

HYDROGENATION PROCESS USING CATALYST COMPRISING ORDERED INTERMETALLIC COMPOUND

FIELD OF THE INVENTION

5 The present invention relates to a process for the hydrogenation, in particular the selective hydrogenation of unsaturated hydrocarbon compounds using a hydrogenation catalyst comprising a specific ordered intermetallic compound, to a catalyst comprising a support and the above
10 specific ordered intermetallic compound supported thereon, and to the use of a binary Pd-Ga ordered intermetallic compound as a catalyst.

BACKGROUND ART

15 Selective hydrogenations of unsaturated hydrocarbon compounds are of high industrial significance. The pyrolysis of naphtha for the production of ethene, propene, butanes, 1,3-butadiene and aromatics is a key process in the modern
20 petrochemical industry. For the nearly complete removal of alkynic compounds from the C₂, C₃ and C₄ cuts, selective hydrogenations are generally used.

For instance, the hydrogenation of acetylene is an important
25 industrial process to remove traces of acetylene in the ethylene feed for the production of polyethylene. Because acetylene poisons the catalyst for the polymerisation of ethylene to polyethylene, the acetylene content in the ethylene feed has to be reduced to the low ppm range.
30 Moreover, economic efficiency requires high selectivity of acetylene hydrogenation in the presence of an excess of ethylene to prevent the hydrogenation of ethylene to ethane.

Typical hydrogenation catalysts contain palladium dispersed
35 on metal oxides. While palladium metal exhibits high activity, e.g. in the hydrogenation of acetylene, it possesses only limited selectivity because of the formation

of ethane by total hydrogenation and C₄ and higher hydrocarbons by oligomerisation reactions.

5 Modification of palladium catalysts by adding promoters or alloying with other metals has been shown to result in an increased selectivity and long-term stability in acetylene hydrogenation. For instance, increased selectivity in semi-hydrogenation of alkynes was reported for Pd combined with Ag
10 (US 4,404,124; and D. C. Huang et al., Catal. Lett. 53, 155 - 159 (1998)), Sn (S. Verdier et al., J. Catal., 218, 288 - 295 (2003)), Au (T. V. Choudhary et al., Catal. Lett., 86, 1 - 8 (2003)), Ni (P. Miegge et al., J. Catal., 149, 404 - 413 (1994), and Pb (W. Palczewska et al., J. Mol. Catal., 25, 307
15 - 316 (1984)). However, the catalytic performance of these modified Pd catalysts remains insufficient and further improvements in selectivity may decrease the costs for the production of polyethylene. In addition to selectivity, the long-term stability of palladium catalysts has to be improved
20 further.

The C₃ cut (propylene) is generally purified by selective hydrogenation of propyne (methylacetylene) and propadiene (allene), and the obtained propylene may be further processed
25 to polypropylene.

Another important selective hydrogenation in industry is the removal of traces of 1,3-butadiene from the C₄ fraction after the extractive separation thereof. Pd/Al₂O₃ catalysts are
30 commonly used in this reaction. Furthermore, the selective hydrogenation of 1,5-cyclooctadiene, obtained by cyclic dimerization of 1,3-butadiene, to cyclooctene on Pd/Al₂O₃ and of benzene to cyclohexene on ruthenium catalysts are of importance.

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In all of these selective hydrogenations, further improvements of the selectivity to the desired product and an

increased long term stability of the used catalyst have been strongly desired.

5 The intermetallic compounds PdGa or Pd₃Ga₇ are described by E. Hellner et al. in Z. Naturforsch. 2a, 177 - 183 (1947) and by K. Khalaff et al. in J. Less-Common Met. 37, 129 - 140 (1974). However, any catalytic potential of these compounds has been unknown so far.

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The use of ordered intermetallic compounds as catalysts in a variety of different reactions is generally described in US 2004/0126267 A1 and WO 2004/012290 A2. However, these documents fail to disclose the application of this type of
15 compounds to hydrogenations, let alone selective hydrogenations. In fact, the focus of these references is on their use in fuel cells. In addition, these patent applications fail to disclose the specific Pd based intermetallic compounds of the present invention.

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It is therefore an object of the present invention to provide a process for the hydrogenation of unsaturated hydrocarbon compounds, in particular of ethyne (acetylene) in admixture with a large excess of ethene (ethylene) to afford ethene,
25 which overcomes the drawbacks of the prior art as outlined above, and which shows an improved selectivity to the target product. It is another object to provide novel catalysts having the above beneficial properties in selective hydrogenation reactions, in particular in the selective
30 hydrogenation of acetylene to afford ethylene when ethylene is present in an excessive amount.

SUMMARY OF THE INVENTION

35 The above objects are attained by a process for the hydrogenation of at least one unsaturated hydrocarbon compound using a hydrogenation catalyst comprising a specific

ordered intermetallic compound. The ordered intermetallic compound used in the process of the invention comprises at least one metal of type A capable of activating hydrogen, and
5 at least one metal of type B not capable of activating hydrogen, and the structure of the intermetallic compound is such that at least one kind of type A metals is mainly surrounded by atoms of the metal of type B. According to another aspect, the present invention is concerned with a
10 catalyst comprising a support and the above ordered intermetallic compound supported thereon.

According to still another aspect, the present invention relates to the use of a binary Pd-Ga ordered intermetallic
15 compound as a catalyst.

Preferred embodiments of the present invention are subject of the dependent claims.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the coordination of Pd atoms in PdGa (Fig. 1a) and in Pd₃Ga₇ (Fig. 1b).

25 Fig. 2 shows the evolution of in situ XRD patterns measured during thermal treatment of PdGa in 50% hydrogen in helium from 323 to 723 K.

Fig. 3 shows the conversion (Fig. 3a) and selectivity (Fig. 3b) of PdGa (40 mg), Pd₃Ga₇ (100 mg), Pd/Al₂O₃ (0.15 mg), and Pd₂₀Ag₈₀ (200 mg) in the hydrogenation of acetylene in admixture with an excess of ethylene at 473 K.
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Fig. 4 shows the conversion (Fig. 4a) and selectivity (Fig. 4b) of as-prepared Pd₂Ga (10 mg), Pd₂Ga milled in argon (0.8 mg) and Pd/Al₂O₃ (0.1 mg) in the hydrogenation of acetylene in admixture with an excess of ethylene at 473 K.
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Fig. 5 shows the conversion (Fig. 5a) and selectivity (Fig. 5b) of Pd₂Ge (0.5 mg) and PdZn (100 mg) in the hydrogenation of acetylene in admixture with an excess of ethylene at 473 K.

Fig. 6 shows the conversion and selectivity of the hydrogenation of acetylene to give ethylene in the presence of an excess of ethylene at 473 K using PtZn as a catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The benefits of the hydrogenation process of the present invention can be achieved preferentially if the hydrogenation proceeds selectively.

Everyone active in the field of hydrogenation catalysis is familiar with the term "selective hydrogenations". Generally, a chemical reaction is referred to as being selective if this reacts preferentially with one of several functional groups of similar reactivity which are present in the molecules of the reaction mixture, whereas the remaining functional groups of this type react to a significantly lower degree, *i.e.* they do hardly react in the case of highly selective reactions. Differently stated, a hydrogenation is selective if this is selecting a certain hydrogenation reaction (or certain hydrogenation reactions) from the various hydrogenation reactions which are possible in the reaction mixture. Consequently, term "selective hydrogenation" as it is used herein covers *e.g.*, the following situations: (1) some of the unsaturations (*e.g.* double and/or triple bonds) of the unsaturated hydrocarbon compound to be reacted are hydrogenated with preference whereas the other unsaturations react to a significantly lower degree, and (2) in the case that one or more unsaturations of the unsaturated hydrocarbon compound to be reacted can be hydrogenated twice (*e.g.* triple bonds), they

are hydrogenated with preference only once, and the 2nd reaction step is hardly observed. For the purpose of the present invention, a hydrogenation is referred to as
5 selective if the molar ratio of the desired target compound to the undesired target compound(s) is larger than 1 : 1, preferably more than 2 : 1, more preferably more than 5 : 1, and most preferably 10 : 1.

10 A typical example of situation (1) is the hydrogenation of an alkadiene to afford mainly, preferably almost exclusively, the corresponding alkene without substantial reaction of the alkene to the corresponding alkane. Situation (2) may be exemplified by the reaction of an alkyne to give mainly the
15 corresponding alkene, whereas the consecutive reaction of the alkene to afford the alkane hardly takes place. As will be appreciated from the above, the two situations are not mutually exclusive. That means, both of the above situations may exist in the selective hydrogenation of a specific
20 molecule. In the case of the acetylene reaction in a large excess of ethylene which corresponds to situation (2), it is important that the ethylene, in spite of its large concentration, is hardly converted to ethane.

25 Examples of selective hydrogenations are described in the Background Art section of the present specification.

The unsaturated hydrocarbon compound used in the selective hydrogenation process of the present invention is not limited
30 in kind as long as this contains one or more unsaturations susceptible to hydrogenation and poses a selectivity problem as outlined above. For example, the unsaturated hydrocarbon compound may be an unsaturated carbonyl compound, e.g. a compound having both a carbonyl moiety and a carbon-carbon
35 double bond in the molecule. However, the unsaturated hydrocarbon compound preferably contains, as unsaturations susceptible to hydrogenation, carbon-carbon double and/or

carbon-carbon triple bonds, and is free from further unsaturations susceptible to hydrogenation, *i.e.* hydrogenable group(s). According to a more preferred embodiment, the
5 unsaturated hydrocarbon compound is selected from the group consisting of alkadienes, alkatrienes and alkapolyenes; alkynes, dialkynes, trialkynes and polyalkynes; and aromatic compounds. The alkadienes, alkatrienes and alkapolyenes, and the alkynes, dialkynes, trialkynes and polyalkynes cover
10 both, alicyclic and cyclic compounds. Still more preferably, the unsaturated hydrocarbon compound is selected from the group of alkadienes, cycloalkadienes, alkynes and benzene.

The alkadiene may be 1,3-butadiene, which will be converted
15 by way of the selective hydrogenation of the present invention, mainly to 1-butene, without being fully hydrogenated to butane to a significant degree. The cycloalkadiene is, for example, 1,5-cyclooctadiene which will afford upon the selective hydrogenation of the invention
20 cyclooctene, while cyclooctane resulting from the full hydrogenation is a minor product. The selective hydrogenation of benzene will afford cyclohexene with minor amounts of cyclohexadiene and cyclohexane. An example of a selective hydrogenation of a triple bond in the presence of a double
25 bond is the purification of 1,3-butadiene by hydrogenation of vinyl acetylene present in the mixture. Still another example of a selective hydrogenation is the reaction of nitrobenzene to aniline.

30 The alkyne is preferable ethyne (acetylene), and this is the most preferred embodiment of the present invention. Through the process for the selective hydrogenation of the invention, ethyne will predominantly be converted to ethene (ethylene) while the hydrogenation of ethene to afford ethane is
35 negligible. This is even so when the selective hydrogenation of ethyne is carried out under reaction conditions where ethyne is present in admixture with an excess of ethene in

relation to ethyne, which is a particularly preferred embodiment of the selective ethyne hydrogenation according to the present invention. Most preferably, ethene is present in
5 the reaction mixture to be hydrogenated in a large excess in relation to ethyne. The ethyne to ethene weight ratio in the starting mixture of the selective ethyne hydrogenation of the invention is preferably 1 : 10 to 1 : 10^6 , more preferably 1 : 50 to 1 : 10^3 . In industrial processes, the ethene to
10 ethyne weight ratio in the mixture obtained after the selective hydrogenation is typically as large as $> 10^6$.

The selective hydrogenation of phenyl acetylene to styrene in excess of styrene is another example of a selective
15 hydrogenation. As will be appreciated, that reaction is the polystyrene counterpart of the selective acetylene hydrogenation in excess of ethylene in the feed used for the preparation of polyethylene.

20 As used herein, the term "ordered intermetallic compound" refers to a compound that consists of more than one metal and has an ordered crystal structure. For the purpose of the present specification, boron (B), silicon (Si) and arsenic (As) are regarded as "metals" since they can form
25 intermetallic compounds. In the ordered crystal structure, substantially all unit cells include the same arrangement of metal atoms.

The catalyst for use in the invention may be an unsupported
30 or a supported catalyst. If it is an unsupported catalyst, the ordered intermetallic compound may make up at least 90%, preferably at least 95%, more preferably at least 99% of the catalyst. The balance to 100% may, for example, consist of volumes of a non-ordered intermetallic compound which may
35 e.g., be due to the preparation method of the ordered intermetallic compound. Most preferably, the catalyst for use

in the selective hydrogenation process of the invention consists entirely of an ordered intermetallic compound.

It will be appreciated that defects which usually cannot be completely avoided in a real crystal may be present in the ordered intermetallic compound. Such defects can cause a small number of unit cells in the ordered intermetallic compound to have a different arrangement of metal atoms than the majority of the unit cells. Defect types include for example vacancies, interstitials, atom substitutions and anti-site defects.

Crystal imperfections due to the presence of defects will lead to a certain homogeneity range of the ordered intermetallic compounds. However, the formulae used in the present specification refer to the ideal crystal structure. As will be appreciated from the above, the stoichiometric ratio of the metals forming the ordered intermetallic compound as used in the formula may vary up and down. To give an example, if a binary ordered intermetallic compound is represented by the general formula A_xB_y , then x and y may independently be an integer of 1 or more. In the present specification, AB (*i.e.* $x = y = 1$) and A_3B_7 represent ordered intermetallic compounds having a certain stoichiometric ratio of the constituent metals (for example, PdGa and Pd_3Ga_7). Taking account of the above homogeneity range the values of x and y may be slightly greater or slightly less than the whole numbers indicated in the formula. For instance, in the case of AB (*i.e.* $x = y = 1$), such as in PdGa, the actual values of x or y may be between about 0.9 and 1.1.

The ordered intermetallic compounds of the invention may have a variety of stoichiometric ratios. Preferably, the ordered intermetallic compounds are binary compounds, *i.e.* those comprising two types of metals, but they may also be ternary or multinary intermetallic compounds. An example of a ternary

ordered intermetallic compound for use in the present invention is Pd_2PtGa_3 .

5 The ordered intermetallic compounds within the meaning of the present invention are to be distinguished from metal alloys and metal solid solutions. Alloys and solid solutions do not have an ordered atomic structure, as described above. Metal atoms are arranged randomly in unit cells of alloys and solid
10 solutions.

Ordered intermetallic compounds also generally have a more stable atomic arrangement in comparison to alloys and solid solutions. This results in an enhanced lifetime of the
15 catalyst under reaction conditions. In alloys and solid solutions, atoms are prone to migration with an associated reduction of catalytic performance.

The ordered intermetallic compound for use in the process
20 according to the present invention comprises at least one metal of type A capable of activating hydrogen, and at least one metal of type B not capable of activating hydrogen, and the structure of the ordered intermetallic compound is such that at least one kind of type A metals, preferably all type
25 A metals, is mainly surrounded by atoms of the metal of type B. In this context, the term "mainly" accounts for the fact that there may be defects due to atom substitutions so that there may be some metals of type A in the crystal structure of the intermetallic compound, in the first coordination
30 sphere of which there are also one or more of type A metal atoms. The above requirement of being mainly surrounded is fulfilled if at least 50%, preferably at least 80%, more preferably at least 90%, and most preferably about 100% of the first coordination sphere of least one kind of the type A
35 metals is occupied by atoms of type B metals. The above situation that the type A metal atoms (Pd) are mainly, more specifically exclusively surrounded by type B metal atoms

(Ga) is illustrated for PdGa in Fig. 1a, and for Pd₃Ga₇ in Fig. 1b. The embodiment of the ordered intermetallic compounds for use in the process of the invention where the type A metal atoms are completely surrounded by type B metal atoms, *i.e.* where about 100% of the first coordination sphere of the at least one kind of type A metal is occupied by atoms of type B metals does, however, not exclude the presence of defects. The feature that the structure of the ordered intermetallic compound is such that at least one kind of type A metals, preferably all type A metals, is surrounded mainly by atoms of the metal of type B indicates that the atoms of type A metal are predominantly coordinated to atoms of type B metals, *i.e.* coordinated at least 50%, preferably at least 80%, and more preferably about 100% to type B metals.

The molar ratio of the metals of type A and B (A:B) may be from 20 : 1 to 1 : 20. Typically it is from 2 : 1 to 1 : 20, preferably from 1 : 1 to 1 : 20, more preferably from 1 : 1 to 1 : 5. The metal of type A is not limited in kind, as long as this is capable of activating hydrogen. However, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au are preferred. Cr, Mo, W, Fe, Co, Rh, Ni, Pd and Pt are more preferred. There is no particular limitation of the metals of type B, either. According to a preferred embodiment, these metals are selected from the group consisting of B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Zn, Cd and Hg, *i.e.* the metals of the groups 12, 13, 14 and 15 of the Periodic Chart. According to a preferred embodiment, the mentioned metals *e.g.* of the groups 12, 13, 14 and 15 of the Periodic Chart as type B metals are combined with palladium and/or platinum and/or another type A metal to form the ordered intermetallic compound, which is more preferably a binary ordered intermetallic compound.

The intermetallic compound for use in the process of the present invention is more preferably selected from

intermetallic compounds of Pd with at least one of B, Al, Ga, In, Tl, Si, Ge, Sn and Zn, intermetallic compounds of Pt with at least one of Al, Ga, In, Tl, Sn and Zn, and intermetallic
5 Pd/Pt compounds with at least one of Al, Ga, In, Tl and Sn, such as Pd_2PtGa_3 . Preferably, the ordered intermetallic compound is a binary compound of Pd in combination with B, Al, Si, Ge, Zn or Ga, more preferably it is a binary compound of Pd in combination with Ge, Zn or Ga. According to a still
10 more preferred embodiment, the ordered intermetallic compound for use in the process of the present invention is an ordered binary Pd-Ga intermetallic compound. According to another preferred embodiment, the ordered intermetallic compound is a binary compound of Pt in combination with Zn. The above
15 intermetallic compounds, in particular ordered binary intermetallic compounds comprising Pd are preferably used in the selective hydrogenation of carbon-carbon multiple bonds, especially the selective hydrogenation of carbon-carbon triple bonds to give the corresponding alkene. The compounds
20 to be hydrogenated are preferably free of any unsaturated groups amenable to hydrogenation other than the carbon-carbon triple bond(s).

The specific ordered intermetallic compound to be used in the
25 selective hydrogenation process of the present invention is preferably Pd_2Ga , PdGa , PdGa_5 , Pd_3Ga_7 , PdSn , PdSn_2 , Pd_2Ge , PdZn , PtGa or PtZn ; more preferably PdGa , Pd_2Ga , PdGa_5 or Pd_3Ga_7 ; and most preferably PdGa , Pd_2Ga or Pd_3Ga_7 . These specific intermetallic compounds may be used in the selective
30 hydrogenation of any unsaturated hydrocarbon, in particular, in the following reactions: (cyclo)alkadiene $\rightarrow$ (cyclo)alkene and alkyne $\rightarrow$ alkene (in particular, ethyne $\rightarrow$ ethene).

In a particular preferred embodiment of the selective
35 hydrogenation process of the invention, the at least one unsaturated hydrocarbon compound is ethyne (acetylene), and the intermetallic compound is an ordered binary Pd-Ga

intermetallic compound, preferably PdGa or Pd₃Ga₇. Even more preferably, the selective hydrogenation of ethyne to ethene is carried out with the above ordered intermetallic compounds under reaction conditions where the ethyne starting material is present in admixture with ethene, the ethene being present in large excess in relation to ethyne.

It was surprisingly found by the present inventors that intermetallic compounds as recited in Claim 1 offer distinct advantages in selective hydrogenations, *e.g.*, over the supported monometallic catalysts of the prior art, such as supported palladium, platinum and rhodium catalysts, and over alloyed or promoted palladium catalysts, in terms of selectivity to the desired product. Without wishing to be bound by theory, it is assumed that the enhanced selectivity is due to the defined structure of active sites allowing only certain adsorption geometries of the unsaturated hydrocarbon compound to be hydrogenated. Because the atoms of at least one metal of type A, preferably all type A atoms in the structure of the ordered intermetallic compound are mainly surrounded by type B atoms, the individual atoms of the type A metals are isolated. This is considered to avoid an oversupply of activated hydrogen, and leads to an enhanced selectivity. Due to the isolation of type A atoms, only some adsorption geometries of the reactants are possible.

According to another aspect, the invention is concerned with supported catalysts comprising the ordered intermetallic compounds as described above in connection with the hydrogenation process of the present invention.

Catalyst screening methods may be used to readily determine which ordered intermetallic compounds are well-suited to catalyse a specific type of (selective) hydrogenation. Suitable screening methods are described in A. Hagemeyer, A. Strasser, P. Volpe, F. Anthony, High-throughput screening in

heterogeneous catalysis: Technologies, strategies and applications, Wiley-VCh, Weinheim, 2004.

5 The skilled person in the field of hydrogenation catalysis will readily select and optimise the reaction parameters for a certain selective hydrogenation reaction. For instance, the temperature range of industrial selective hydrogenations is typically 10° to 300°C, preferably 20° to 250°C, most
10 preferably 30° to 200°C. The pressure is generally 1 to 100 bar, preferably 2 to 75 bar, most preferably 5 to 50 bar. For more details, reference is made to WO 03/106020.

The present inventors have found that binary ordered
15 intermetallic compounds comprising palladium and gallium are especially useful selective hydrogenation catalysts, in particular in the selective hydrogenation of acetylene to ethylene. Accordingly, the present invention is directed in another aspect to the use of a binary Pd-Ga ordered
20 intermetallic compound as a catalyst. The present inventors have found that this type of ordered intermetallic compounds offers particular advantages in catalysis, in particular, in the field of selective hydrogenations. Due to their ratio of electronegativities (Pd: 1.4; Ga: 1.8), the palladium is
25 retained in the metallic state but at the same time, a covalent Pd-Ga bond of sufficient strength can be formed. It is considered that these electronic factors lead to the high structural stability of binary Pd-Ga ordered intermetallic compounds. In addition, the covalent bonds are likely to
30 suppress or prevent hydride formation. This avoids an oversupply of active hydrogen which may reduce the selectivity.

For the above reasons, binary Pd-Ga ordered intermetallic
35 compounds were found to be excellent hydrogenation catalysts (in particular, in selective hydrogenation reactions) due to their excellent selectivity and stability. Of course, due to

their outstanding stability, they are also promising candidates as catalysts for further types of reactions.

5 The stoichiometric ratio of Pd and Ga in the ordered intermetallic compound of the invention may be in the range of 20 : 1 to 1 : 20. The Pd : Ga range is preferably from 2 : 1 to 1 : 20, more preferably from 1 : 1 to 1 : 5. Examples of the binary Pd-Ga ordered intermetallic compounds are PdGa, 10 PdGa₅, Pd₃Ga₇, and Pd₂Ga. PdGa, Pd₂Ga and Pd₃Ga₇ are particularly preferred. These binary Pd ordered intermetallic compounds, and also Pd₂Ge and PdZn have been found to be highly selective hydrogenation catalysts, *e.g.* in the selective hydrogenation of acetylene to ethylene, even when 15 the acetylene in the feed is admixed with a large excess of ethylene. In addition, PdGa and Pd₃Ga₇ proved to have an excellent structural stability under various reaction conditions, *e.g.* in reactive gas atmospheres of hydrogen, various hydrocarbons, carbon monoxide and oxygen, in 20 particular under reaction conditions which are typically employed in industrial selective hydrogenations, *e.g.* temperatures from room temperature to about 500 K. This renders PdGa and Pd₃Ga₇ (*e.g.* in unsupported state) highly attractive catalysts in general, particularly for selective 25 hydrogenations, and especially for the industrial hydrogenation of acetylene in admixture with a large excess of ethylene to afford ethylene with high selectivity.

The ordered intermetallic compounds for use in the process of 30 the invention can for instance be manufactured by melting an amount of the constituent metals suitable to form the intermetallic compound. The metals subjected to the thermal treatment are present in a molar ratio corresponding to their molar ratio in the intermetallic compound. Preferably, the 35 melting of the metals is carried out under inert gas atmosphere, such as argon and nitrogen, preferably argon. This manufacturing method is standard in solid state

chemistry. The method of preparing PdGa and Pd₃Ga₇ is, for example, described in the working examples of the present application, and in more detail in R. Giedigkeit, Diploma
5 thesis, Technische Universität Darmstadt (Germany), 1998, the contents of which is herewith incorporated by reference in its entirety.

The preparation of some ordered intermetallic compounds may
10 involve annealing steps, *e.g.*, where the respective compound does not crystallize from the melt. To give an example, this is necessary for Pd₃Ga₇ which does not show congruent melting behavior. Looking at the phase diagram of the respective intermetallic system, the skilled person will conclude where
15 annealing is necessary to achieve the thermodynamic equilibrium of the sample so that the thermodynamically most stable modification is formed. The annealing is preferably carried out for an amount of time and temperature as large as possible.

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As mentioned earlier, the ordered intermetallic compound for use in the process of the invention may be used in the as-synthesized form as an unsupported catalyst. In this case, the specific surface area (BET method, N₂ adsorption, for
25 more details see the Examples) is typically in the range of 0.001 to 0.1 m²/g. To increase the catalyst surface area, so as to enhance the activity of the catalyst, it proved beneficial to comminute (*e.g.* pulverize) the ordered intermetallic compound. For example, the ordered
30 intermetallic compound obtained by melting the constituent metals as explained above may be comminuted with an associated increased catalyst activity. The means to be used for comminuting (*e.g.* pulverizing) the ordered intermetallic compound are not limited in kind, and may be ball mills,
35 swing mills, cryo mills, planetary mills, etc. optionally in an argon atmosphere. In the alternative, the ordered intermetallic compounds may be ground by hand, *e.g.* using a

mortar. The above comminution treatments result in a specific surface area of the ordered intermetallic compound which is typically in the range of 0.05 to 20 m²/g, preferably 0.1 to 10 m²/g, and most preferably of 0.2 to 5 m²/g.

To increase the catalytic activity of the ordered intermetallic compounds of the invention, their surface may be subjected to surface etching before they are used as a hydrogenation catalyst in the selective hydrogenation. The surface etching may be carried out prior to or after the comminution treatment; it is preferred to do the etching subsequent to the comminution treatment. However, the ordered intermetallic compounds, e.g., the binary Pd-Ga compounds, are preferably used as catalysts in the unetched state.

The surface etching may be achieved by chemical etching, e.g. by using alkaline etching solutions and complexing amines, such as EDTA and derivatives, dependent on the particular ordered intermetallic compound to be etched. Useful alkaline etching solutions are, for example, aqueous alkali hydroxide (e.g. sodium and potassium hydroxide) and alkaline earth hydroxide solutions, and aqueous ammonia solutions. In the case of ordered intermetallic palladium gallium compounds, in particular of PdGa and Pd₃Ga₇, the use of an alkaline etching solution having a pH in the range of 8.0 to 10.5 afforded hydrogenation catalysts showing in the selective hydrogenation of acetylene a higher activity while maintaining an excellent selectivity and catalyst lifetime. In the case of PdGa a pH of about 9.0 and in the case of Pd₃Ga₇ a pH of 10.5 gave the best results in terms of activity in the selective hydrogenation of acetylene.

While the catalytic activity of the ordered intermetallic compounds can be increased by way of the surface etching, the selectivity, e.g., in the acetylene reaction, may be slightly

reduced upon etching. To regain the selectivity of the unetched ordered intermetallic compound, a tempering at reduced temperature to effect a sintering of the palladium particles can be carried out. Suitable temperatures for the tempering are 50 - 500 °C, preferably 80 - 400 °C, most preferably 100 - 300 °C.

The surface area of the hydrogenation catalyst for use in the process of the present invention may also be increased by using precipitation methods, sol-gel chemistry and inert supports.

According to another aspect, the present invention is concerned with the use of PdGa and Pd₃Ga₇ as a catalyst, and to a supported catalyst comprising any of the ordered intermetallic compounds as recited in Claim 1, or a mixture of these, provided on a support. Preferred embodiments of the ordered intermetallic compounds in the supported catalysts are the same as those described herein in connection with the hydrogenation process. Suitable supports are those commonly used in catalysis, *e.g.* compounds having a high surface area, such as active carbon, alumina, silica, silicates, etc.

The following Examples are given for illustration of the invention and must not be construed as limiting the present invention.

EXAMPLES

30

Preparation of catalysts

Binary palladium gallium intermetallic compounds were prepared by melting the corresponding amounts of Pd and Ga in glassy carbon crucibles under argon atmosphere in a high-frequency induction furnace. 1.2083 g palladium (ChemPur 99.95%) and 0.7917 g gallium (ChemPur 99.99%) were used to

obtain 2 g PdGa (11.354 mmol). 0.7909 g Pd (7.432 mmol) and 1.2091 g Ga (17.340 mmol) yielded 2 g Pd₃Ga₇. Pd₂Ga was prepared in a similar way. The crystal structure of the
5 obtained products was controlled by X-ray diffractometry using a STOE STADI P diffractometer (Cu K α ₁ radiation, curved Ge monochromator) in transmission geometry with a linear position sensitive detector and comparison with reference data from literature.

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After melting, Pd₃Ga₇ was annealed at 673 K for 800 h in a glassy carbon crucible sealed in a silica tube filled with argon. Pd₂Ga was annealed at 1073 K for 170 h in evacuated and sealed quartz ampoules. PdGa was used without further
15 annealing.

The samples were powdered in a swing mill (Retsch MM 200, 4 ml WC pot, 2 WC balls) for 2 × 30 min for PdGa and 2 × 10 min for Pd₃Ga₇ at 25 Hz. Pd₂Ga was either used as prepared
20 after grinding in a mortar or after milling in Ar atmosphere using the above swing mill for 2 × 30 min.

Pd₂Ge was prepared by melting the corresponding amounts of Pd and Ge metals in glassy carbon crucibles under argon
25 atmosphere in a high-frequency induction furnace. After the melting the ingot of intermetallic compound was annealed at 1073 K for 170 h in a sealed and evacuated quartz glass ampoule.

PdZn and PtZn were prepared by annealing of the corresponding amounts of metals in evacuated quartz glass ampoules. First ampoules were heated up to 873 K for 24 h and annealed at this temperature for additional 24h. Then ampoules were heated up to 1173 K for 24 h and annealed at this temperature
30 for 72 h. According to XRD, PtZn appeared to be a single phase after such temperature treatment, while PdZn was not.

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Therefore, PdZn was ground, pressed in a pill and additionally annealed at 1173 K for 3 days. After second annealing single phase material was obtained.

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In order to increase the active catalyst surface, chemical etching was performed by ammonia solution at various pH. Commercial ammonia solution (Merck, 25% p.a.) was diluted with water to the required pH value. PH-measurements were performed with a Knick pH-Meter 761 Calimatic and a Mettler-Toledo Inlab 422 electrode calibrated with buffer solutions (Merck centiPUR pH = 7 and pH = 9). 50 mg PdGa or Pd₃Ga₇ were added to 75 ml of the diluted ammonia solution and stirred for 10 minutes at 300 K. The solution was filtrated under Argon flow and washed with additional 50 ml of the diluted ammonia solution. The etched sample was dried by evacuation for 120 min in a desiccator and stored under Ar in a glove box.

20 Characterization of catalysts

In the present specification the specific surface area of the intermetallic compounds was measured according to the BET method (Quantachrome Quantasorb Jr.). The samples (200 mg) were treated over night at 393 K in helium flow (20 ml/min) and measurements were performed by determining the total amount of nitrogen adsorbed using three different nitrogen concentrations.

In situ X-ray diffraction (XRD) experiments were conducted on a STOE diffractometer (Cu-K α) in Bragg Brentano geometry equipped with a secondary monochromator, a scintillation counter, and a Bühler HDK high temperature diffraction chamber mounted onto the goniometer. The gases were mixed by Bronkhorst mass flow controller and introduced in the experimental chamber at a total flow of 100 ml/min. The

exhaust gas composition was continuously monitored with a mass spectrometer (QMS 200, Pfeiffer). For the in situ experiments usually 50 mg of the samples was dispersed onto a steel band.

The thermal stability of PdGa and Pd₃Ga₇ was studied in helium, 20% oxygen in He, or 50 % H₂ in helium. The in situ XRD patterns for PdGa and Pd₃Ga₇ were measured in the 2θ range from 35.5° to 48.5° and from 22.5° to 52.5°, respectively, with a step width of 0.02 and a counting time of 3 sec/step. PdGa and Pd₃Ga₇ were heated from 323 K to 723 K and from 323 K to 693 K, respectively, and XRD patterns were measured isothermally every 50 K. The effective heating rate amounted to 0.5 K/min.

Both, PdGa and Pd₃Ga₇ showed a remarkable stability and structural integrity upon the above thermal treatment in various reactive gas atmospheres at temperatures commonly used for selective hydrogenations. This could be demonstrated for example by in situ X-ray diffraction (as described above), as well as by thermal gravimetric analysis (TG and DSC). Representative XRD patterns measured during thermal treatment of PdGa in 50 % hydrogen in helium from 323 to 723 K are shown in Fig. 2. As can be seen, no additional diffraction lines corresponding to Pd metal, PdO, or Ga₂O₃ were detected. The observed narrowing of the diffraction lines is indicative of crystallite growth of the PdGa material. However, up to 500 K which is the typical temperature employed for selective hydrogenations, the crystallite growth is small.

Catalytic measurements

Catalytic investigations were performed in a plug flow reactor consisting of a quartz tube with a length of 300 mm, an inside diameter of 7 mm and equipped with a sintered glass

frit to support the catalyst bed. For temperature control, a thermocouple was located next to the heating wire wound around the reactor. A second thermocouple was placed inside
5 the reactor to measure the temperature of the catalyst bed. The reactant gases were mixed with Bronkhorst mass flow controllers (total flow 30 ml/min). A Varian CP 4900 Micro gas chromatograph (GC) and a Pfeiffer omnistar quadropol mass spectrometer (MS) were used for effluent gas analysis. The
10 Varian MicroGC contains three modules, each with an individual column and a thermal conductivity detector. Hydrogen and helium of the feed gas, and possible oxygen and nitrogen impurities because of leaks in the set-up were separated on a molsieve column. Acetylene, ethylene, and
15 ethane were separated on an alumina column. The total concentration of C₄ hydrocarbons (1-butene, 1,3-butadiene, n-butane, trans and cis-2-butene) was determined using a siloxane (dimethylpolysiloxane) column. Higher hydrocarbons were also separated on the siloxan column but not further
20 quantified because of the presence of many different C₆ and C₈ hydrocarbons and their low total concentration (less than 0.1% of absolute product stream concentration). Argon (6.0) and helium (6.0) were used as carrier gases for the molsieve column and for the other columns, respectively. A
25 measurement cycle including stabilization, sampling, injection, and separation took between 4 and 5 minutes.

Acetylene hydrogenation experiments were carried out under the condition of 0.5% acetylene, 5% hydrogen, and 50%
30 ethylene in helium. All gases were obtained from Westfalen Gas (Germany).

Activity and selectivity of the materials in the hydrogenation of acetylene were measured by temperature-
35 programmed and by isothermal experiments. The experiments were performed at 473 K in the isothermal mode. The conversion rate was calculated using the following equation:

$$\text{Conv} = \frac{(C_{\text{bypass}} - C_x)}{C_{\text{bypass}}}$$

5 where C_x is the acetylene concentration in the product stream and C_{bypass} is the acetylene concentration in the feed before the reaction. The selectivity was calculated from the following equation, with C_{bypass} being the acetylene concentration before the reactor and C_x the acetylene
10 concentration after the reactor:

$$\text{Sel} = \frac{(C_{\text{bypass}} - C_x)}{C_{\text{bypass}} - C_x + C_{\text{ethane}} + 2xC_{\text{C}_4\text{H}_x}}$$

15 Calculation of the selectivity assumes that acetylene is only hydrogenated to ethylene, which may be further hydrogenated to ethane. The amount of C_4 hydrocarbons and carbon deposits formed was supposed to be negligible. In addition to hydrogenation of acetylene to ethane, ethylene from feed may
20 be hydrogenated to ethane, which is included in the selectivity equation. In order to measure selectivity in acetylene hydrogenation at the same conversion, different amounts of catalysts were used according to their specific activity determined in a previous experiment.

25

Activity of the samples was calculated using following equation:

$$\text{Act} = \frac{\text{Conv } C_{\text{feed}} C_{\text{exp}}}{m_{\text{cat}}}$$

30

where *Conv* is the calculated acetylene conversion, C_{feed} is the concentration of acetylene in feed, i.e. 0.5 %, m_{cat} the amount of used catalyst in g and constant C_{exp} is 1.904 g/h
5 and contains experimental parameters like total gas flow (30 ml), temperature (300 K) and pressure (1013 mbar) and is based on the perfect gas model.

The samples were diluted with 50 mg boron nitride (hexagonal,
10 99.5%, 325 mesh, Aldrich). A commercial Pd on alumina catalyst (5 wt% Pd, Aldrich) was used as a reference. Additionally, an unsupported palladium silver alloy was used as a benchmark catalyst. The Pd-Ag alloy ($\text{Pd}_{20.28}\text{Ag}_{79.72}$, referred to as $\text{Pd}_{20}\text{Ag}_{80}$ in the following) was prepared by
15 melting the corresponding physical mixture of the elements 1.20405 g Ag (99.995% ChemPur) and 0.30348 g Pd (99.95% ChemPur)) three times in an arc melter under argon. Subsequently, the regulus obtained was enclosed in an evacuated quartz glass ampoule and heated at 800°C for six
20 days. After the heat treatment, the regulus was powdered and phase purity of the Pd-Ag alloy obtained was confirmed by X-ray powder diffraction.

In the case of Pd_2Ge , PdZn and PtZn , the intermetallic
25 compound was ground in a mortar and the amount of catalyst was adjusted to reach more than 90 % conversion.

Examples 1 and 2, Comparative Examples 1 and 2

30 The activity, selectivity, and long-term stability of untreated Pd-Ga intermetallic compounds (PdGa , Example 1 and Pd_3Ga_7 , Example 2) in acetylene hydrogenation were determined in an excess of ethylene (0.5% C_2H_2 + 5% H_2 + 50% C_2H_4) and compared to the catalytic performance of $\text{Pd}/\text{Al}_2\text{O}_3$
35 (Comparative Example 1) and a $\text{Pd}_{20}\text{Ag}_{80}$ alloy (Comparative Example 2).

Isothermal catalysis experiments were performed by heating the untreated intermetallic compounds and the reference materials (PdGa: 40 mg, Pd₃Ga₇: 100 mg, Pd/Al₂O₃: 0.15 mg, and Pd₂₀Ag₈₀: 200 mg) in helium to a reaction temperature of 473 K followed by switching to the ethylene-rich feed.

The acetylene conversion and the corresponding selectivity obtained are plotted in Figure 3a and Figure 3b. During 20 hours time on stream Pd₃Ga₇ showed a constant acetylene conversion of 99%. PdGa reached a constant acetylene conversion of about 90 % after two hours time on stream. Pd₂₀Ag₈₀ showed a nearly constant conversion level at 85%, whereas Pd/Al₂O₃ exhibited a strong deactivation from 100% to 40% conversion during 20 hours time on stream. In addition to a high conversion of acetylene, the untreated intermetallic compounds PdGa and Pd₃Ga₇ possessed a high long-time stable selectivity of about 70% compared to 50% selectivity of Pd₂₀Ag₈₀, and only 20% selectivity of Pd/Al₂O₃ (see also Table 1 the rows with "-" in the column "pH of etching solution").

Examples 3 and 4

Isothermal catalysis experiments were performed by heating the chemically etched (by means of aqueous ammonia solution) intermetallic compounds in helium to a reaction temperature of 473 K followed by switching to the ethylene-rich feed. The results are shown in the following Table 1, which also includes data obtained for the above (Comparative) Examples 1 and 2.

Table 1: Acetylene conversion and selectivity of untreated and chemical etched PdGa, Pd₃Ga₇, Pd/Al₂O₃, and Pd₂₀Ag₈₀ after 20 h in an excess of ethylene at 473 K.

5

Sample	pH of etching solution	sample mass [mg]	acetylene conversion %	Selectivity %	Activity [g/g _{cat} ·h]
PdGa	-	40.0	86	75	0.205
PdGa (Ex. 3)	9.0	5.00	93	64	1.771
Pd ₃ Ga ₇	-	100	99	71	0.094
Pd ₃ Ga ₇ (Ex. 4)	10.5	7.00	98	55	1.333
Pd/Al ₂ O ₃	-	0.15	43	17	27.29
Pd ₂₀ Ag ₈₀	-	200	83	49	0.040

Chemical etching of PdGa at a pH of 9.0 (m = 5 mg) resulted in 93% acetylene conversion and 64 % selectivity after 20 hours time on stream. This corresponds to an eight times higher activity compared to untreated PdGa (m = 40 mg).

Chemically etched Pd₃Ga₇ also exhibited an increased activity in acetylene hydrogenation. 7 mg of Pd₃Ga₇ etched at a pH of 10.5 were sufficient to reach a similar acetylene conversion like 100 mg untreated Pd₃Ga₇.

The above shows that the activity of PdGa and Pd₃Ga₇ in the selective acetylene hydrogenation can be increased by chemical etching while maintaining a selectivity superior to conventional hydrogenation catalysts.

Examples 5 and 6, Comparative Example 3

The activity, selectivity and long-term stability of Pd₂Ga
5 intermetallic compounds in as-prepared form after grinding in
a mortar (Example 5) and after milling (Example 6) in
acetylene hydrogenation with an excessive amount of ethylene
(0.5 % C₂H₂ + 5 % H₂ + 50 % C₂H₄) were determined and
compared to the catalytic performance of Pd/Al₂O₃
10 (Comparative Example 3).

Isothermal catalysis experiments were performed by heating
the intermetallic Pd₂Ga compounds and the reference materials
(Pd₂Ga as prepared: 10 mg; Pd₂Ga milled using a swing mill:
15 0.8 mg; Pd/Al₂O₃: 0.1 mg) in helium to a reaction temperature
of 473 K, followed by switching to the ethylene-rich feed.

Figs. 4a and 4b show the acetylene conversion and the
corresponding selectivity obtained in the above experiments.
20 As can be seen, Pd₂Ga shows excellent activity, stability and
selectivity.

The catalytic results after 20 h time on stream are compiled
in the following table. As can be seen, the activity of Pd₂Ga
25 can be increased significantly by milling (note that only
0.8 mg milled Pd₂Ga was used in Example 6) so as to increase
the specific surface area, while retaining the high
selectivity.

30

35

Table 2: Acetylene conversion, selectivity and activity of as-prepared and milled Pd₂Ga and Pd/Al₂O₃ after 20 h in an excess of ethylene at 473 K.

5

Sample	Sample treatment	Sample mass [mg]	Acetylene conversion [%]	Selectivity [%]	Activity [g/g _{cat} ·h]
Pd ₂ Ga (Ex. 5)	None	10	94	74	0.89
Pd ₂ Ga (Ex. 6)	Milled in argon	0.8	84	77	10.0
Pd/Al ₂ O ₃ (Comp. Ex. 3)	None	0.1	44	20	41.89

Examples 7 and 8

10 Catalytic experiments were carried out using Pd₂Ge (0.5 mg) and PdZn (100 mg) as ordered intermetallic compounds in the hydrogenation of acetylene in the presence of excessive ethylene at 473 K. Isothermal catalysis experiments were performed similar to Examples 1 and 2. The results are shown
15 in Figs. 5a and 5b.

As can be seen, Pd₂Ge which is used in Example 7 in an amount of only 0.5 mg is highly active. Moreover, Pd₂Ge and PdZn exhibit a high selectivity in the conversion of acetylene to
20 ethylene in the presence of a large excess of ethylene.

Example 9

Acetylene was hydrogenated in the presence of an excess of
25 ethylene at 473 K using 100 mg PtZn ordered intermetallic compound as a catalyst. Isothermal catalysis experiments were

performed similar to Examples 1 and 2. As shown in Fig. 6, a high selectivity to the desired ethylene at a high conversion is achieved.

CLAIMS

1. A process for the hydrogenation of at least one
5 unsaturated hydrocarbon compound using a hydrogenation
catalyst comprising an ordered intermetallic compound wherein
the intermetallic compound comprises at least one metal of
type A capable of activating hydrogen, and at least one metal
of type B not capable of activating hydrogen and the
10 structure of the intermetallic compound is such that at least
one kind of type A metals is mainly surrounded by atoms of
the metal of type B.
2. The process according to Claim 1, wherein the
15 hydrogenation is a selective hydrogenation.
3. The process according to Claim 1 or 2, wherein the
unsaturated hydrocarbon compound has carbon-carbon double
and/or triple bond(s) but no other hydrogenable group(s).
- 20 4. The process according to any one of Claims 1 to 3,
wherein the unsaturated hydrocarbon compound is selected from
the group consisting of alkadienes, cycloalkadienes, alkynes
and aryls.
- 25 5. The process according to Claim 4, wherein the
unsaturated hydrocarbon is ethyne which is converted to
ethene through the selective hydrogenation.
- 30 6. The process according to Claim 5, wherein the ethyne is
present in admixture with an excess of ethene.
- 35 7. The process according to any one of the preceding
claims, wherein the structure of the ordered intermetallic
compound is such that at least 80% of the first coordination
sphere of the at least one kind of type A metals is occupied
by atoms of type B metals.

8. The process according to Claim 7, wherein 100% of the first coordination sphere of the at least one kind of type A metals is occupied by atoms of type B metals.

5

9. The process according to any one of the preceding claims, wherein the metals of type A are selected from the group consisting of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au. .

10

10. The process according to any one of the preceding claims, wherein the metals of type B are selected from the group consisting of B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb Bi, Zn, Cd, and Hg.

15

11. The process according any one of the preceding claims, wherein the molar ratio of the metals of type A and B (A : B) is from 20 : 1 to 1 : 20.

20

12. The process according to any one of the preceding claims, wherein the intermetallic compound is selected from the group consisting of Pd₂Ga, PdGa, PdGa₅, Pd₃Ga₇, PdSn, PdSn₂, Pd₂Ge, PdZn, PtZn and PtGa.

25

13. The process according to Claim 12, wherein the intermetallic compound is PdGa, Pd₂Ga or Pd₃Ga₇.

30

14. The process according to any one of the preceding claims, wherein the intermetallic compound is subjected to surface etching prior to use as a hydrogenation catalyst in the selective hydrogenation.

15. The process according to Claim 14, wherein the etching is carried out using an alkaline etching solution.

35

16. The process according to Claim 15, wherein the intermetallic compound is PdGa or Pd₃Ga₇ and the pH of the alkaline etching solution is in the range of 8.0 to 10.5.

5

17. The process according to any one of the preceding claims, wherein the intermetallic compound is comminuted prior to use as a hydrogenation catalyst in the selective hydrogenation.

10

18. A use of a binary Pd-Ga ordered intermetallic compound as a catalyst.

19. The use according to Claim 18, wherein the molar ratio of Pd and Ga in the ordered intermetallic compound is 20 : 1 to 1 : 20.

20. The use according to Claim 18 or 19, wherein the ordered intermetallic compound is PdGa or Pd₃Ga₇.

20

21. A catalyst comprising a support and an ordered intermetallic compound supported thereon, wherein the intermetallic compound comprises at least one metal of type A capable of activating hydrogen, and at least one metal of type B not capable of activating hydrogen and the structure of the intermetallic compound is such that at least one kind of type A metals is mainly surrounded by atoms of the metal of type B.

22. The catalyst according to Claim 21, wherein the ordered intermetallic compound is a binary Pd-Ga ordered intermetallic compound.

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