

Ni/TiO₂ for ethanol steam reforming: which is the best synthetic approach?

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The performance of Ni/TiO₂ catalysts in ethanol steam reforming (SR) was considered in this study; in particular, the effects of both the methodology of Ni introduction and calcination temperature were deeply investigated. Activity strongly depends on the physico-chemical properties of the catalyst, that greatly change according to the synthetic approach.

Introduction

Ethanol SR for a cleaner hydrogen production is an attracting topic for researchers and the design of a highly active and selective catalyst is a key point for the fulfilment of this process on industrial scale. Nickel is known to be both active and selective in the SR reactions, but also the support plays an essential role. The aim of this work is the investigation of the effect of the synthetic parameters on the physico-chemical properties of the sample and on its catalytic performance.

Experimental

TiO₂ support was prepared by a conventional precipitation method¹. Ni (10 wt%) was added to the support by means of incipient wetness impregnation with an aqueous solution of the metallic precursor, either before (NiC) or after (CNI) the calcination of the support. Samples were calcined at 500 °C (NiC500 and CNI500) or at 800 °C (NiC800). The samples were characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), high-resolution transmission electron microscopy (HR-TEM) and N₂ physisorption. Activity tests were performed after reduction of the catalysts in H₂ flow for 1h at 500 °C for samples calcined at 500 °C, at 800 °C for NiC800. The activity tests were carried out at atmospheric pressure by feeding a 3:1 (mol/mol) H₂O:CH₃CH₂OH mixture at 500 °C.

Results and discussion

The characterization measurements we carried out reveal marked differences among the samples, in particular for what concerns the interactions between the active phase and the support and, as a consequence, Ni availability to the reaction.

XRD pattern on NiC500 before the reduction reveals only nanocrystalline anatase. This suggests that all nickel species have been incorporated in the anatase lattice^{1, 2}, thus making Ni unavailable for the reaction. In fact, this sample is almost completely inactive in ethanol SR. Ni incorporation in TiO₂ is due to Ni impregnation before the calcination of the support. When Ni is added to the calcined support (CNiC500), no incorporation in the anatase lattice is detected. This sample is more active than NiC500 (EtOH conversion: 82%; H₂ productivity: 0.21 mol min⁻¹ kg_{cat}⁻¹), but it is not stable. The calcination treatment at high temperature (NiC800) stabilizes the active phase by strengthening the interactions of Ni species with the support (SMSI), with the formation of an ilmenite-type structure (NiTiO₃) in which nickel is still reducible to Ni⁰. The catalytic performance of this catalyst is satisfactory, with an ethanol conversion of 99% and a H₂ productivity of 0.84 mol min⁻¹ kg_{cat}⁻¹.

Conclusions

The ability of the support to increase Ni availability to the reaction and to stabilize the active phase is of primary importance to achieve both high ethanol conversion and H₂ productivity. The results indicate that TiO₂-supported Ni systems are very sensitive to the synthetic procedure. The best catalytic performances are obtained by calcining at the highest temperature.

¹ V. Nichele, M. Signoreto, F. Menegazzo, A. Gallo, V. Dal Santo, G. Cruciani, G. Cerrato, Appl. Catal. B: Environ. doi:10.1016/j.apcatb.2011.10.003.

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