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Innovative catalysts for the steam reforming of ethanol and glycerol

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The goal of this project is to produce efficient catalysts for H₂ production. This would allow to develop a fully Italian technology for the energetic valorisation of renewable feedstocks. The latter will be constituted by second generation bioethanol and by-product glycerol, to be converted into a clean energy vector by Steam Reforming. A specific aim of the project will also be the simplification of the H₂ purification section, by catalysts able to integrate as much as possible the reforming stage with the water gas shift reaction. This would also allow considerable energy saving through the thermal integration of two reactions, endothermic the former, exothermic the latter. Particular care will be paid to the feedstock purification section (both for bioethanol and glycerol), since on one hand it is an energy demanding task, its integration with the process being envisaged for process intensification purposes. On the other hand, poor knowledge is available on the effect of possible impurities present in the feed on catalyst performance and durability.

The catalysts will be prepared by means of an innovative flame pyrolysis (FP) method, allowing to obtain nanostructured single or mixed oxides, characterised by high surface area (beneficial for catalyst activity), accompanied by suitable thermal resistance. The latter is imparted by the flash calcination in the hottest part of the synthesis flame and it is a key feature for reforming, a high temperature application. New catalyst formulations will be proposed, as better described in the following, as well as known compositions (e.g. the well established Ni/Al₂O₃), now prepared by one-pot FP synthesis to obtain mixed oxides, to be subsequently reduced in situ to achieve high Ni dispersion and peculiar metal support-interaction. The same approach will be adopted also for different supports and active phases. Care will be put into the selection of the support, by tuning its acidity to limit catalyst deactivation by coking.

Catalyst characterisation will allow to spread light on the reaction mechanism and to support both the development of new formulations and a final kinetic modelling. Suitable theoretical modelling of the surface interaction between reactants and products and the active sites will accompany the whole activity for the same reasons. For all these reasons a detailed knowledge of the morphological and structural properties of the catalyst is a must. The basic idea is to improve the dispersion of the active phase on the support to increase activity and resistance towards coking. It is indeed known that small Ni particle size unfavour the formation of coke filaments. This can be effectively achieved by preparing the catalyst in form of mixed oxide, which will be transformed into the active form by reduction in situ in the reaction environment. Therefore, a set of Ni based samples, supported over supports (titania, zirconia, alumina, silica, lanthana) differing for acidity, redox properties and prepared in different ways, will be synthesised and characterised. For comparison also Fe and Co-based catalysts

will be prepared, mostly supported on lanthana starting from a common precursor (LaNiO₃, LaCoO₃, LaFeO₃).

XRD analysis will be a pivotal characterization tool to get structural information on the catalyst precursor (mixed oxide) and of the finally activated catalyst. Also, it will give important notice on the metal dispersion.