni/CeO₂-SiO₂ catalyst in the FBR was carried out for almost 400 h and only a partial deactivation was observed (Figure 1), which resulted in ethanol conversion as well as hydrogen yield lowering from 100% to 80% and 43.5 to 36%, respectively. In fact, after 300 h of TOS, the system reached a stationary condition with no more activity decay. The test was performed for further 100 h and the system was found to hold the plateau condition. These results suggest that coke deposition does not follow a constant trend during the test; conversely, it is supposed that carbon progressively deactivate the most reactive catalytic sites, involved in reforming and by-products formation.

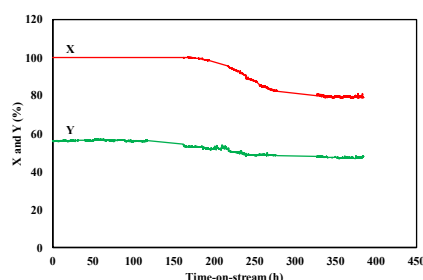


Figure 1. C₂H₅OH conversion (X) and H₂ yield (Y) in FBR, 500°C, H₂O/C₂H₅OH=4, O₂/C₂H₅OH=0.5, WHSV=4.1 h⁻¹.

As a result, catalyst activity remained unchanged with no further increase in catalyst deactivation. In order to investigate the above hypothesis, a further test in FBR was performed over the Pt-Ni/CeO₂-SiO₂ catalyst: at regular intervals, the test was stopped and a sample was withdrawn and characterized by TGA to study the variation of carbon formation rate (CFR, the ratio between coke mass and the product of catalytic mass, the total mass of carbon fed as ethanol during the test and the time-on-stream) with TOS (time-on-stream). However, in order to accelerate the achievement of the stationary condition, WHSV was fixed to 12.3 h⁻¹: the system reached a stationary condition after almost 150 h; CFR was quite high at the beginning of the test and displayed a decreasing trend with TOS. The CFR after 175 and 200 h were almost the same, proving that the net rate of carbon formation (i.e. the difference between coke formation and gasification rate) was equal to zero. Also other authors studied reforming reaction in FBR over Ni-based catalysts [3]. However, a different behavior was found: almost steady performances were followed by a severe drop in ethanol conversion and finally a slow decrease in ethanol conversion until total deactivation of the catalyst. Conversely, in this work, coke deposition was drastically attenuated and a satisfactory activity was still observed after 200 h of test.

4. Conclusions

In this work, OESR was studied over a Pt-Ni/CeO₂-SiO₂ catalyst in fixed and fluidized bed reactors at 500°C. In FBR, superior performance was observed with a coke selectivity reduction of almost 4 times. The catalyst in FBR reached a plateau condition after 300 h of test at 4.1 h⁻¹, where ethanol conversion and hydrogen yield were equal to 80% of the equilibrium values. This behavior was linked to the coke formation rate lowering during the test, which was attested to $0.00000162 \text{ g}_{\text{coke}} \cdot \text{g}_{\text{catalyst}}^{-1} \cdot \text{g}_{\text{carbon, fed}}^{-1} \cdot \text{h}^{-1}$ after 175 h at 12.3 h⁻¹.

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Keywords

Hydrogen, reforming, fluidization, coke.