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# **INNOVATIVE CATALYSTS FOR PROCESS INTENSIFICATION OF METHANE REFORMING AND PROPANE DEHYDROGENATION REACTIONS**

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## *Abstract*

In the early decade, a rapid increase in oil consumption was recorded, that led to a widening between the predicted demand for oil and the known oil reserves. Such trend, mainly due to the growing new economies, is causing a quick increasing in oil price, that effect on European chemical industry competitiveness. In this dramatic scenario, characterized by higher cost of naphtha from crude oil, the ability to exploit novel feeds such as natural gas, coal and biomass may be the keystone for the chemical industry revival. Innovating chemical processes are thus essential for the future of the chemical industry to make use of alternative feedstock in the medium and long term future. In this direction, to open new direct routes with rarely used and less reactive raw feedstock such as short-chain alkanes and CO<sub>2</sub> appears one of the most promising breakthrough, since in one hand it may reduce the current dependency of European chemical industry on naphtha, in the other hand may reduce the energy use and environmental footprint of industry.

Despite light alkanes (C1–C4) and CO<sub>2</sub> are stable molecules hard to activate and transform directly and selectively to added-value products, these challenges could be overcome thanks to relevant process intensifications along with the smart implementation of catalytic membrane reactors. Process intensification consists of the development of novel apparatuses and techniques, as compared to the present state-of-art, to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment size/production capacity ratio, energy consumption, or waste production. The past decade has seen an increase in demonstration of novel membrane technology. Such developments are leading to a strong industrial interest in developing membrane reactors for the chemical industry.

The main target of the CARENA is to address the key issues required to pave the way to marketing CMRs in the European chemical industry. The UNISA contribution in CARENA project is to study and optimize supported and unsupported catalysts in order to match to membrane reactors aimed to methane reforming and propane dehydrogenation processes. The guideline of this work was fully jointed to the UNISA involving in CARENA project.

The methane reforming routes (steam- and/or auto-thermal-) are processes widely analyzed in the literature, and many studies identified Ni and Pt-group as most active catalysts, as well as the benefits of bimetallic formulation. Moreover, the crucial role of ceria and zirconia as chemical supports was demonstrated, due to their oxygen-storage capacity. In this work, great effort was spent in the reforming process intensification, in order to maximize catalyst exploit in reforming process.

In order to minimize mass transfer limitations, without precluding the catalyst-membrane coupling, several foams were selected as catalytic support, and were activated with a catalytic slurry. The performances of such catalysts in the auto-thermal reforming and steam reforming of methane were investigated. Catalytic tests in methane auto-thermal reforming conditions were carried out in an adiabatic reactor, investigating the effect of feed ration and reactants mass rate. Tested catalysts showed excellent performances, reaching thermodynamic equilibrium even at very low contact time. By comparing foams catalyst performances to a commercial honeycomb catalyst, the advantages due to the foam structure was demonstrated. The complex foam structure in one hand promotes a continuous mixing of the reaction stream, in the other hand

allows conductive heat transfer along the catalyst resulting in a flatter thermal profile. As a result, the reaction stream quickly reaches a composition close to the final value.

Steam reforming catalytic tests were carried out on foam catalysts at relatively low temperature (550°C) and at different steam-to carbon ratios and GHSV values. The catalytic tests evidenced the relevance of heat transfer management on the catalytic performances, since the samples characterized by the highest thermal conductivity showed the best results in terms of methane conversion and hydrogen yield. The beneficial effect was more evident in the more extreme conditions (higher S/C ratios, higher reactants rates), in which the heat transfer limitations are more evident.

The selective propane dehydrogenation (PDH) was one of the most attractive challenges of the CARENA project, that points to insert a membrane-assisted PDH process in a wider scheme characterized by the process stream recirculation. This approach requires to minimize inerts utilization and side-products formation. Moreover, no papers are present in literature on the concentrated-propane dehydrogenation, due to the severe thermodynamic limitations. A wide study is present in this work aimed to identify and select an optimal catalytic formulation and the appropriate operating conditions that allows the process intensification for the PDH reaction by means of a membrane reactor.

In a first stage, the relevance of side-reactions in the catalytic volume and in the homogeneous gas phase was analyzed, resulting in the optimization of the reaction system. Platinum-tin catalysts were prepared, in order to study the role of each compound on the catalytic performances and lifetime. Preliminary studies have defined the optimal operating conditions, able to minimize the coke formation and then to slow down catalyst deactivation. Several studies on catalyst support highlighted the requirement to use a basic supports with a high specific surface, able to minimize cracking phenomena.

Basing on such indications, CARENA partners provided two catalytic formulations optimized with respect the indicated operating conditions, that showed excellent activity ad selectivity. On these catalyst, the effect of the water dilution, the operating pressure and the presence of CO and CO<sub>2</sub> was investigated, in order to understand the catalytic formulation behavior in the real scheme conditions.