

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

Foreword

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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 800-1200 °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 on 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.

2 Description of the nanocatalysts

2.1 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.

2.2 Nanoparticle description

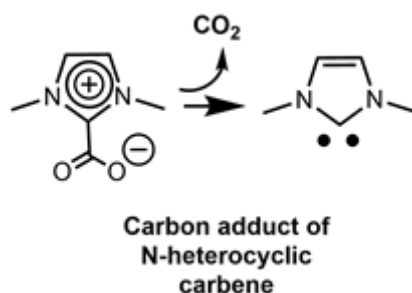
a) Composition

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 coalesce with other nanoparticles of the surroundings and also including the element atoms and the said organic molecules. Thus, these organic compounds behave as nanofabrication controlling agents in the nanoparticles to avoid coalescence or agglomeration with other nanoparticles. This assures that the nanoparticles are small and well-dispersed in a predetermined volume or area. In addition, the final composition of the nanoparticles is controlled by the presence of these organic molecules (i.e., nanoparticle mean diameter and size distribution, shape and crystallinity in alloy and core-shell, well-distributed on the support, uniform compositions on different regions of the support and improved catalyst performance by control of the reactivity of the nanoparticle sites).

- The “organophosphorus compound”, also referred as “P-coordinating compound” relates to organic compounds comprising phosphorus (P). An example of organophosphorus compound are the phosphines. Phosphines (or phosphane) results from replacement of one or more hydrogen centers by an organic substituents R (alkyl, aryl) in PH_3 molecule, which gives $\text{PH}_{3-x}\text{R}_x$ (or $\text{PR}_1\text{R}_2\text{R}_3$ if all H are substituted), an organophosphine, generally referred to as phosphines, which can be primary, secondary, or tertiary phosphines depending on the number of hydrogen replacements. A particular and exemplified organophosphine is triphenylphosphine (PPh_3).
- The “C-coordinating N-heterocyclic carbenes”, also referred as “carbon adducts of N-heterocyclic carbenes” are carbenes of formula $\text{RN}_2\text{C:}$, where the 'R' is a ($\text{C}_2\text{-C}_n$)-alkyl forming with the two N atoms an heterocycle, and the C atom coordinates (i.e. adducts) with another carbon atom containing compound (i.e. a carbon dioxide). The carbon dioxide adducts of N-heterocyclic carbenes reacts under the reaction conditions used for the catalyst preparation forming N-heterocyclic carbene ($\text{RN}_2\text{C:}$) and another carbon atom containing compound (i.e., carbon dioxide). A particular

carbon adduct of N-heterocyclic carbenes is the 1,3-dimethylimidazoliumcarboxylate (NHC-CO₂), illustrated below, and which gives the 1,3-dimethylimidazoliumcarbene.



iii) One or more metallic elements selected from the group consisting of tin (Sn), gallium (Ga), and indium (In) are cocatalysts in the catalyst composition. Thus, they also increase the rate of the chemical reaction catalyzed by the metallic elements of the group 10 in the nanoparticle and cooperate improving each other catalytic activity (better yield and/or selectivity).

b) Size

The nanoparticles in the catalyst have a diameter from 0,5 nm to 15 nm. Nanoparticles comprising Ni as only element of group 10, and Sn and/or Ga have a diameter from 10,0 nm to 15,0 nm. Nanoparticles comprising Pt have diameter sizes from 1,0 nm to 5,0 nm. The process allows obtaining nanoparticles of PtSn with a mean diameter of 1,42 nm.

In general, the smaller the size of the nanoparticles resulted in better the performance of the catalyst because the dispersion of the number of available active metal sites is maximized. This results in a more efficient use of the precious metals.

2.3 Porous support description

The porous support shall be selected from:

- Alumina-based (Al₂O₃): gamma-Al₂O₃, theta-Al₂O₃ and alumina with alkaline elements (Li-Al₂O₃ and Na-Al₂O₃).
- Silica-based (SiO₂).
- Zeolites-based and related aluminosilicates of several chemical formulas.

Pore diameter is between 1-50 nm so, according to the IUPAC definition, the support is mesoporous.

3 Process for the preparation of catalysts

3.1 General description

The process comprises, in a one-pot step, the decomposition of:

- one or more organometallic precursor compounds (bis- and tris(dibenzylideneacetone) and, 1,5-cyclooctadienedimethyl) of one or more elements of group 10, and

- one or more organometallic precursors ((C₁-C₄)-alkyl complexes) compounds of metallic elements selected from the group consisting of Tin (Sn), Gallium (Ga), and Indium (In).

These precursor compounds provide the metallic elements to the reaction.

This is made in the presence of:

- an organic solvent, selected from the group consisting of ether containing solvents (in particular tetrahydrofuran, methyl-tetrahydrofuran, dioxane and diethyl ether), aromatic solvents (in particular benzene, toluene, anisole, methyl anisole and xylenes) and alkanes (in particular cyclohexane, hexane, pentane) and mixtures thereof.
- a porous support, and
- one or more organic molecules selected from the group consisting of an organophosphorus compound and an N-heterocyclic carbene.

The one-pot decomposition is carried out at the following physical condition ranges:

- Temperature: from 20 °C (room temperature) to 100 °C
- Time: from 30 minutes to 70 hours
- Pressure: from 1,0 x 10⁵ Pa to 5,0 x 10⁵ Pa

It is performed in hydrogen gas atmosphere, which allows a reductive environment that starts reducing the organometallic compounds to obtain the metals that will conform the nanoparticles and/or will be deposited onto the surface of the selected support.

All the operations for the syntheses of nanoparticles can be carried out using standard Schlenk tubes, Fisher-Porter vessels or gloveboxes under nitrogen atmosphere.

3.2 Preparation of reactivities

- Tris(dibenzylideneacetone)diplatinum (Pt₂(dba)₃) can be prepared adapting the reported procedure [1] using potassium tetrachloroplatinate(II) (K₂PtCl₄), dibenzylideneacetone (dba).
- Sodium acetate with metal trace levels (NaOAc), can be used without further purification.
- The tin precursors (SnBu₄ and N,N'-Di-t-butyl-2,3-diamidobutanetin(II)), and stabilizing agents (triphenylphosphine (PPh₃)) can be used without further purification.
- The imidazolium carboxylate (NHC-CO₂) can be prepared following reported procedures in [2] and [3].
- Solvents (Toluene, tetrahydrofuran (THF) and hexane) can be purified by solvent purification systems (e.g. MBRAUN SPS or equivalent) and degassed by freeze-pump-thaw cycles prior use.
- High purity gas such as hydrogen (H₂), nitrogen (N₂) and argon (Ar) shall show a purity >99,999%, and hydrocarbons (propane) a purity of 99,9999%.
- Pyrogenic γ-Al₂O₃ (100 m² g⁻¹) can be pre-treated as reported in [4] to obtain Al₂O₃ and LiAl₂O₃.

3.3 Catalyst preparation process

a) Supported nanoparticles:

The process to prepare the bimetallic PtSn-NPs ligand capped (L), Pt-(2 wt.)/Sn-(1 wt.)-NPs supported onto Al₂O₃ (**PtSn-L@Al₂O₃**), is the following:

- The platinum precursor (i.e., for Pt₂dba₃, 0,274 mmol, 150 mg), the tin precursor (i.e., for SnBu₄, 0,274 mmol, 101 mg), the selected stabilizing agent (L: none, PPh₃, NHC·CO₂) (i.e., for PPh₃, 0,054 mmol, 14,35 mg), the corresponding support (i.e., for Al₂O₃, 2,57 g) and solvent (i.e., 37,5 mL toluene) shall be introduced in a Fisher Porter vessel.
- The mixture shall be pressurized with 3 bars of H₂ and stirred at 700 rpm at 100 °C during 40 h.
- After this period, it shall be filtered with a 14-15 μm pore filter, washed with toluene and hexane and dried under vacuum.
- The resulting supported **PtSn^{IV}-P@Al₂O₃** is isolated in high yields (ca. 90-95%) and can be stored under inert atmosphere.

Same procedure shall be followed to obtain **PtSn^{IV}-NHC@Al₂O₃**, using the NHC·CO₂, or **PtSn^{IV}@Al₂O₃**, without adding any stabilizing agent.

To obtain the **PtSn^{IV}-P@LiAl₂O₃**, LiAl₂O₃ shall be used as support.

PtSn^{II}-P@Al₂O₃ and **PtSn^{II}-NHC@Al₂O₃** shall be prepared using the as-described methodology with Sn (II) precursor (N,N'-Di-t-butyl-2,3-diamidobutanetin(II)).

1Pt0.5Sn^{IV}@Al₂O₃ shall be prepared using a theoretical content of Pt-(1 wt.)/Sn-(0,5 wt.).

b) Colloidal nanoparticles:

The process to prepare PtSn-L NPs ligand capped (L: none, PPh₃, NHC·CO₂), **PtSn^{IV}-L**, is the following:

- The Pt precursor (Pt₂dba₃, 0,274 mmol, 150,0 mg), the tin precursor (i.e., for SnBu₄, 0,274 mmol, 101,0 mg), the selected stabilizing agent (i.e. for PPh₃, 0,054 mmol, 14,35 mg), and toluene (37,5 mL) shall be introduced in a Fisher Porter vessel.
- The mixture shall be pressurized at 3 bars of H₂ and stirred at 700 rpm at 100 °C during 40 h.
- After this period, it shall be washed with toluene and hexane and dried under vacuum.
- The resulting colloidal **PtSn^{IV}-P** is isolated in low yields (20-30%) and can be stored under inert atmosphere after precipitation.

Same procedure shall be followed for the obtention of **PtSn^{IV}-NHC** (adding 0,2 equivalents of NHC·CO₂) and **PtSn^{IV}** (without any stabilizing agent).

PtSn^{II}-L colloids shall be prepared following the same methodology described, changing the Sn (N,N'-Di-t-butyl-2,3-diamidobutanetin(II)). **PtSn^{II}-P**, **PtSn^{II}-NHC** and **PtSn^{II}** are obtained in low yields (20-30%) and can be stored under inert atmosphere after precipitation.

4 Catalyst Characterization

For complete characterization purposes, the use of colloidal nanoparticles, see 3.3 (b), is recommended as they allow obtaining better accuracy for the metallic contents.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses shall be performed on digested samples of the materials. The digestions shall be carried out using a microwave digestion system.

As a general procedure, 50 mg of sample shall be charged in Teflon liners followed by 12 mL of a concentrated acid mixture of aqua regia (3 mL HNO₃ 69% and 9 mL HCl 37%). The mixture shall be heated from room temperature to 200 °C during 30 min (approx. 6 °C/min) and then kept isotherm at 200 °C during 1 h more.

After a typical digestion, the reactor is open and the homogeneity of the solution examined. The solutions shall be transferred to volumetric flasks of 50 mL and the liners washed exhaustively with deionized high purity water with electrical resistance $R > 18,2 \text{ M}\Omega/\text{cm}$ (at 25 °C) (e.g. Milli-Q water).

Finally, the obtained solutions shall be analyzed by ICP-OES. Quantification of Pt and Sn is performed by comparison with the respective calibration curve constructed in the range of 0-20 ppm.

Transmission Electron Microscopy (TEM) experiments shall be performed at with an electron microscope operating at 100 kV with resolution of 3 Å. The particles size distributions can be determined by a manual analysis of enlarged images. At least 200 particles on a given grid shall be measured to obtain a statistical size distribution and a mean diameter.

Scanning Transmission Electron Microscopy - High Angle Annular Dark Field (STEM-HAADF) images shall be obtained in a probe-corrected microscope at a working voltage of 300 kV, coupled with a HAADF detector. X-ray Energy Dispersive Spectra (EDS) can be obtained with a detector. High Resolution TEM (HRTEM) imaging of the nanoparticles shall be performed in an image-corrected operated at a working voltage of 300 kV, equipped with a S-FEG and a spherical aberration corrector of the objective lens. TEM and HRTEM images can be acquired with a bottom mounted 2Kx2K CCD camera. The samples can be dispersed in absolute ethanol or hexane, using ultrasonication. A drop of this solution shall be then deposited on a Holey carbon 300 mesh copper grid.

5 Example: Preparation of nanocatalysts of PtSn with Sn(III and IV) precursors, using different combinations of agents

5.1 Effect of the organic stabilizing agents

Preparation of bimetallic PtSn nanoparticles (labelled Pt10), using:

- Organometallic precursors: Pt₂(dba)₃ and SnBu₄ in a Pt/Sn molar ratio 1:1.
- Stabilizing agent: Phosphine PPh₃ (although all phosphines are valid).
- Solvent: Toluene.
- Atmosphere of H₂ at 3 bar and room temperature.

Pt10 displayed small and well-dispersed nanoparticles size of 2,0-2,3 nm.

Preparation of bimetallic PtSn nanoparticles (labelled Pt11), using:

- Organometallic precursors: $\text{Pt}_2(\text{dba})_3$ and SnBu_4 in a Pt/Sn molar ratio 1:1.
- Stabilizing agent: None.
- Solvent: Toluene.
- Atmosphere of H_2 at 3 bar and room temperature.

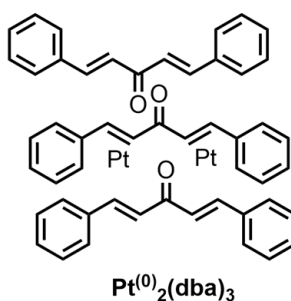
Pt11 displayed the formation of aggregates, thus showing the relevant positive effect of the phosphines (i.e., PPh_3) stabilizing agent.

5.2 Effect of different precursors

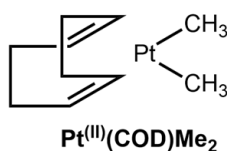
Decomposition of Pt and Sn precursors at 100 °C.

The metallic precursors were, for Pt:

- Tris(dibenzylideneacetone)dipalladium(0), $\text{Pt}^{(0)}_2(\text{dba})_3$

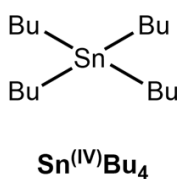


- (1,5-Cyclooctadiene)dimethylplatinum(II), $\text{Pt}^{(\text{II})}(\text{COD})(\text{Me})_2$

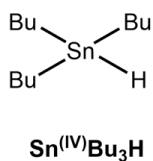


And for Sn(III) and Sn(IV):

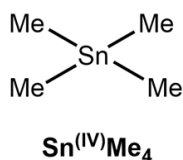
- Tin (IV) bromide, SnBu_4



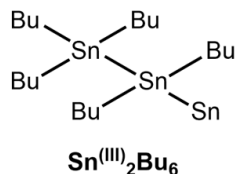
- Tributyltin hydride, HSnBu_3



- Tetramethyltin, SnMe_4



- Bis(tributyltin), Sn₂Bu₆



The results showed that in presence of SnBu₄, the Pt precursor, either Pt⁽⁰⁾₂(dba)₃ (labelled Pt12) or Pt^(II)(COD)(Me)₂ (labelled Pt13), decomposes quantitatively over a period of time of <15-20 h and the SnBu₄ partially decomposes (2-4% for Pt12 and 7-10% for Pt13) over a period of time of >40 h.

For Pt^(II)(COD)(Me)₂ and over period of time of >40 h, the Sn(III) and Sn(IV) precursors decompose at an extent of less than 15%, for example, the SnBu₄ decomposes 5-10% (Pt13) and HSnBu₃ (labelled Pt14), SnMe₄ (labelled Pt15) and Sn₂Bu₆ (labelled Pt16) decompose 10-15%.

5.3 Effect of different porous supports

Decomposition of the Pt(0 and II) and Sn(III and IV) precursors onto four different supports:

- Mesoporous alumina, Al₂O₃ (labelled Pt6c)
- Mesoporous lithiated alumina, Li- Al₂O₃ (labelled Pt7c)
- Sodium mesoporous zeolite, Na-ZSM-5 (labelled Pt8c) ¹
- Acid mesoporous zeolite, H-ZSM-5 (labelled Pt9c)

Conditions:

- 100 °C.
- organometallic precursors: Pt₂(dba)₃ and SnBu₄.
- organic stabilizing agent: phosphine (PPh₃).
- Nominal metal loading: Pt 2% wt-Sn 1% wt (Pt/Sn molar ratio 1:1).

The results obtained revealed that:

- Pt precursor is quantitatively decomposed forming small Pt nanoparticles and the decomposition rate is not affected by the nature of the support.
- Sn precursor is partially decomposed, and the decomposition rate varies depending on nature of the support in the following order Al₂O₃ (Pt6c) >> Li-Al₂O₃ (Pt7c) = Na-ZSM-5 (Pt8c) >> H-ZSM-5 (Pt9c) >>>no support.

¹ ZSM-5, Zeolite Socony Mobil-5 (framework type MFI from ZSM-5), is an aluminosilicate zeolite belonging to the pentasil family of zeolites. Its chemical formula is Na_nAl_nSi_{96-n}O₁₉₂·16H₂O (0<n<27). Patented by Mobil Oil Company in 1975, it is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions.

- The Sn(III and IV) precursors (for example, SnBu_4) in the presence of Al_2O_3 decompose quite fast (70-100 % after 40 h).
- Small nanoparticles well dispersed on the support are found with distinct Pt/Sn ratios depending on the analyzed region. In some regions, more Sn than Pt can be present, which means that the decomposition of Sn precursors occurred also on the support sites.

5.4 Effect of different organophosphorus compounds in catalysts characteristics

Catalysts samples of PtSn nanoparticles supported onto alumina (Al_2O_3) with a nominal Pt and Sn loading of 2.0 % w/W and 1.0 % w/W respectively.

Prepared by decomposition of the organometallic Pt and Sn precursors at 100 °C under 3 bar of hydrogen during 40 h in presence of 0.2 equivalents of phosphorous organic stabilizing agents from 6 different functional groups (Cat0 prepared in absence of organic stabilizing agent).

	Cat 0	Cat 1	Cat 2	Cat 3	Cat 4	Cat 5	Cat 6
Organic stabilizing agent	None	Monophosphine (PPh3)	Diphosphine (bidentate ligand)	Phosphoramidite	Phosphite	Secondary phosphine oxyde	Tertiary phosphine oxyde
PtSn-Nanoparticle Mean diameter (nm)	1,42 ± 0,35	1,33 ± 0,31	Below detection limit of or electron microscopy (< 1 nm).	1,66 ± 0,28	2,63 ± 0,68	1,50 ± 0,24	2,05 ± 0,53
Pt content by ICP (wt. %)	1,328	1,744	1,038	1,012	1,413	0,652	0,805
Sn content by ICP (wt. %)	1,381	1,111	0,322	1,046	1,074	0,042	1,050
Sn/Pt molar ratio (mol/mol)	1,71	1,04	0,509	1,643	1,249	0,107	2,143

Table 1 – Characteristics of different nano catalysts for different organic stabilizing agents

6 Example: Effect of different nanocatalyst in non-oxidative dehydrogenation (nODH) of light alkanes

Several catalysts evaluated in the following non-oxidative dehydrogenation of propane for the selective production of propylene.

The laboratory set up for the catalytic nODH reactions consists in a stainless-steel fixed bed reactor system on-line connected to a GC-TCD/MS system. The reaction is carried out under O_2 and H_2O exclusion conditions. Argon (5,0, purity 99,999%), N_2 (5,0, purity 99,999%), H_2 (5,0, purity 99,999%), propane (3,5, purity 99,95%), butane (3,5, purity 99,95%) and 2-butene (3,5, purity 99,95%) are purified in line with molecular sieves and BTS-catalysts traps to ensure high

purity is maintained. Mass flow controllers and by-pass 3 port valve system control the composition and the flow to the reactor or directly to the analysis system. Pressure is monitored and controlled: pressure transducer at the entrance of the reactor, pressure regulator with a manometer at the exit of the reactor, and safety valves to avoid overpressures (adjusted to a maximum of 5 bars). Temperature is controlled with a temperature heating jacket Hobersal with a thermocouple inside the reactor. The catalyst preparation is carried out in a glovebox for avoiding oxidation. The catalyst 1 - 100 mg (i.e., 25,0 mg cat., 0,1 mg Pt) is dispersed in a known amount of silicon carbide ($\varnothing \approx 150\text{-}300 \mu\text{m}$) and placed in the reactor. Catalyst pre-treatment consists in a reduction program at 500-600 °C (1 °C/min) under H₂ flow for 4-16h at a pressure comprised between 0,5 and 3 absolute bars.

In this example, the selected initial conditions for the non-oxidative dehydrogenation (n-ODH) of propane are: temperature, 530 °C; pressure, 1 bar; and gas flow: 3 mL/min of Propane, 21 mL/min of Ar and 1 mL/min H₂.

The propane conversion and propene selectivity are determined by gas chromatographic (GC-TCD) analysis of gas samples taken at regular intervals (each 14 min). The response factor of the propane and propene are determined using argon as internal standard. The mathematical formula for the determination of the conversion and selectivity are:

$$\text{Propane conversion (\%)} = \frac{\text{Total Propane}_{out}}{\text{Total Propane}_{in}} \times 100$$

$$\text{Propylene selectivity (\%)} = \frac{\text{Total propylene}_{out}}{\text{Total propane}_{in} - \text{Total propane}_{out}} \times 100$$

Table 2 lists the results obtained on propane non-oxidative dehydrogenation with some of the catalysts compositions. Comparative data with the benchmark Statoil catalyst (currently termed LINDE-BASF Statoil) are also included.

Nanocatalyst composition	Initial conv. –to – conv. After 900 min (%)	Selectivity (%)
PtSn/Mg(Al)O (STATOIL Reference)	26-to-3	83
PtSn-PPh ₃ /Al ₂ O ₃	24-to-15	98
PtSn-PPh ₃ /Li- Al ₂ O ₃ ;	20-to-10	97
PtSn-PPh ₃ /Al ₂ O ₃	23-to-12	99
PtGa-PPh ₃ /Al ₂ O ₃	23-to-14	99
NiSn-PPh ₃ /Al ₂ O ₃	2-to-1,5	75

Table 2 - Propane dehydrogenation catalyzed by PtSn and NiSn nanocatalyst

This example clearly illustrates that nODH of alkanes in which the defined catalyst compositions were employed, provided high conversion indexes as well as very high selectivities for propene.

Bibliography

- [1] Ould Ely, T.; Pan, C.; Amiens, C.; Chaudret, B.; Dassenoy, F.; Lecante, P.; Casanove, M. J.; Mosset, A.; Respaud, M.; Broto, J. M. Nanoscale Bimetallic CoPt_{1-x} Particles Dispersed in Poly(Vinylpyrrolidone): Synthesis from Organometallic Precursors and Characterization. *J. Phys. Chem. B* 2000, 104 (4), 695–702. <https://doi.org/10.1021/jp9924427>.
- [2] De Los Bernardos, M. D.; Pérez-Rodríguez, S.; Gual, A.; Claver, C.; Godard, C. Facile Synthesis of NHC-Stabilized Ni Nanoparticles and Their Catalytic Application in the: Z -Selective Hydrogenation of Alkynes. *Chem. Commun.* 2017, 53 (56), 7894–7897. <https://doi.org/10.1039/c7cc01779k>.
- [3] Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O.; Crabtree, R. H. Imidazolium Carboxylates as Versatile and Selective N-Heterocyclic Carbene Transfer Agents: Synthesis, Mechanism, and Applications. *J. Am. Chem. Soc.* 2007, 129 (42), 12834–12846. <https://doi.org/10.1021/ja0742885>.
- [4] Rouge, P.; Garron, A.; Norsic, S.; Larabi, C.; Merle, N.; Delevoye, L.; Gauvin, R. M.; Szeto, K. C.; Taoufik, M. A Smarter Approach to Catalysts by Design: Combining Surface Organometallic Chemistry on Oxide and Metal Gives Selective Catalysts for Dehydrogenation of 2,3-Dimethylbutane. *Mol. Catal.* 2019, 471 (January), 21–26. <https://doi.org/10.1016/j.mcat.2019.04.011>.