Transformation of biomass waste to obtain catalysts of interest to the chemical industry

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TECHNICAL DESCRIPTION

New process has developed to prepare **heterogeneous catalysts** consisting of **carbonaceous materials derived from biomass residues and highly dispersed metal nanoparticles with low transition metal content**. It 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.

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) I**t 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**.

CURRENT STATE OF THE TECHNOLOGY

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.

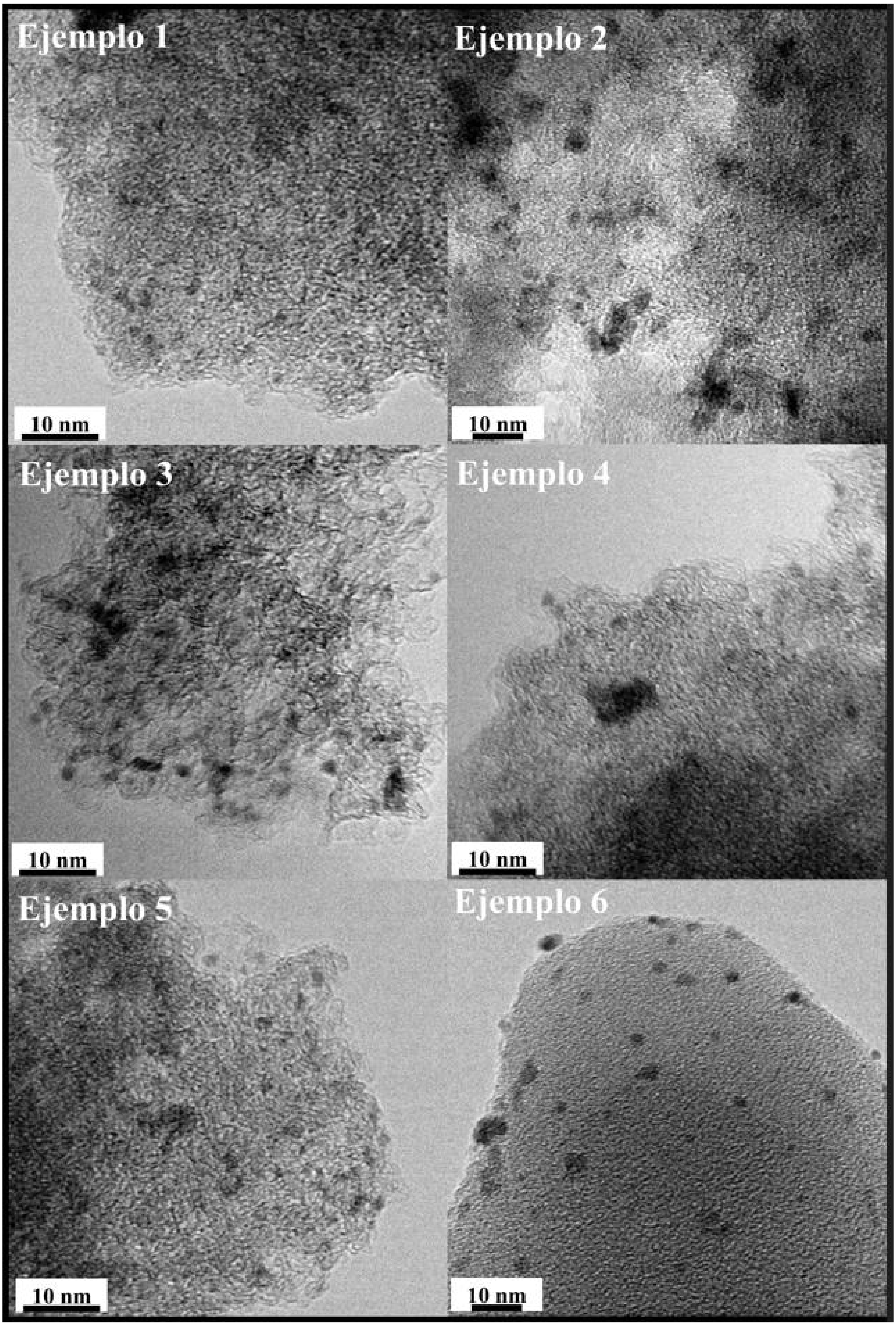
The catalysts obtained have been characterised using various techniques to determine their structure and composition, among them:

- 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.

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.*

KEYWORDS

Catalyst, residue, biomass, transition metal, ruthenium, activated carbon, hydrogenation, levulinic acid, gamma-valerolactone, organic compound.