

# Hybrid Catalysts for the Thermo-Catalytic Cracking process : effect of the hydrogen spillover species of the co-catalyst on the product selectivities and on-stream stability

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## Introduction

Ethylene and propylene are the major precursors of plastics, synthetic fibers and other large-volume products of the petrochemical industry. In the next 10 years, it is predicted that the production of these two olefins will constantly be increasing because of growing market demands, mostly for propylene. This trend induces the industrial sector to develop new catalytic processes such as the TCC, Thermo-Catalytic Cracking. The latter, with respect to the current steam-cracking technology, shows higher yields of light olefins, less energy consumption and less emission of greenhouse gases.

Hybrid catalysts used in TCC include two components: a) a main component possessing cracking properties (acid sites) and b) a co-catalyst showing hydrogen formation capability (by steam-reforming). The use of a special binding agent (bentonite clay) results in the formation of a pore continuum [1], allowing the hydrogen newly formed on the co-catalyst to spill over to the main component surface. These hydrogen spilt-over species (HSO) contribute to the reduction of coke formation, thus increasing the catalyst on-stream stability [2].

This work aims at ascertaining the action of these HSO species and showing their beneficial effects on both the catalyst activity and (on-stream) stability.

## Materials and methods

### 1) Main catalyst component:

This contains Mo-Ce mixed oxides, doped with P and supported on Ytria-stabilized alumina.

### 2) Co-catalyst having HSO properties

This contains Ni oxide, highly dispersed on Ytria-stabilized alumina and eventually doped with Ce or Re.

These two components (the co-catalyst being in a proportion of 20-30 wt %) are subsequently extruded with a pressurizing and binding agent (bentonite clay). The extrudates are finally activated at 750 °C.

Catalyst testing: The tests were performed with the experimental set-up (fixed-bed reactor) and testing procedure, similar to those reported in ref. [2]. The feeds used were an atmospheric gas oil (AGO), mainly and a light naphtha (L-NAP) in some conditions.

## Results and discussion

NiO was used as a non-noble metal oxide which could lead to the formation of hydrogen species on the co-catalyst surface, most probably by hydrocarbon steam-reforming. Hybrid catalysts using such Ni-based co-catalysts, when compared to the mono-component catalyst (reference sample not containing any co-catalyst), showed a reduced formation of polyaromatics and simultaneously an enhanced production of light olefins.

This effect on the product selectivities (and yields) increased with the increased “strength” of hydrogen formation and spill-over capability of the co-catalyst. As a final result, the catalyst activity and selectivity could be kept almost constant for a longer period of time of continuous reaction.

On the other hand, it was possible to incorporate NiO directly onto the main catalyst component. However, there was an upper limit for NiO loading (ca. 2 wt %), over which the effect of NiO was exactly the reverse, i.e. a larger amount of heavy hydrocarbons formed and a significantly rapid activity decay. This was ascribed to a too rapid sintering of Ni species on the too “crowded” surface.

## Conclusion

The presence of the co-catalyst having hydrogen formation and hydrogen spill-over properties enhances the production of light olefins while the formation of coke precursors (and finally, coke) is significantly reduced. These co-catalysts when tested on hydrocarbon feeds containing various polyaromatic hydrocarbons (PAH) and in the TCC conditions (i.e. presence of steam at high reaction temperatures), shows some ring-opening properties which are nowadays actively searched for their very favourable impact on the up-grading of heavy hydrocarbon distillates such as those produced from sand oils [3].

## References

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