

SUPPORTED CARBONYLATION CATALYST

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The invention relates to a supported catalyst, in which a metal of Group VIII of the periodic system (CAS version as printed in Chemical Engineering News, 63(5), 27, 1985) is immobilized on a carbon support. The invention also relates to the preparation of the supported catalyst and its use in a carbonylation process.

In EP-B-405433, the use of an iodide or bromide promoted rhodium catalyst system is disclosed in the carbonylation of butadiene to pentenoic acid in the presence of acetic acid and water. According to this disclosure the rhodium source is preferably $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{cyclooctadiene})\text{Cl}_2]_2$, $[\text{Rh}(\text{cyclooctadiene})-(\text{acetylacetonate})]$, RhI_3 and $\text{Rh}(\text{CO})_2\text{I}_3$. Thus, the rhodium is present in the reaction mixture as a component of a homogeneous catalyst system. Semi-heterogeneous catalyst systems are also mentioned. These systems have as a rhodium source a supported rhodium catalyst, for example Rh/C and Rh/alumina.

As a rule homogeneous catalyst systems are preferably used for the process of EP-B-405433 in spite of the apparent advantages of a heterogeneous catalyst system. This apparent advantage is the more simple catalyst-product separation of a heterogeneous catalyst system. The reason for this preference is that the heterogeneous carbonylation catalyst systems are usually not stable over a longer period of time. Leaching of the Group VIII-metal is the main reason for the poor catalyst stability.

The object of this invention is to provide a Group VIII metal-supported catalyst which is stable over a longer period of time when used as carbonylation catalyst.

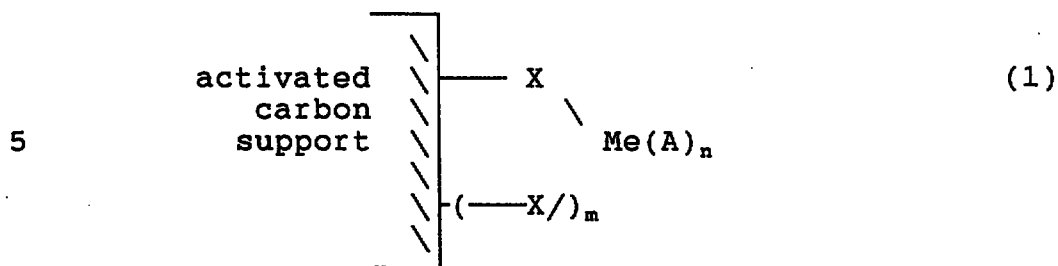
This object is achieved in that the catalyst comprises halogen atoms, the Group VIII metal and an

activated carbon support which support has a more hydrophobic surface than normal activated carbon, obtainable by subjecting the activated carbon to a temperature treatment in an inert medium, in which the
5 temperature is between 500 and 1100°C.

The catalyst according to the invention is more stable than the conventional Group VIII metal-supported carbon catalyst. The leaching of the Group VIII is almost totally avoided. Furthermore it has been observed that
10 almost no adipic acid is formed as by-product when carbonylating butadiene to pentenoic acid using a Rh-supported catalyst according to the invention in the process of EP-B-405433. When using homogeneous catalyst systems in the process of EP-B-405433 a considerable
15 amount of adipic acid is formed. The low selectivity to adipic acid is advantageous if the preferred product is pentenoic acid.

US-A-4158643 describes the preparation of a heterogeneous catalyst in which activated carbon is used
20 as support for a catalyst composition, particularly $\text{PdCl}_2\text{-CuCl}_2$, with which modified activated carbon is to be impregnated. The modification of the activated carbon comprises of an oxidative modification in which chemisorption of the oxygen by the activated carbon
25 support takes place. The present invention is different in that a temperature treatment of the activated carbon is performed.

Without being limited to theory it is believed that the catalyst has a structure according the following
30 general formula (1):



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in which X represents a halogen atom, Me represents a Group VIII metal atom, A represents one or more different organic or anorganic ligand groups in which n is 0 - 4 and m is 0 - 3.

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The Group VIII metal (Me) can be for example rhodium, palladium, platinum, ruthenium, iridium, nickel or cobalt. The halogen atom (X) can be for example F, Cl, Br, or I. Preferably X is Br, I or Cl and more preferably I.

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Group A may be one or more coordinating ligand groups, for example CO, H, halogen, for example F, Cl, Br, or I, or alkenes, for example the alkenically unsaturated substrate of the carbonylation reaction in which the supported catalyst is used for example butadiene.

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It is not fully understood how the halogen and Group VIII metal atoms are bonded to the activated carbon surface. Electrostatic and/or covalent bounds are believed to exist in this system. The catalyst is stable under reducing conditions. Oxidizing conditions may deactivate the catalyst. The catalyst is preferably stored under reducing conditions, for example, optionally in a solvent, under a carbon monoxide, nitrogen and/or hydrogen atmosphere.

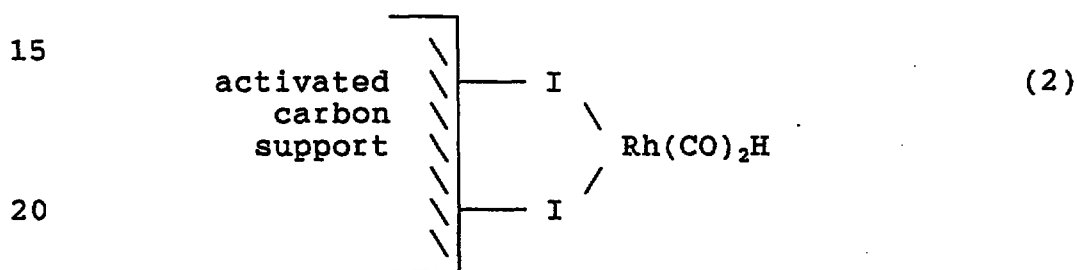
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An example of an interesting supported catalyst according to the invention is a catalyst in which the Group VIII metal is rhodium and X is I (iodine), in which m is preferably 0, 1 or 2. Other examples are (Me/X): the (Pd/Cl)-supported catalyst, in which m is preferably 0 or 1 and the (Rh/Br)-supported catalyst, in which m is

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preferably 0, 1 or 2. The description shall describe the Rh/I-supported catalyst in more detail. This does not mean that the invention is limited to this particular supported catalyst. The below described composition and the process to prepare the (Rh/I)-supported catalyst will in general also apply to other supported catalysts according to the invention.

It is believed that the activated configuration of the (Rh/I) supported catalyst during the carbonylation reaction is represented by the following general formula ($m=1$, $n=3$):



25 On the activated support iodine atoms may be present which do not bind with any rhodium atom. Therefore the amount of iodine atoms on the support will generally be larger than the amount of rhodium atoms which can be calculated according to formula (1). The amount of iodine can be for example between 50 and 3000 mmol/kg and the amount of rhodium can be for example between 10 and 1000 mmol/kg of supported catalyst.

35 The carbon support of the catalyst can be made starting from any ordinary activated carbon. The preparation of activated carbon is for example described in Active Carbon, by J.B. Donnet, R.C. Bansal and F.Stoecklin, Marcel Dekker, New York 1988: Activated carbon is usually prepared by first carbonization of any source of carbonaceous raw material, e.g. (pit)coal, wood,

sugar or vegetable oil. The carbonization is generally accomplished by heating the source in an inert atmosphere to a temperature not exceeding 600°C. The thus carbonized product is subsequently activated at temperatures between
5 400 and 900°C in the presence of a suitable oxidizing agent, e.g. steam, air, oxygen or carbon dioxide or any mixtures of these gasses. The active oxygen in the activating agent burns away the more reactive portions of the carbon skeleton as carbon monoxide. Two types of
10 activated carbon are generally known: Low (400-575°C) and High (575-900°C) Temperature Activated Carbon. These Activated Carbon supports can be obtained from companies like for example Lurgi (DESOREX ED 47®), American Norit Company (NORIT RB-1, SORBONORIT B-3) or the Kennecott
15 Corporation (CARBORUNDUM GAC-616GA) (product names between brackets). Other surface treatments are liquid phase treatments with HNO₃, H₃PO₄ or hydrogen peroxide. Preferably High Temperature Activated Carbon is used as the carbon support. Other examples of carbon support
20 material are graphite and graphite fibrils. The hydrophobicity of the carbon, obtained by heat treatment between 400-900°C in the presence of a suitable oxidizing agent is the hydrophobicity of "normal activated carbon" according to this invention.

25 Preferably the activated carbon support should not contain high amounts of impurities, for example SiO₂, Fe₂O₃ or Al₂O₃. Preferably the total amount of these impurities should be less than 1 wt%. These impurities may for example be present in commercially available activated
30 carbon which is originally obtained from pitcoal.

To obtain the most stable (with regard to Group VIII metal leaching) supported catalyst according to the invention it has been found that the choice and pre-treatment of the carbon support is very important. This
35 pre-treatment shall be described below.

As already explained above the content of SiO₂,

Fe₂O₃ and/or Al₂O₃ impurities in the carbon support should preferably be lower than 1 wt%. When a as such contaminated activated carbon is used the carbon should first be treated in order to remove these impurities. An
5 example of such treatment is described by L. Daza, S. Mendrioroz and J.A. Pajares, Carbon, 24, 1986, page 33. This treatment comprises two steps in which first the (Al) silicates are removed by a treatment with hot 20% aqueous NaOH and second the transition metal oxides are removed by
10 extraction with aqueous HCl.

Activated carbon with a more hydrophobic surface than normal activated carbon is obtainable by subjecting the activated carbon to a temperature treatment in an inert medium, in which the temperature is between 500 and
15 1100°C and preferably between 600 and 1000°C. The inert medium is usually an inert gas, for example nitrogen.

Preferably the activated carbon supported obtained with the above temperature treatment is subjected to a mild oxidation, preferably by contacting the
20 activated carbon with oxygen in water. For example by mixing the support particles in water and bubbling oxygen through this mixture at about room temperature and atmospheric pressure.

The activated carbon support used to prepare the
25 supported catalyst is preferably free of any free oxygen (O₂). To remove any free oxygen the activated carbon support is preferably heated under vacuum at a temperature between 20 and 200°C and flushed several times with an inert gas, for example nitrogen. During the actual loading
30 of the halogen and Group VIII metal the presence of any free oxygen should also be avoided in order to obtain the most active catalyst. The use of inert or (with oxygen) reactive gases, for example nitrogen, or hydrogen and/or carbon monoxide, during the preparation may ensure that no
35 free oxygen is present.

The actual Group VIII metal-supported catalyst

is preferably prepared by first promoting the thus pre-treated activated carbon support by contacting the carbon support with a strong acid with a $pK_a < 3$. The reaction conditions of this first step are not very critical. The temperature will generally be between 20 and 250°C. The pressure will generally be about atmospheric or slightly higher. It may be advantageous to use a solvent during this first step. Suitable solvents are water, and the solvents mentioned which can be used for the Group VIII metal loading. The acid is generally an anorganic acid, for example sulphuric acid or phosphoric acid. Preferably the acid is the corresponding hydrogen halide (HX), for example HI, HBr, HCl or HF. When using the corresponding hydrogen halide the support is simultaneously promoted and loaded with the halogen atoms. When a different acid is used the halogen atoms may be loaded in a next step, for example, simultaneously with the Group VIII metal loading. Separate loading of the halogen atoms is performed by contacting the promoted support with hydrogen halide.

In a next step the Group VIII metal is loaded on to the thus obtained halogen-carbon support by contacting the carbon support with a mixture comprising a Group VIII metal (Me) source dissolved in a suitable solvent.

The Group VIII metal source can be any material which will produce Group VIII metal ions when contacting the mixture with the carbon support. Among the materials which can be employed as the source of the Group VIII metal are their salts, oxides, Group VIII metal carbonyl compounds and coordination compounds of the Group VIII metals. Examples of Rh-sources are RhI_3 , $Rh(CO)_2I_3$, $Rh(III)nitrate$ trihydrate, $Rh(CO)I_3$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(acac)_3$, $Rh(CO)_2(acac)$, $Rh(C_2H_4)_2(acac)$, $[Rh(C_2H_4)_2Cl]_2$, $[Rh(CO)_2Cl]_2$, $[Rh(COD)Cl]_2$, $Rh_2[O_2C(CH_2)_6CH_3]_4$, $Rh_2(acetate)_4$, $[Rh_2Cl_2(CO)_4]$ or $RhCl_3 \cdot 3H_2O$, where acac is acetylacetonate and COD is 1,5-cyclooctadiene.

Suitable solvents are solvents in which the

Group VIII metal source can readily dissolve under the conditions of contacting the mixture with the carbon support. The choice of the solvent is not critical. It has been found that the solvents which can be used in the carbonylation reaction as described in the earlier mentioned EP-B-405433 are also examples of suitable solvents for the Group VIII metal loading step. Examples of solvents are water, acetone, C_1 - C_{10} halocarbon solvents, for example the chlorocarbon solvents, for example methylene chloride or ethylene chloride and C_2 - C_{20} carboxylic acids and mixtures thereof. Suitable carboxylic acids are aliphatic C_2 - C_{20} monocarboxylic acid, aliphatic C_4 - C_{20} dicarboxylic acids, benzoic acid, C_1 - C_3 alkyl-substituted benzoic acids and mixtures thereof. Preferred carboxylic acids are aliphatic C_2 - C_6 monocarboxylic acid, C_4 - C_7 dicarboxylic acid, benzoic acid and mixtures thereof. The most preferred acids are acetic, propionic, butyric, 2-methylbutyric, valeric and caproic acids and mixtures thereof.

The concentration of the Group VIII metal source is not critical. Higher concentrations are favorable because the loading of the Group VIII metal will be more efficient. The maximum concentration will depend on the solubility of the Group VIII metal source in the mixture.

The promoting step and the loading of the support with the halogen and Group VIII metal may be advantageously performed in one step. To perform this in one step the corresponding hydrogen halide is added to the mixture of the dissolved Group VIII metal.

The concentration of hydrogen halide during promoting and/or during the Group VIII metal loading is preferably between 1 and 100 mmol/l.

The temperature at which the Group VIII metal loading is performed is preferably between 20 and 250°C. Lower temperatures are possible but the increased contact time would not be practical.

Preferably the Group VIII metal loading is performed in the presence of hydrogen at a pressure of between 0.1 and 10 MPa. This is advantageous because any unwanted Rh(III) species are thus converted to the preferred Rh(I) species.

Preferably the loading of the Group VIII metal is performed in the presence of carbon monoxide, because a more stable catalyst is obtained. Preferably the carbon monoxide pressure is between 0.1 and 10 MPa. The use of carbon monoxide is especially advantageous when a Group VIII metal source is used in which 2 or more Group VIII metal atoms are present in the molecule of the Group VIII metal source. For example 2 rhodium atoms are present in an example of a possible rhodium source $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ and 1 rhodium atom is present in another possible rhodium source: RhI_3 . Furthermore by treating the catalyst with carbon monoxide the active carbonylation catalyst of formula (2) is obtained. Such an active supported catalyst may however also be formed in situ during the carbonylation reaction when starting from a supported catalyst in which other ligand groups than carbon monoxide are bound to the Group VIII metal. This means that during transportation or storage of the supported catalyst other ligand groups than carbon monoxide may be present.

The molar ratio between the Group VIII metal source and the hydrogen halide in the mixture is preferably between 1 : 1 and 1 : 20.

In view of the favourable results obtained with the catalyst, the invention also relates to a supported catalyst on a carbon support material obtainable by the method of preparing the catalyst as described above.

The supported catalyst according to the invention can advantageously be used as catalyst for various carbonylation reactions of organic compounds. An example of a possible carbonylation reaction is a reaction between an alkenically unsaturated substrate or an

alkyliodide, carbon monoxide and a reactive compound, for example water or carboxylic acids, alkanols, for example methanol, ethanol or propanol. Examples of suitable alkyl iodides are C_1 - C_{15} alkyl iodides, for example

5 methyl iodide, 2-iodobutane, 1-iodobutane, 2-iodobutene, 1-iodobutene or iodovaleric acid and isomers thereof.

Examples of suitable alkenically unsaturated organic compounds are C_1 - C_{15} alkenes, for example ethene, propene, 1-butene, butadiene, 1-hexene, 1-heptene or 1-octene or

10 functionalized C_1 - C_{15} allylic compounds, for example 1-methoxy 2-butene, 3-methoxy 1-butene, 1-ethoxy 2-butene, 3-methoxy 1-butene, 2-butenyl acetate, 1-butene 3-carbonate, 2-butene 1-carbonate, 3-hydroxy 1-butene and 1-hydroxy 2-butene. Another example of a possible

15 carbonylation reaction is the carbonylation in the liquid phase of methanol with carbon monoxide and a hydrogen iodide or methyl iodide in a process to prepare acetic acid, methyl acetate or acetic acid anhydride.

The supported catalyst is especially
20 advantageous when used for the carbonylation of alkenically unsaturated organic compounds in a process to prepare the corresponding carboxylic acids or alkyl esters.

A preferred carbonylation process, in which the
25 Rh/I-supported catalyst according to the invention is used, is the bromide or iodide promoted carbonylation of butadiene and water as for example described in the above mentioned EP-B-405433. The resulting pentenoic acid is an important intermediate in a process to prepare adipic acid
30 (precursor for Nylon-6.6) or ϵ -caprolactam (precursor for Nylon-6). The pentenoic acid may also be esterified with an alkanol to an alkyl pentenoate. The reaction conditions to perform the carbonylation are generally as described in the aforementioned EP-B-405433. The pentenoic acid is
35 prepared by reacting butadiene in a solvent, carbon monoxide and water in the presence of the Rh/I-supported

catàlyst according the invention and a promoter selected from the class consisting of bromide and iodide, at a temperature in the range of 40 to 200°C and at a carbon monoxide partial pressure in the range of 0.5 to 20 MPa in
5 a suitable organic solvent. The solvent which can be used are the same as described above for the solvents which may be used during the Group VIII metal loading. The solvent is preferably acetic acid, the saturated carboxylic acids which are formed as by-products in the carbonylation and
10 high boiling carboxylic acids (with a boiling point higher than that of pentenoic acid). For example adipic acid, valeric acid and/or C₉-carboxylic acids, alkyl iodides, for example methyl iodide, 2-iodobutane, 1-iodobutane, 2-iodobutene or 1-iodobutene.

15 The promoter can be those promoters as mentioned in EP-B-405433 (with the exception of the RhI₃ for obvious reasons) and H₂SO₄, HBF₄ or HFSO₃. Preferred promoters are HI, HBr or methyl iodide. The molar ratio (dissolved) promoter and (heterogeneous) rhodium (on the supported
20 catalyst) is preferably between 1:1 and 20:1 calculated for a volume of reaction mixture and supported catalyst.

The concentration of promoter is preferably between 0 and 5000 ppm.

25 Water should preferably not be present in a large excess. Preferably water is present in less than 15 wt% and more preferably in less than 10 wt% calculated on the total liquid reaction mixture including the solvent(s), promoter(s) and reactants but without the supported catalyst.

30 The process may be performed in for example a slurry reactor or a packed bed reactor. After the reaction the pentenoic acid can be isolated by for example extraction.

35 The invention shall be elucidated with the following non-limiting examples.

Example I

100 gram of activated carbon (DESOREX ED 47 of the LURGI company) was treated with an aqueous NaOH (20%) solution at 90°C for two weeks. Subsequently the carbon
5 was subjected to a Soxleth-extraction with water for one week. Subsequently the carbon was subjected to a Soxleth-extraction with 2N HCl for four weeks. Subsequently the carbon was subjected to a Soxleth-extraction with water for three weeks. The thus obtained carbon had less than 1
10 wt% of SiO₂, Fe₂O₃, and Al₂O₃ impurities.

The carbon support obtained was subsequently dried and heated in an inert nitrogen atmosphere (0.3 MPa), in which the temperature was increased with 100°C per hour to 600°C. The temperature was kept at 600°C for
15 16 hours. After cooling the carbon was contacted with water for two weeks in which water mixture oxygen was bubbled through.

In a 100 ml autoclave 15 g of this carbon support was contacted with a solution of 50 ml acetic
20 acid, 0.67 g of 56% HI (3.0 mmol) and 146 mg of [Rh₂(CO)₄Cl₂] (0.38 mmol) at a pressure of 0.3 MPa H₂ and 1.7 MPa CO and at a temperature of 130°C for 72 hours. The liquid solution was removed from the catalyst while the pressure was maintained at 0.5 MPa. The thus obtained
25 catalyst will be referred to as T-600. See also Table 1.

Example II

Example I was repeated except that the temperature was increased at the same rate to 900°C
30 instead of 600°C and kept at that temperature for 16 hours. The thus obtained catalyst will be referred to as T-900. See also Table 1.

Example III

35 Example I was repeated except that the temperature was increased at the same rate to 1100°C

instead of 600°C and kept at that temperature for 16 hours. The thus obtained catalyst will be referred to as T-1100. See also Table 1.

5 Comparative experiment A

Example I was repeated except that no temperature treatment was performed prior to the Rh-loading. The thus obtained catalyst will be referred to as T-0. See also Table 1.

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Table 1

example	A	I	II	III
catalyst	T-0	T-600	T-900	T-1100
I (mmol/g)	370	650	770	310
Rh (mmol/g)	29	61	79	17

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Example IV

In the autoclave of Example II, which contained about 15 g of the Rh supported catalyst (T-900), was filled with a solution of 39 g acetic acid (99.8%), 0.51 g H₂O, 292 mg (56%) HI (1.28 mmol) and 240 mg of propionic acid (internal standard). The autoclave was pressurized to 4.0 MPa with CO and heated to 130°C. Butadiene (0.6 g) was injected immediately and the pressure was increased to 7.0 MPa with additional CO. After 300 minutes a sample was taken and analyzed by gas chromatography. Subsequently the pressure was let off to 0.5 MPa and the liquid solution was separated from the catalyst which remained in the autoclave. The above sequence was repeated 7 more times (resulting in runs 1-8). See table 2 for results.

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Comparative experiment B

Example IV was repeated, except that now the autoclave containing the supported catalyst (T-0) obtained

in Comparative experiment A was used. The results are shown in Table 2.

Table 2

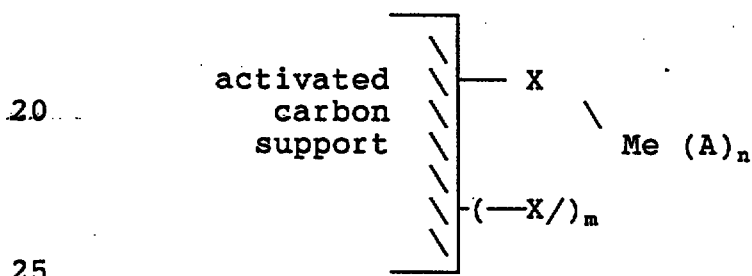
5	example	B	IV
	catalyst	T-0	T-900
	sel 3PA in first run (1)	91	91
	sel adipic acid (2)	0	0
10	conversion of butadiene in first run (%)	70	70
	leaching after one run (3)	10	1.2
	after 4 runs	9.5	0.8
	after 6 runs	9.5	0.4
15	after 8 runs	8.8	0.4

- (1) selectivity of pentenoic acid in (mol pentenoic acid)/(mol butadiene converted)*100%
 - (2) selectivity adipic acid. See (1)
 - (3) leaching in ppm Rh in reaction mixture after one run. The sample for measuring the Rh concentration was taken under reaction conditions at 130°C.
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C L A I M S



1. Supported catalyst, in which a metal of Group VIII of the periodic system is immobilized on a carbon support, characterized in that the catalyst comprises halogen atoms, the Group VIII metal and an activated carbon support which support has a more hydrophobic surface than normal activated carbon, obtainable by subjecting the activated carbon to a temperature treatment in an inert medium, in which the temperature is between 500 and 1100°C.
2. Supported catalyst according to claim 1, characterized in that the metal of Group VIII is bound to the activated carbon support as shown in the following general formula:



- in which X represents the halogen atom, Me represents the Group VIII metal, A an organic or anorganic group, n is 0-4 and m is 0-3.
3. Supported catalyst according to any one of claims 1-2, characterized in that the Group VIII metal is rhodium.
 4. Supported catalyst according to any one of claims 1-3, characterized in that the halogen is iodine, bromide or chloride.
 5. Process to prepare a supported catalyst, by (a) subjecting activated carbon to a temperature treatment in an inert medium, in which the temperature is between 500 and 1100°C, and performing



- the next steps separately or simultaneously: (b) promoting the thus treated activated carbon support by contacting the carbon support with a strong acid with a $pK_a < 3$, (c) contacting the promoted support with hydrogen halide corresponding with the halogen atoms of the catalyst, (d) contacting the promoted carbon support with a mixture of a Group VIII metal source dissolved in a solvent.
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6. Process according to claim 5, characterized in that the strong acid is the hydrogen halide of step (c) and that step (b) and step (c) are combined in one step.
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7. Process according to any one of claims 5-6, characterized in that carbon monoxide is present in step (d).
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8. Process according to any one of claims 5-7, characterized in that the contacting with the group VIII metal source (d) is performed in the presence of hydrogen at a pressure of between 0.1 and 10 MPa.
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9. Process according to any one of claims 5-8, characterized in that the strong acid and the hydrogen halide is HI and the metal of the group VIII metal source is rhodium.
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10. Process according to any one of claims 5-9, characterized in that the activated carbon obtained in step (a) is contacted with oxygen in water prior to step (b).
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11. Supported catalyst on a carbon support material obtainable by any one of the processes according to claims 5-10.
12. Use of the supported catalyst according to any one of claims 1-4 or 11 or as obtained by the process according to any one of claims 5-10 as a catalyst in a carbonylation reaction.
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13. Process to prepare pentenoic acid by a bromide or iodide promoted carbonylation of butadiene with



5 carbon monoxide and water in which a supported catalyst according to any one of claims 1-4 or 11 or as obtained by the process according to any one of claims 5-10, in which the Group VIII metal is Rh and the halogen is I, is used.