

CO₂ Sorption Enhanced Steam Reforming of Ethanol

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Introduction

The interest in using hydrogen as an energy carrier has increased considerably in the last years. Therefore, systems for efficient H₂ production are of great importance. In this respect, production of hydrogen from bio-ethanol via steam reforming has shown a great potential, with the advantage that bio-ethanol is considered as a CO₂ neutral energy source. Several catalysts with adequate properties in terms of activity and hydrogen selectivity has been proposed, however, catalyst stability still remains a problem, in particular is deactivation due to coke formation a serious issue [1]. At the same time the concept of multifunctional reactors combining reaction and separation, especially the idea of sorption enhanced steam methane reforming (SESMR), has received a growing attention during the last years [2]. A CO₂ acceptor can be installed together with the catalyst in order to remove CO₂ from the gas phase. Thus, normal equilibrium limits of reforming and shift reaction are removed, and a product containing H₂ in concentrations above 95% is possible.

The objective of this work has been to test the concept of sorption enhanced steam reforming of ethanol (SESRE) and study the possible benefits of introducing a CO₂ acceptor in the reaction bed. With this purpose, a synthetic CaO composite material has been used as CO₂ acceptor and hydrotalcite-based (HT) Ni-Co catalysts have been used as reforming catalysts. This system was chosen since HTs are known to result in catalysts with small metal particle sizes and an enhanced resistance to sintering as well as low coke formation due to its basicity [3].

Materials and Method

A series of five different hydrotalcite-based Ni-Co catalysts were prepared by a co-precipitation technique. The catalysts differed in the Ni-Co loading, varying from 40-0, to 30-10, 20-20, 10-30 and 0-40. The catalytic activity and stability was screened by conventional steam methane reforming in a fixed-bed reactor at 848 K, 1 bar and a steam-ethanol-ratio of 6. SESRE was performed in a fixed-bed reactor using the same conditions. A mixture of the steam reforming catalyst and the CO₂ acceptor was placed in the reactor. Previous to the reaction, the sample was reduced in a mixture of Ar and H₂ at 923 K for 10 h, using a heating rate of 2 K/min from ambient temperature to 923 K. After reduction, the temperature was decreased to 848 K and the reactive mixture was introduced in the reactor (3.6 g ethanol+water / h.g catalyst). The reaction was continued until the saturation of the acceptor, which corresponds with the breakthrough of the CO₂ concentration on the products stream. At this point, the ethanol/steam mixture was switched to Ar and the temperature was increased to 973 K for regeneration of the acceptor. The same cycle was carried out several times in order to study the stability of the process. The downstream gas composition was monitored using an online microGC.

Results and Discussion

All the hydrotalcite supported Ni-Co catalysts showed good activity and stability in conventional steam-reforming at the studied conditions. The activity increased in the order 10Ni-30Co > 40Co ~ 20Ni-20Co ~ 30Ni-10Co > 40Ni. The catalysts suffered initial deactivation during the first operation hours, but good stability was observed after more than 40 hours on stream.

The 10Ni-30Co catalyst was selected for SESRE since it was the catalyst with best stability and activity. Figure 1 shows a typical effluent concentration profile on a water free basis. A H₂ yield close to 98% was obtained for a period of time of 50 min. The downstream composition (~0.3% CH₄, ~0.8% CO, ~0.9% CO₂) remained unchanged until the saturation of the acceptor. At this point, breakthrough of the CO₂ took place and the composition was close to that expected from the thermodynamics of conventional ethanol steam reforming. It should be also noted that the small amount of CH₄ formed most likely results from the methanation reaction rather than the decomposition of ethanol. The selection of a different catalyst might result in different compositions and this is a parameter that will be studied.

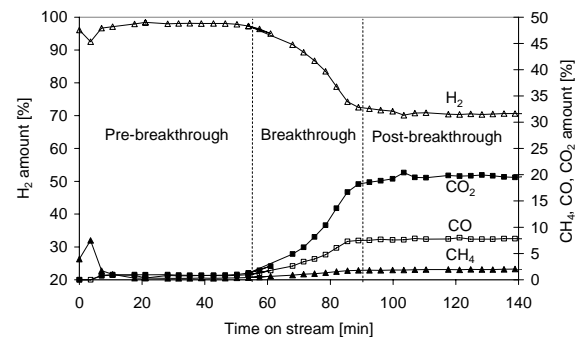


Fig. 1. Effluent concentration profiles on water free basis. 7.9 g CO₂ acceptor, 1.6 g 10Ni-30Co catalyst, 848 K, steam/ethanol: 6, 1 bar, 5.7 g/h ethanol + water. Regeneration: 973 K in Ar.

Significance

SESRE is reported as a promising route for production of high purity hydrogen in a single step. In addition, the study of this process opens new opportunities to understand the reaction mechanism of ethanol reforming.

References

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