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(54) Title: A METHOD FOR PRODUCING PHENOLIC COMPOUNDS

(57) Abstract: The present invention relates to a method for producing phenolic compounds from bio-based materials. The method features high selectivity and/or yield, mild reaction conditions, high concentration of starting reactants and therefore is more suitable for industrialization.



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A method for producing phenolic compounds

TECHNICAL FIELD

The present invention relates to a method for producing phenolic compounds from bio-based materials.

BACKGROUND

The following discussion of the prior art is provided to place the disclosure in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of common general knowledge in the field.

Fossil fuels are widely used in the industry and for domestic purposes. Disadvantageously, they are non-renewable, unsafe and environmentally unfriendly. Currently, some researches are focusing on developing alternatives for fossil fuels. An increasing attention has been paid to convert lignocellulosic biomass into liquid fuels and value-added chemicals.

Bio-based charcoal oil is produced via a thermochemical route by fast pyrolysis of lignocellulosic biomass, such as eucalyptus and spruce wood chips. Prior practice usually includes one or more separation step(s) to isolate the components of pyrolysis oil. The components can be processed by hydrodeoxygenation (HDO) to obtain valuable aromatic compounds. Crude pyrolysis oil mixture is initially separated by distillation into two fractions of organic lights or phenolics, and tars or heavies. An industrial representative light fraction of syringol-catechol cut of the bio-based charcoal oil mixture contains syringol (36.6%), 3-methoxycatechol (13.4%) and catechol (6.7%). These three components can be converted to phenolic compounds by HDO after separation. However, it is difficult to separate this light fraction by distillation as syringol and 3-methoxycatechol, form azeotropes with catechol.

Journal of Industrial and Engineering Chemistry 122 (2023) 138-151 teaches the application of Ni catalysts supported by activated carbon (AC) and $\text{TiO}_2\text{-SiO}_2$ for highly effective hydrodeoxygenation of syringol-a lignin-derived model compound. However, the concentration of syringol in their bio-oil composition is quite low (7.54% for bamboo and 5.89% for oak wood). The best result was obtained in 0.009 g/mL syringol solution dissolved in octane at 400 °C over Ni/AC with 99.33% syringol conversion, 39.32% phenol yield, 23.80% p-xylene yield, 22.89% cresols yield and only 3.79% guaiacol yield. In addition, non-oxygenated compounds e.g. mesitylene, naphthalene and multi-alkyl-substituted benzene derivatives e.g. tetramethylbenzene, pentamethylbenzene were observed. The selectivity of phenol is not ideal and thus the technology is not suitable for industrialization. From a mechanism point of view, the high yield of p-xylene was because of a consecutive series of reactions including demethoxylation, methylation/transalkylation and dehydration. Acidic oxide $\text{TiO}_2\text{-SiO}_2$ and AC favored transalkylation reactions. Moreover, Ni/AC displayed higher CO and moisture content, and high selectivity of hydrocarbon gasses C_2H_4 , C_2H_6 and C_3H_6 .

The Applicant perceived that there is still the need for an improved method for producing phenolic compounds from bio-based materials in high selectivity and/or yield.

SUMMARY

The present invention provides a method for producing a phenolic compound, comprising reacting a material, in particular a bio-based material which contains a benzene compound comprising at least one hydroxyl group and one methoxy group [Compound A] with molecular hydrogen in the presence of a catalyst comprising a support and Ni, wherein the support comprises at least one oxide of Period 3 element and is free or substantially free of titanium.

High selectivity and/or yield of phenolic compounds can be produced directly from bio-based materials, especially light fractions of charcoal oil, thereby avoiding separation step(s) of bio-based material components.

In comparison with the catalysts reported, such as Ni/AC and Ni/ $\text{TiO}_2\text{-SiO}_2$, the catalyst used in the invented method is selective in phenolic compounds. Less

or even no non-oxygenated compounds and alkyl- or multi-alkyl-substituted benzene derivatives were produced.

Unlike Ni/AC, no further degradation to hydrocarbon gasses was observed when using a specific catalyst as mentioned above.

It is possible to obtain high yield of phenolic compounds at low reaction temperature and/or low gas pressure by using the invented method.

The Applicant also surprisingly found that the invented method allows the use of high concentration of the Compound A, in particular syringol, for the production of phenolic compounds.

Other subjects and characteristics, aspects and advantages of the present invention will emerge even more clearly on reading the detailed description and the examples that follow.

BRIEF OF DESCRIPTION OF DRAWINGS

Fig.1 H₂-TPR profile of Ni 52/49, Ni Sat 310 and Ni 6215P;

Fig.2 CO-pulse chemisorption of Ni 52/49.

DEFINITIONS

Throughout the description, including the claims, the term "comprising one" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified, and "between" should be understood as being inclusive of the limits.

As used herein, the terminology "(C_n-C_m)" in reference to an organic group, wherein n and m are both integers, indicates that the group may contain from n carbon atoms to m carbon atoms per group.

The articles "a", "an" and "the" are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article.

The term "and/or" includes the meanings "and", "or" and also all the other possible combinations of the elements connected to this term.

It is specified that, in the continuation of the description, unless otherwise indicated, the values at the limits are included in the ranges of values which are given.

Ratios, concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such a range format is used

merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also all the individual numerical values or sub-ranges encompassed within that range as if each numerical value or sub-range is explicitly recited.

DETAILS OF THE INVENTION

The present invention provides a method for producing a phenolic compound, comprising reacting a material containing a benzene compound comprising at least one hydroxyl group and one methoxy group [Compound A] with molecular hydrogen in the presence of a catalyst comprising a support and Ni, wherein the support comprises at least one oxide of Period 3 element and is free or substantially free of titanium.

Compound A

As used herein, the term "benzene compound comprising at least one hydroxyl group and one methoxy group [Compound A]" means a benzene compound in which at least one hydroxyl group and one methoxy group are bonded to the benzene ring. Other functional group may be bonded to the benzene ring, as long as its presence does not prevent hydrodeoxygenation reaction by which the phenolic compound is obtained. The functional group is notably a straight or branched alkyl and preferably a C₁-C₁₀ straight or branched alkyl. Representative straight chain alkyls include methyl, ethyl, n-propyl, n-butyl, n-pentyl, and the like; while branched alkyls include isopropyl, sec-butyl, isobutyl, tert-butyl, isopentyl, and the like.

In some embodiments, the Compound A is a benzene compound comprising one hydroxyl group and two methoxy groups [Compound A1]. Non-limitative example of such Compound A1 is syringol.

Preferably, the material preferably contains at least 10 wt%, preferably at least 20 wt% and more preferably at least 30 wt% of the Compound A1, based on the weight of the material.

Advantageously, the material contains 10 to 55 wt%, preferably 20 to 50 wt% of the Compound A1, based on the weight of the material.

In some embodiments, the Compound A is a benzene compound comprising two hydroxyl groups and one methoxy group [Compound A2]. Non-limitative example of such Compound A2 is 3-methoxycatechol.

Preferably, the material contains at least 2 wt%, preferably at least 5 wt% and more preferably at least 10 wt% of the Compound A2, based on the weight of the material.

Advantageously, the material contains 2 to 20 wt%, preferably 5 to 15 wt% of the Compound A2, based on the weight of the material.

In a particular embodiment, the material contains a benzene compound comprising one hydroxyl group and two methoxy groups [Compound A1] and a benzene compound comprising two hydroxyl groups and one methoxy group [Compound A2].

Compound B

The material may further contain a benzene compound comprising at least two hydroxyl groups [Compound B].

As used herein, the term "benzene compound comprising at least two hydroxyl groups [Compound B]" means a benzene compound in which at least two hydroxyl groups are bonded to the benzene ring. Other functional group may be bonded to the benzene ring, as long as its presence does not prevent hydrodeoxygenation reaction by which the phenolic compound is obtained. The functional group is notably a straight or branched alkyl and preferably a C₁-C₁₀ straight or branched alkyl. Representative straight chain alkyls include methyl, ethyl, n-propyl, n-butyl, n-pentyl, and the like; while branched alkyls include isopropyl, sec-butyl, isobutyl, tert-butyl, isopentyl, and the like.

In some embodiments, the Compound B comprises two hydroxyl groups. Non-limitative example of such Compound B is catechol.

The material preferably contains at least 1 wt%, preferably at least 2 wt% and more preferably at least 5 wt% of the Compound B, based on the weight of the material.

Advantageously, the material contains 1 to 10 wt%, preferably 2 to 8 wt% of the Compound B, based on the weight of the material.

The weight ratio of the Compound A and the Compound B is not limited. In a particular embodiment, the Compound A and the Compound B has a weight ratio which can form an azeotrope. The weight ratio of the Compound A to the Compound B can be from 1:1 to 75:1 and preferably from 7.5:1 to 12:1.

In particular, the material can be a composition comprising syringol 10 to 55 wt%, 3-methoxycatechol 2 to 20 wt%, and catechol 1 to 10 wt%, based on the weight of the material.

The material includes those commercially or industrially available, such as products obtained by extraction of Biocarbo's commercial products. The skilled person can use any technology of extraction, such as organic solvent, water, supercritical fluid, distillation or adsorption to obtain the material.

Phenolic compound

As used herein, the term "phenolic compound" means a benzene compound in which at least one hydroxyl group is bonded to the benzene ring. Other functional group, which does not prevent hydrodeoxygenation reaction, may be bonded to the benzene ring. The functional group is notably a straight or branched alkyl and preferably a C₁-C₁₀ straight or branched alkyl. Representative straight chain alkyls include methyl, ethyl, n-propyl, n-butyl, n-pentyl, and the like; while branched alkyls include isopropyl, sec-butyl, isobutyl, tert-butyl, isopentyl, and the like.

Preferably, the phenolic compound comprises one or two hydroxyl group(s) and more preferably one hydroxyl group.

The phenolic compound may comprise a methoxy group. Preferably, the phenolic compound does not comprise a methoxy group.

Said phenolic compound is preferably selected from the group consisting of phenol, catechol and guaiacol and preferably phenol and guaiacol and more preferably phenol.

The skilled person can understand that the Compound A and/or the Compound B are/is converted to the phenolic compound through hydrodeoxygenation reaction. Non-limitative examples of such conversion are as follows:

- conversion of syringol to guaiacol and/or phenol;

- conversion of 3-methoxycatechol to catechol and/or phenol, and
- conversion of catechol to phenol.

In a preferred embodiment, the yield of phenol is at least 50%, at least 60%, or at least 70%.

Catalyst

Period 3 element is an element found on the third row (or period) of the periodic table. They are sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), and argon (Ar).

Said oxide is preferably selected from the group consisting of silicon oxide (SiO_2), aluminum oxide (Al_2O_3), magnesium oxide (MgO) and more preferably SiO_2 and Al_2O_3 .

In one embodiment, the support comprises one oxide of Period 3 element. Said oxide in this embodiment is SiO_2 or Al_2O_3 and preferably SiO_2 .

In another embodiment, the support comprises at least two oxides of Period 3 elements. Said two oxides in this embodiment are SiO_2 and Al_2O_3 . The weight ratio of SiO_2 is at least 60 wt%, preferably at least 80 wt%, based on the weight of the support. The weight ratio of Al_2O_3 is less than 40 wt%, preferably less than 20 wt%, based on the weight of the support.

As used herein, the term "free of Ti", when used with reference to the support, means that the support does not comprise Ti at all.

As used herein, the term "substantially free of Ti" when used with reference to the support means that the support comprises less than 5 wt%, preferably less than 1 wt%, more preferably less than 0.5 wt%, most preferably less than 0.1 wt% of Ti, based on the weight of the support.

In some preferred embodiments, the support comprises 0 to 5 wt%, preferably 0 to 1 wt%, more preferably 0 to 0.5 wt%, most preferably 0 to 0.1 wt% of Ti, based on the weight of the support.

The loading of Ni is from 50 to 80 wt%, preferably from 50 to 65 wt%, based on the weight of the catalyst.

The average diameter of Ni particles on the support can be from 5 nm to 50 nm, preferably from 10 nm to 30 nm, as determined by CO-pulse chemisorption.

The Ni dispersion on the support can be from 3 to 10%, preferably from 4 to 9%, as determined by CO-pulse chemisorption.

The supported Ni catalyst is characterized by the presence of a reduction peak at a temperature below 300°C, or below 280°C, or even below 250°C, preferably at a temperature from 180°C to 250°C, more preferably from 200°C to 250°C, as determined by H₂-TPR analysis.

The supported Ni catalyst is characterized by the presence of a H₂ consumption of at least 2 mmol /g, preferably from 2 to 10 mmol /g at one or more temperature(s) in the reduction from 200°C to 250°C, as determined by H₂-TPR analysis.

The Brunauer-Emmett-Teller (BET) surface area of the supported Ni catalyst is from 100 to 300 m²/g, preferably from 120 to 280 m²/g and more preferably from 140 to 260 m²/g.

The catalyst can be commercial products, such as Ni 52/49 from BASF, Ni Pricat 6215P from Johnson Matthey and Ni Sat 310 catalyst from Clariant.

The catalyst can be reduced and stabilized by known methods before use.

Advantageously, the catalyst is reduced under H₂ flow by raising the temperature before the reaction. For example, the catalyst can be reduced under H₂ flow by raising the temperature from room temperature to 150 to 250°C with a heating rate of 0.5 to 1°C/min, holding the temperature at 150 to 250°C for a certain time, such as 300 to 600 mins, and finally raising the temperature to reaction temperature with a heating rate of 0.5 to 1°C/min.

Molecular Hydrogen

As used herein, molecular hydrogen is a diatomic molecule that is composed of two hydrogen atoms held together by a covalent bond with the chemical formula H₂. Molecular hydrogen is normally called hydrogen gas (H₂) as it is present in gas form.

Advantageously, the reaction can be carried in the presence of a gas mixture of hydrogen gas (H₂) and an inert atmosphere such as nitrogen gas (N₂) or argon gas (Ar). Good results can be obtained when a mixture of hydrogen gas (H₂) and nitrogen gas (N₂) is present. The volume ratio of hydrogen gas (H₂) to the inert atmosphere is from 0.1:1 to 1:1 and preferably from 0.3:1 to 0.9:1.

The gas pressure in the reactor is not particularly limited. Gas pressure less than 5 bar, or less than 2 bar, or even less than 1.5 bar is preferred. Good results can be obtained at atmospheric pressure (1 bar).

Reaction conditions

The reaction temperature can be from 250 to 350°C and preferably from 305 to 350°C.

Advantageously, before contacting hydrogen gas (H₂), the material is preheated in the presence of hydrogen gas or a mixture of hydrogen gas (H₂) and nitrogen gas (N₂) at a temperature from 100 to 200°C and preferably from 140 to 160°C.

The method of the present invention can be readily adapted for a batch, a fed-batch or a continuous mode.

The equipment used is not particularly limited. Fixed-bed reactors are preferably used.

The amount of the catalyst generally depends on the mode adapted. For example, in the fixed-bed reactors, the amount of the catalyst is preferably such that weight hourly space velocity (WHSV), based on the material, is from 0.1 to 10 g·g_{Cat.}⁻¹·h⁻¹ and preferably from 0.4 to 2 g·g_{Cat.}⁻¹·h⁻¹.

As used herein, weight hourly space velocity (WHSV) is the weight of feed per hour per unit weight of the catalyst loaded in the reactor.

The following examples are included to illustrate embodiments of the disclosure. Needless to say, the disclosure is not limited to describe examples.

EXAMPLES

Materials

- Charcoal oil mixture (36.6% syringol, 13.4% 3-methoxycatechol, 6.7% catechol) , a product obtained by extraction of Biocarbo's commercial product, from Solvay;
- 64 wt.% Ni/SiO₂, Ni 52/49, from BASF;
- 60 wt.% Ni/Al₂O₃-Kieselguhr, Pricat Ni 6215P, from Johnson Matthey;
- 52 wt.% Ni/SiO₂-Al₂O₃, Ni Sat 310, from Clariant;
- Quartz sand, CAS No. 14808-60-7, from Aladdin;
- Ethanol absolute >99.8%, CAS No. 64-17-5, from Sinopharm Chemical Reagent.

Catalyst Characterization: BET Surface Area

The Brunauer-Emmett-Teller (BET) surface area of the different Ni catalysts was determined by using a Micromeritics HAM-TriStar II 3020 surface area analyser. The samples were pretreated at 350°C under vacuum before analysis. The BET surface area of Ni 52/49, Ni Sat 310 and Pricat Ni 6215P is shown in Table 1.

Catalyst Characterization: H₂-TPR

The temperature programmed reduction (H₂-TPR) of different Ni catalysts was conducted to evaluate the reducibility of Ni species and interaction of NiO with support materials. Fig.1 shows the TPR profiles obtained in the temperature range from 50°C to 900°C. All the Ni catalysts show a main reduction peak at temperatures below 290°C, indicating weak NiO-support interactions with the support. Strong NiO-support interaction is typically characterized by a large reduction peak around 500°C to 600°C, which is absent in all the Ni catalysts tested. The reduction peaks and H₂ consumption for all the Ni catalysts are shown in Table 1.

H₂-TPR and CO-pulse chemisorption analysis of a catalyst were performed in a Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD). For each experiment, approximately 100 mg catalyst was placed

in a U-shaped quartz tube (i.d. = 10 mm) and reduced in a flow of 10% H₂/Ar while ramping the temperature up to 300 °C at the rate of 10 °C /min, and then held at 300 °C for 30 min (this part corresponds to the H₂-TPR analysis). After that, the sample was cooled down to 50 °C and flushed with He for 30 min. The loop gas of 10% CO/He was pulsed over the sample and the TCD signal was recorded until the peak area became constant (this part corresponds to the CO-TPD analysis).

Catalyst Characterization: CO-Pulse Chemisorption

CO-pulse chemisorption was carried out to measure the metal dispersion and active metal particle size of the catalysts. A CO-pulse profile of Ni 52/49 catalyst is shown in Fig.2. The catalyst was first reduced under H₂ flow and then CO loop gas was pulsed over the sample. The peak area increases until it reaches a constant value.

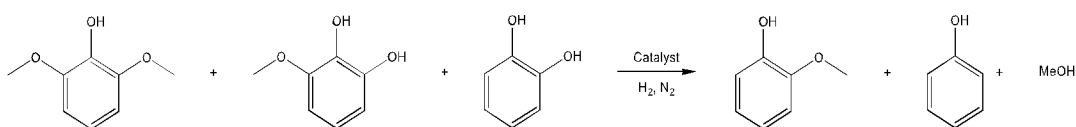
Table 1. Summary of BET surface area, H₂-TPR and CO-pulse chemisorption for all the Ni catalysts.

Catalyst	BET surface area (m ² /g)	H ₂ - TPR (°C)	H ₂ Consumption(mmol/g)	CO-pulse chemisorption	
				Metal dispersion (%)	Particle diameter (nm)
Ni 52/49 (BASF)	235	242	5	4.7514	21
Ni Sat 310 (Clariant)	145	215	2	7.5015	13
Pricat Ni 6215P (Johnson Matthey)	177	216	3	8.4259	12

These commercial Ni catalysts are pre-reduced and stabilized.

Example 1

In a typical experiment, 0.50 g of Ni 52/49 catalyst (BASF) was diluted with 2.00 g of quartz sand and placed at the isothermal zone of the stainless steel reactor (internal diameter 0.9 mm). The catalyst was reduced under 50 mL/min H₂ flow by raising the temperature from 25°C to 200°C at 0.5°C/min, holding the temperature at 200°C for 450 min, and finally raising the temperature to 305°C at 0.5°C/min. The temperature of the reactor was maintained at 305°C during the reaction. After the catalyst reduction, 50 mL/min H₂ and 55 mL/min N₂ gas flow rates were used. Charcoal oil mixture (Solvay) was preheated at 150°C and fed into the reactor by a syringe pump at 0.5 mL/min. During the reaction, liquid samples were collected in a cold trap at 0-4°C at the bottom of the reactor and the gasses were evacuated to the scrubber. Liquid samples were collected each hour, diluted in ethanol solvent and analyzed by gas chromatograph on a HP-5 column equipped with a flame ionization detector. 92% syringol conversion, 70% 3-methoxycatechol conversion, 70% phenol yield, 12% guaiacol yield and 11% cresol yield were obtained.



Reaction scheme for the hydrodeoxygenation of charcoal oil containing syringol, 3-methoxycatechol and catechol to guaiacol, phenol and methanol.

Example 2

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 1.5 g of Ni 52/49 catalyst (BASF), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 305°C and 1 bar. 95% syringol conversion, 95% 3-methoxycatechol conversion and 70% phenol yield were obtained.

Example 3

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 0.5 g of Pricat Ni 6215P catalyst (Johnson

Matthey), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 305°C and 1 bar. 91% syringol conversion, 70% 3-methoxycatechol conversion, 67% phenol yield, 11% guaiacol yield and 9% cresol yield were obtained.

Example 4

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 0.5 g of Ni Sat 310 catalyst (Clariant), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 305°C and 1 bar. 76% syringol conversion, 70% 3-methoxycatechol conversion, 51% phenol yield, 11% guaiacol yield and 7% cresol yield were obtained.

Example 5

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 1.0 g of Ni 52/49 catalyst (BASF), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 305°C and 1 bar. 95% syringol conversion, 77% 3-methoxycatechol conversion, 60% phenol yield, 6% guaiacol yield and 9% cresol yield were obtained.

Example 6

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 1.0 g of Ni 52/49 catalyst (BASF), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 320°C and 1 bar. 95% syringol conversion, 71% 3-methoxycatechol conversion, 70% phenol yield, 5% guaiacol yield and 10% cresol yield were obtained.

Example 7

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 1.0 g of Ni 52/49 catalyst (BASF), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 335°C and 1 bar. 98% syringol conversion, 75% 3-methoxycatechol conversion, 79% phenol yield, 4% guaiacol yield and 11% cresol yield were obtained.

Example 8

Experimental procedure is same as Example 1. Hydrodeoxygenation reaction was conducted using 1.0 g of Ni 52/49 catalyst (BASF), 0.5 mL/min charcoal oil mixture (Solvay), 50 mL/min H₂, 55 mL/min N₂, 350°C and 1 bar. 98% syringol conversion, 77% 3-methoxycatechol conversion, 79% phenol yield, 5% guaiacol yield and 11% cresol yield were obtained.

CLAIMS

1. A method for producing a phenolic compound, comprising reacting a material containing a benzene compound comprising at least one hydroxyl group and one methoxy group [Compound A] with molecular hydrogen in the presence of a catalyst comprising a support and Ni, wherein the support comprises at least one oxide of Period 3 element and is free or substantially free of titanium.
2. The method according to claim 1, wherein the oxide is selected from the group consisting of SiO₂, Al₂O₃, MgO, more preferably SiO₂ and Al₂O₃.
3. The method according to claim 1 or 2, wherein the support comprises one oxide of Period 3 element and said oxide is SiO₂ or Al₂O₃ and preferably SiO₂.
4. The method according to claim 1 or 2, wherein the support comprises two oxides of Period 3 elements and said two oxides are SiO₂ and Al₂O₃.
5. The method according to any one of claims 1 to 4, wherein the Compound A is a benzene compound comprising one hydroxyl group and two methoxy groups [Compound A1] and preferably syringol, or a benzene compound comprising two hydroxyl groups and one methoxy group [Compound A2] and preferably 3-methoxycatechol.
6. The method according to any one of claims 1 to 5, wherein the material contains a Compound A1 and a Compound A2.
7. The method according to any one of claims 1 to 6, wherein the material further contains a benzene compound comprising at least two hydroxyl groups [Compound B] and preferably catechol.

8. The method according to any one of claims 1 to 7, wherein the phenolic compound comprises one or two hydroxyl groups and preferably one hydroxyl group.
9. The method according to any one of claims 1 to 8, wherein the phenolic compound is phenol, catechol or guaiacol and preferably phenol or guaiacol and more preferably phenol.
10. The method according to any one of claims 1 to 9, wherein the support comprises less than 5 wt%, preferably less than 1 wt%, more preferably less than 0.5 wt%, most preferably less than 0.1 wt% of Ti, based on the weight of the support.
11. The method according to any one of claims 1 to 10, wherein the loading of Ni is from 50 to 80 wt%, preferably from 50 to 65 wt%, based on the weight of the catalyst.
12. The method according to any one of claims 1 to 11, wherein the material contains at least 10 wt%, preferably at least 20 wt% and more preferably at least 30 wt% of the Compound A1, based on the weight of the material.
13. The method according to any one of claims 1 to 12, wherein the material contains at least 2 wt%, preferably at least 5 wt% and more preferably at least 10 wt% of the Compound A2, based on the weight of the material.
14. The method according to any one of claims 1 to 13, wherein the material contains at least 1 wt%, preferably at least 2 wt% and more preferably at least 5 wt% of the Compound B, based on the weight of the material.
15. The method according to any one of claims 1 to 14, wherein the weight ratio of the Compound A and the Compound B is from 1:1 to 75:1 and preferably from 7.5:1 to 12:1.

16. The method according to any one of claims 1 to 15, wherein the material reacts with molecular hydrogen at a temperature from 250 to 350°C and preferably from 305 to 350°C and/or a gas pressure of less than 5 bar, or less than 2 bar, or less than 1.5 bar, or even atmospheric pressure.

DRAWINGS

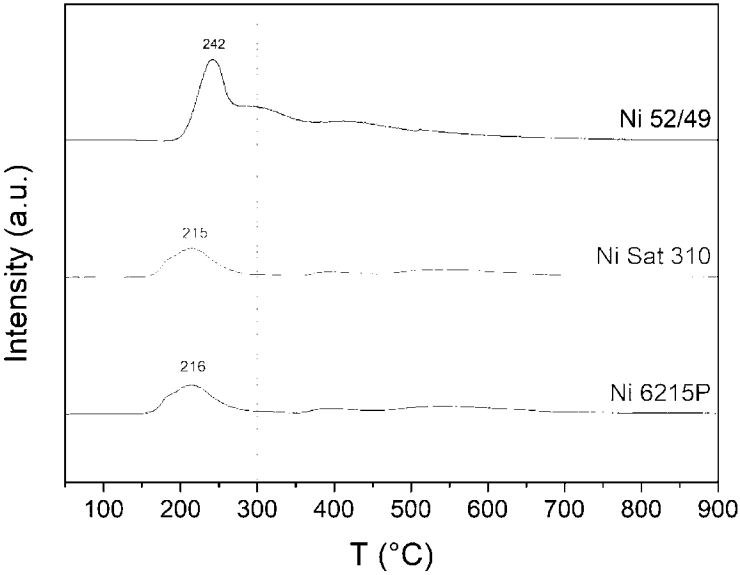


Fig. 1

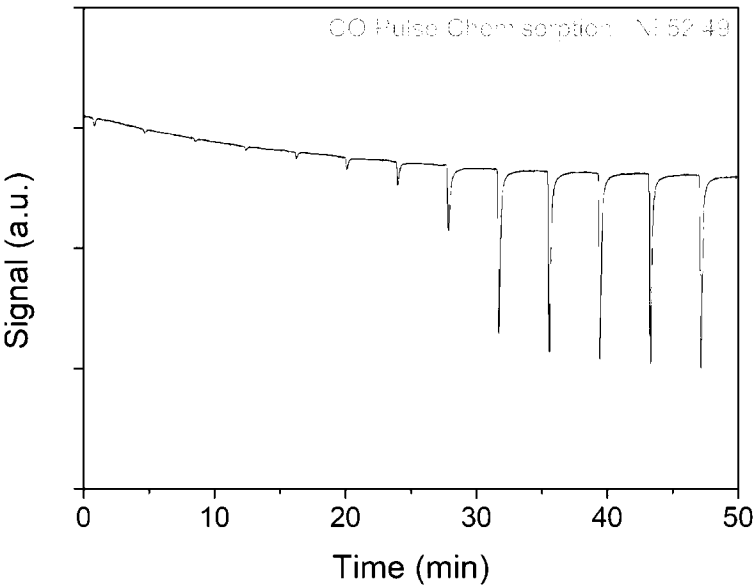


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/139909

A. CLASSIFICATION OF SUBJECT MATTER

C07C37/50(2006.01)i; C07C39/02(2006.01)n; C07C39/04(2006.01)n; B01J23/755(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C07C, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNTXT,CNKI,ENTXTC,VEN,CASREACT: phenol+, methoxy+, hydrodeoxygenation, hydrogen, syringol, +catechol, nickel, support, carrier, Al₂O₃, alumina, SiO₂, silica**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 110152672 A (ZHEJIANG NORMAL UNIVERSITY) 23 August 2019 (2019-08-23) claims 1-9, paragraphs 44-56, 86-89; example 10	1-4, 8-11, 16
X	Haowei Li et al. "Upgrading lignin bio-oil for oxygen-containing fuel production using Ni/MgO: Effect of the catalyst calcination temperature" <i>Applied Energy</i> , No. 253, 31 July 2029 (2029-07-31), 113613 part 3.4, Fig.6	1-2,5, 8-10, 12
A	CN 105189413 A (THE PROCTER & GAMBLE COMPANY) 23 December 2015 (2015-12-23) claims 1-25; paragraphs 15-16	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 September 2024

Date of mailing of the international search report

14 September 2024

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/139909

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	110152672	A	23 August 2019	None			
CN	105189413	A	23 December 2015	MX	2015012182	A	26 July 2016
				CA	2901590	A1	02 October 2014
				CA	2901590	C	05 September 2017
				JP	2016513626	A	16 May 2016
				US	2014275468	A1	18 September 2014
				US	9452422	B2	27 September 2016
				BR	112015023228	A2	18 July 2017
				EP	2970040	A1	20 January 2016
				EP	2970040	B1	15 November 2017
				ZA	201505967	B	29 March 2017
				WO	2014159040	A1	02 October 2014