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Valorization of light hydrocarbons - One-pot method for the preparation of nanocatalysts for non-oxidative dehydrogenation (nODH) of light alkanes

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European foreword

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The final text of this CEN Workshop Agreement was provided to CEN for publication on 2022-11-11.

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In particular, the one-pot method described in this CWA is subject of international patent application PCT/EP2022/054574 (2022) Claiming priority of the European Patent application no.: EP21382154.9 (2021) held by EURECAT.

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Introduction

Olefins, also commonly named alkenes, are hydrocarbons containing one or more carbon-carbon double bond. Light olefins are strategic chemical building blocks that produce a broad range of extensively high-value-added products such as polymers, or other interesting chemical intermediates.

Propylene (C_3H_6) is a particularly interesting raw material due to its high versatility for the production of materials such as polypropylene (PP) for the production of plastic materials, acetone, isoprene for synthetic rubber, acrylonitrile, acrolein, acrylic acid and acrylates for the production of acrylic fibres, among others and propylene oxide.

The worldwide demand for propylene (C_3H_6) is expected to grow at an average annual rate around 2-3 % between 2021-2035 (from 90,6 tons/year to 132,1 tons/year) that will exceed the current production capacity.

Traditionally, the production of alkenes is carried out by cracking processes of fossil naphtha. These cracking processes produce large CO_2 emissions due to its high-energy demanding nature (i.e., reaction temperatures 800-1 200 °C).

Recently, the dehydrogenation of light alkanes (C_1-C_8 alkanes) emerged as a more efficient and sustainable alternative to produce these alkenes. However, the non-oxidative dehydrogenation (nODH) process is up to now applied at industrial scale only with limited success due to:

- Technical limitations – The reaction is operated at high temperatures (550-700 °C) hindering the selectivity and favouring metal sintering and coke formation affecting catalyst stability. The reaction as well has thermodynamic limitations (maximum conversion 30-45 %) depending on temperature.

- Economical limitations – i.e., high operational expenditures (OPEX) related with the need of regeneration cycles due to the quick catalyst deactivation.

- Sustainability limitations – i.e., large greenhouse gases emissions associated with poor catalyst performances and catalyst regeneration process.

Although good catalysts for nODH of alkanes have already been provided, there is still a need of additional ones with high catalytic conversion, activity and selectivity, and/or with a catalytic conversion. The selection of certain metals in combination with other elements, all of them stabilized with particular organic compounds and adsorbed on porous supports, gave rise to highly active catalytic surface areas that, in addition, not only are selective for propene selectivity in nODH, but also are highly stable and free from the main drawbacks of other catalysts for the same reaction (i.e. coke formation, by-side deactivating reactions, etc.).

The methodology in this CWA describes a process for the preparation of a catalyst composition as defined above. By means of this one-pot synthesis method, these catalysts are highly active due to the small-variation of the surface areas caused by the homogeneous distribution of the elements on the supports, and due to the synthesis of well-dispersed nanoparticles (1-15 nm, more particularly 1-5 nm), controlled by the presence of an organic molecule. The one-pot reaction runs at relatively low temperatures (room temperature to 100 °C), thus making the production process more affordable and reproducible than other methods for obtaining similar catalysts.

The use of this method for the preparation of the catalysts results in lower reaction temperature (≈500 °C), higher selectivity to propylene (>99 %) and higher conversion and stability (up to 23 % and maintained at 21 % after 24 h on stream). The one-pot organometallic approach allows to explore new horizons in the preparation of other catalyst for propane dehydrogenation with a very easy one-step methodology.

This CWA includes results from the European research and innovation BIZEOLCAT project (*Bifunctional Zeolite based Catalysts and Innovative process for Sustainable Hydrocarbon Transformation*). This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814671.

BIZEOLCAT's main objective is to obtain light olefins and aromatics using light hydrocarbons (C1, C3 and C4) by implementing new procedures, involving innovative catalysts synthesis methodologies and novel reactor design and processing, demonstrating their improvement in sustainability and economic scalability in existing industrial processes.

1 Scope

This CWA describes a one-pot synthesis method to produce nanocatalysts composed of metallic (Pt-Sn) nanoparticles adsorbed on the surface area of a porous support.

These nanocatalysts are used for the non-oxidative dehydrogenation of alkanes (saturated hydrocarbons) to obtain light alkenes (olefins) and aromatic hydrocarbons.

NOTE 1 Methodology and descriptions in this document are suitable to laboratory scale.

NOTE 2 Safety aspects are not included in this document. General laboratory safety and related nanosafety measures from suitable national or international standards, regulations or literature should be applied.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp/

— IEC Electropedia: available at https://www.electropedia.org/

4 Description of the nanocatalysts

4.1 General description

Catalyst compositions comprises:

a) a metallic nanoparticle; and

b) a porous support with a surface area; wherein the nanoparticle (a) is adsorbed on the surface area of the porous support.

The nanoparticles shall be well-distributed all through the porous support surface.

The amount of nanoparticle is typically between 1 and 5 wt.% of the total catalyst.

4.2 Nanoparticle description

a) Composition

The nanoparticle shall comprise:

i) One or more metallic elements of group 10 of the periodic table: nickel (Ni), palladium (Pd) and platinum (Pt). These elements are, as such, the atoms that catalyze the reaction.

ii) One or more organic molecules selected from the group consisting of an organophosphorus compound, and an N-heterocyclic carbene, acting as “nanofabrication controlling agents”, “organic ligands” or “organic stabilizing agents”. They are organic compounds that are adsorbed onto the metal atoms that will form part of a nanoparticle, in such a way that during the preparation process of the catalyst composition or once prepared, the element atoms will neither agglomerate nor coalescence with other nanoparticles of the surroundings and also including the element atoms and