TECHNOLOGY OFFER **PORTAL**

TRANSFORMATION OF BIOMASS WASTE TO OBTAIN CATALYSTS OF INTEREST TO THE CHEMICAL INDUSTRY

PATENTED TECHNOLOGY

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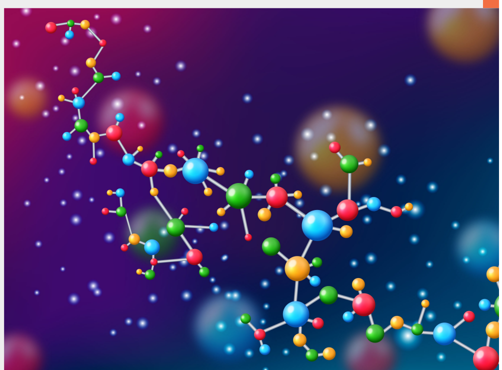
ABSTRACT

The *Materiales Carbonosos y Medio Ambiente* (MCMA) research group at the University of Alicante has developed a new procedure to prepare heterogeneous catalysts from biomass waste based on highly dispersed metal nanoparticles.

This procedure is characterised by the fact that it is very simple, involves few synthesis steps, the synthesis conditions are mild and it is environmentally friendly. Moreover, it is easy to scale up to an industrial level, allows the revalorisation of any type of biomass-derived waste and has a low manufacturing cost. The synthesised catalysts show excellent catalytic behaviour using low noble transition metal contents and could become very promising candidates to replace current commercial catalysts in the production of molecules of great interest to the chemical sector, such as, for example, in the conversion of levulinic acid to gamma-valerolactone. Companies interested in acquiring this technology for commercial exploitation are sought.



INTRODUCTION

The bioeconomy is about providing sustainable solutions and enabling the transformation towards a sustainable economy. In this sense, biorefineries are essential for the development of the bioeconomy, as they replace fossil resources with renewable resources, converting biomass into fuels, electricity and chemicals. In this context, the importance of "platform molecules", which are molecules derived from biomass that serve as starting materials for the preparation of chemicals of various kinds, should be highlighted. These "platform molecules" include: succinic, fumaric, maleic, aspartic, glucaric, glutamic, itaconic, levulinic acids, glycerol, sorbitol, xylitol, ethanol, etc.

In the specific case of levulinic acid, the reactivity of the ketone and carboxylic functional groups gives it great versatility, and a large number of molecules of great interest can be prepared from it, such as esters, acrylic acid, gamma-valerolactone, etc.

Gamma-valerolactone (hereinafter GVL) can be obtained from the catalytic hydrogenation of levulinic acid. GVL is a molecule of great interest, both for its properties (it is water miscible, biodegradable and not very volatile), and for its wide range of applications: as an additive in food and cosmetics, as a green solvent, as a precursor in the synthesis of high value-added molecules (e.g. butene, valeric acid, etc.), in the preparation of fuels or fuel additives (valeric esters), etc.

The most commonly used heterogeneous catalysts for the hydrogenation of levulinic acid to GVL are ruthenium-based. Most of these catalysts contain relatively high amounts of ruthenium (between 1-5 wt.%), and the catalytic reaction is carried out using temperatures above 100 °C, both of which are critical factors in the high costs of the overall process, both from an economic and energy point of view.

Studies have been carried out in which the carbonaceous material used as catalytic support has been prepared from a biomass residue. For example, rice husks, almond shells, cotton reeds, etc. have been used, whose transformation requires high temperatures, numerous experimental steps, long synthesis times and environmentally hazardous activating agents, obtaining moderate levulinic acid conversions and selectivities towards GVL, with the consequent disadvantages in economic and energy terms.

It is therefore necessary to find a suitable process to prepare heterogeneous catalysts with low metal phase contents that can be used in processes such as the selective hydrogenation of levulinic acid to GVL under mild reaction conditions, in a way that minimises the economic and energy cost of the overall process, and that is aligned with the objectives of the circular economy.

TECHNICAL DESCRIPTION

In order to solve the problems described above, a new process has been developed to prepare **heterogeneous catalysts** consisting of **carbonaceous materials derived from biomass residues and highly dispersed metal nanoparticles with low transition metal content**.

The process to obtain these novel catalysts comprises the following **steps**:

1. **Process the biomass**. Biomass waste rich in lignocellulose (it can be any type of biomass, for example: cocoa shells, almond shells, hemp, eucalyptus, etc.) is subjected to a grinding and sieving process to achieve an optimum particle size. Subsequently, they are washed to remove inorganic matter. Finally, they are dried in an oven.

2. **Carbonising the processed biomass residues** in an autoclave reactor in the presence of an aqueous solution (this process is called hydrothermal carbonisation). The heat treatment is carried out at a moderate temperature for a certain time.

3. **Activating the carbonised** product obtained in the previous stage. The carbonised product is subjected to an activation heat treatment in a tube furnace using a specific heating ramp until a certain temperature is reached, which is maintained for a certain period of time. This process is carried out in an inert atmosphere.

4. **Washing the activated carbon** resulting from the previous stage. For this purpose, different washes are carried out with distilled water at moderate temperature until a neutral pH is reached.

5. **Dry the activated carbon**. The activated carbon obtained in the previous step is dried at a certain temperature for a specific time.

6. **Impregnate the activated carbon with the metal precursor**. To an aqueous dispersion of activated carbon, an aqueous solution of an inorganic salt of a transition metal (ruthenium, palladium, iron or rhenium) is added and stirred at room temperature for a specified time.

7. **Reduce the metal phase with a reducing agent**. To the above suspension, an aqueous solution of a reducing agent (preferably a metal hydride) is added at a given concentration and stirred at room temperature for a specified time. Subsequently, the catalyst obtained is filtered and washed with distilled water to remove the solvent.

8. **Dry the obtained heterogeneous catalyst**. For this purpose, a moderate temperature is used for a specified time.

TECHNOLOGY ADVANTAGES AND INNOVATIVE ASPECTS

ADVANTAGES OF THE TECHNOLOGY

The main **advantages** of this novel procedure are listed below:

1) It comprises **few steps** and is **very simple**.

2) It is carried out under **mild reaction conditions**: low pressure, moderate temperature and short reaction times.

3) It **avoids the use of hydrogen gas** at high temperatures.

4) The formation of **small metal nanoparticles** is favoured.

5) **High dispersion** of the metal nanoparticles on the carbonaceous supports is achieved.

6) **No aggregates** of metal particles are obtained.

7) The catalyst offers **many active sites** for the chemical reaction in which it is to be used, which gives **better results** than with commercial catalysts.

8) Drying of the catalyst is carried out at a lower temperature than conventional methods, which **prevents the electronic properties of the surface of the metal nanoparticles from changing substantially**.

9) It allows the **recovery of abundant biomass waste** (cocoa shells, almond shells, hemp, eucalyptus, etc.).

10) The catalysts obtained can be used in the **chemical conversion** of a multitude of **molecules of great industrial interest**.

11) **Lower production costs** than current synthesis methods.

12) **Lower environmental impact** than current synthesis methods.

13) **Porosity is achieved equal to or higher** than with the conventional activation process.

14) **Higher yields** are achieved compared to conventional chemical activation.

15) The process is **easily scalable to industrial scale**.

16) **Versatility** of the synthesis method: different types of hard or soft lignocellulosic biomass residues can be used (regardless of their composition and moisture content).

17) **Low metal content** (ruthenium, etc.) compared to commercial catalysts.

18) **Higher** levulinic acid **conversions** (98.4%) and **selectivities** towards GVL (100%) are achieved than in the current state of the art.

19) The catalysts show **excellent catalytic activity** under mild reaction conditions (low temperatures, etc.).

20) **High stability** of the catalysts obtained after several consecutive reaction cycles.

21) **No special equipment is required**: the equipment used is commercially available and affordable for any laboratory or industry.

22) The **precursors** used are **very cheap and abundant**.

INNOVATIVE ASPECTS OF THE TECHNOLOGY

The main innovation lies in the **use of agricultural waste** (lignocellulosic biomass) to obtain **heterogeneous catalysts** containing **low concentrations of ruthenium in the form of highly dispersed metal nanoparticles**.

The present invention differs from current synthesis methods in that:

1) Activated carbons obtained from **biomass residues rich in lignocellulose** are used as support for the active phase.

2) **Ruthenium contents are much lower** than those present in commercial catalysts.

3) **Mild reaction conditions** are used.

4) The low temperature used for catalyst drying **prevents the electronic properties of the surface of the metal nanoparticles from changing substantially**.

5) The **metal nanoparticles are highly dispersed** on the surface of the activated carbon support, allowing **many active sites** for the chemical reaction of interest to take place with **high efficiency and selectivity**.

6) The **activating agents** used **are not dangerous for the environment** and, moreover, very low concentrations are used compared to conventional chemical activation, which **reduces synthesis costs and environmental impact**.

7) The method is **very simple**, with **few steps** and **short synthesis times**.

CURRENT STATE OF DEVELOPMENT

These novel heterogeneous catalysts (*see Picture 1*) have been **successfully synthesised at laboratory level**. This technology is at a stage of maturity **TRL = 4** (Technological Readiness Level).

Picture 1: Synthesised catalyst in fine powder form.

The heterogeneous catalysts obtained by this novel process are characterised by the following features:

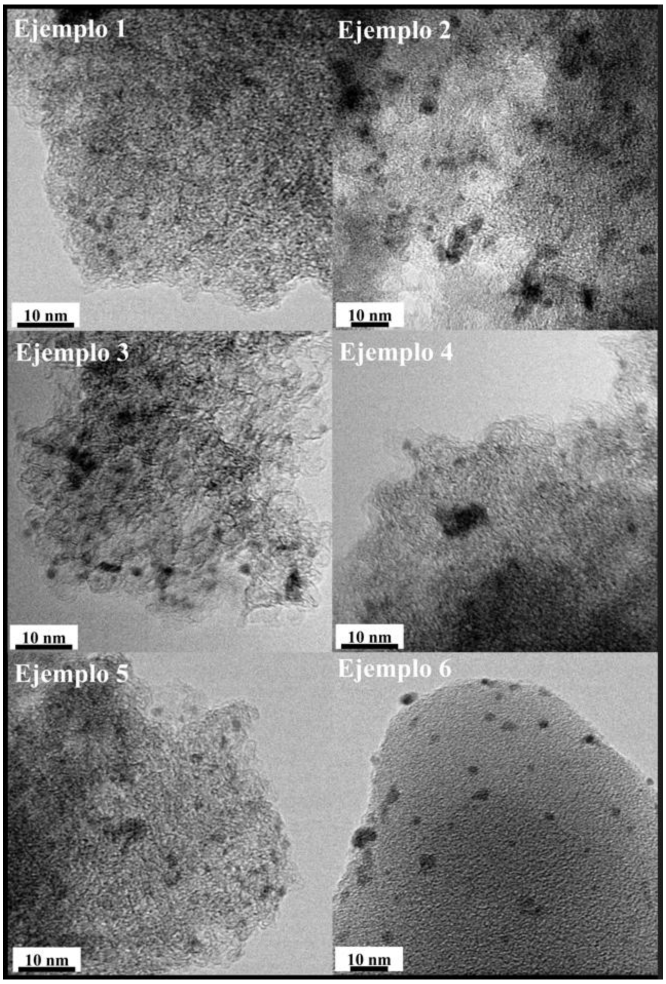
- They have **surface areas** between **700-2.000 $m^2 \cdot g^{-1}$**.
- The active metal phase is highly dispersed in the form of **nanoparticles** with an **average size** between **1.6-3.0 nm**.
- The final **transition metal content** is between **0.1-0.60% weight**.
- In the different reaction conditions tested, the **catalytic activity** in the hydrogenation of levulinic acid to GVL has values **very close to 100%**.

Some examples of different biomass residues used in the laboratory tests to synthesise these novel catalysts are shown below (*see Picture 2*):

Picture 2: Different biomass residues used in the laboratory tests, including cocoa shells, eucalyptus wood and almond shells, respectively.

The catalysts obtained have been characterised using various techniques to determine their structure and composition, among them:

- N_2 adsorption isotherms to determine the porous texture.
- Transmission Electron Microscopy (TEM) to determine the morphology of the active metal phase and the average size of the nanoparticles (*see Figure 3*).
- Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to determine the final transition metal content.
- X-ray Photoelectron Spectroscopy (XPS) to determine the different transition metal species and their surface content.



Picture 3: TEM micrographs of the different catalysts synthesised.

MARKET APPLICATIONS

The present invention is framed both in the **Circular Economy** sector and in the **obtaining of high added value chemical products**.

Specifically, a novel process has been found to prepare heterogeneous catalysts with low transition metal content from lignocellulosic biomass residues that can be successfully used in the **conversion of organic compounds** under mild reaction conditions, such as:

- In the selective hydrogenation of levulinic acid to GVL.

- In the decomposition of hydrogen-bearing molecules.
- In the production of ammonia.
- Other applications of interest.

This technology makes it possible to obtain carbonaceous materials with very low transition metal content, making them very promising **catalysts to replace those currently used in the conversion of organic compounds of interest** (for example, in the conversion of levulinic acid to GVL).

In this respect, the main sectors of interest are:

- The chemical industry.
- Pharmaceutical industry.
- Waste management (conversion of lignocellulosic biomass).

COLLABORATION SOUGHT

Companies interested in acquiring this technology for **commercial exploitation** are sought:

- Patent licensing agreements.
- Development of new applications.
- Technology and knowledge transfer agreements.

Company profile sought:

- Catalyst manufacturers.

INTELLECTUAL PROPERTY RIGHTS

This invention is protected through **patent application**:

- *Title of the patent: "Procedimiento de preparación de catalizadores derivados de biomasa lignocelulósica para la conversión de compuestos orgánicos".*
- *Application number: P202331075.*
- *Application date: 22nd December, 2023.*

MARKET APPLICATION (2)

Materials and Nanotechnology
Chemical Technology

TECHNICAL IMAGES (1)