

HYDROGEN STORAGE BASED ON AQUEOUS FORMATE-BICARBONATE (HYDROGEN CARBONATE) EQUILIBRIUM

The subject of the invention is a process for the hydrogenation of hydrogen carbonate in an aqueous reaction system, where the process comprises contacting the hydrogen carbonate, hydrogen and catalyst with each other while carbon dioxide is present in the gas space. In this phase of the process, formate is produced. The subject of the invention is also a process for the catalytic decomposition of formate in an aqueous reaction system and the hydrogenation of hydrogen carbonate produced in the same reaction system according to the invention, where the reactants and reaction products are formed in a reversible reaction cycle using the reaction system according to the invention, and this reaction cycle is repeated in the required number of times.

In the mentioned formate decomposition process, the formate and the catalyst come into contact, so that hydrogen gas and hydrogen carbonate free of CO_x by-products are produced as the product of the reaction. The subject of the invention is also the hydrogen storage system based on the process according to the invention, preferably a hydrogen accumulator. The subject of the invention is also the use of the hydrogen storage system according to the invention, preferably hydrogen accumulator for the storage of hydrogen required for the operation of a fuel cell (or other device requiring H₂) and, optionally, for its release as needed.

THE STATE OF THE ART

Hull et al. in their publication (Nature chemistry, 2012, 4(5), 383-388) [1] disclose a reversible hydrogen storage system using CO₂ and an iridium catalyst, which operates under near-ambient conditions. In the demonstrated system, CO₂ is converted to formate/formic acid at alkaline pH. Although the authors state that dissolved CO₂ was essential for the production of formate, and a very small amount of the product was formed when only bicarbonate was used, they even suggest that the catalyst tested there reduces CO₂ and not bicarbonate; at the same time, they do not provide the numerical data supporting these findings or the experiments carried out. Table 1 in the referenced publication does not indicate the experimental conditions under which the results cited from the literature were obtained, although the text of the referenced publication indicates that the conditions (pressure, temperature) used in the cited publications are stronger than those used in the referenced publication used by the authors of the article (*Hull et al.*).

Joó et al. in their publication (Chemical Communications 1999, 971-972) [2], disclosed the homogeneous hydrogenation of aqueous hydrogen carbonate to formate with different catalysts

and investigated the effect of the carbon dioxide present. On one hand, they found that for the $[\text{RhCl}(\text{mtppps})_3]$ catalyst, CO_2 in the gas phase was essential for high reaction rates (although a much slower reaction still occurred in its absence). On the other hand, it was also found that CO_2 decreased the rate of reactions carried out with $[\text{RuCl}_2(\text{mtppps})_2]_2$ and $[\text{RuCl}_2(\text{pta})_4]$ catalysts. As a consequence, the effect of CO_2 on the rate of hydrogenation of bicarbonate cannot be predicted in advance even in the case of catalysts with apparently very similar composition and structure, such as the two catalysts mentioned above, thus the rate-increasing or decreasing effect can only be determined based on experiments. In other words, it is not obvious to one skilled in the art that, for a given catalyst, CO_2 present in the gas space will increase or decrease the rate of hydrogenation of bicarbonate.

In their publication *Elek et al.* (Applied Catalysis A: General 2003, 255, 59-67) [3], disclose that the rate of NaHCO_3 hydrogenation catalyzed by the $[\text{RuCl}_2(\text{mtppps})_2]_2$ complex at constant NaHCO_3 concentration and (at also constant) 6 bar H_2 pressure using 5 bar CO_2 was 10% lower than in the absence of CO_2 .

In general, it can be stated that it is difficult to compare the large number of results collected in the literature, that the experimental conditions used were significantly different. This does not only mean the difference in pressure, temperature, and reaction time, but also the difference in the concentration and concentration ratios of the substances used in the reactions. Thus, e.g. starting from the fact that theoretically both HCO_3^- and CO_2 can be hydrogenated, during the experiments described in several publications, for example in the publication of *Laurenczy et al.* (Inorg. Chem. 2000, 39, 5083-5088) [4], the combined dissolved CO_2 and HCO_3^- concentration (i.e. the total concentration of carbonaceous inorganic particles in solution) was kept constant during certain experiments. This e.g. had the consequence that in order to examine the CO_2 effect, when increasing the CO_2 pressure, the amount of measured NaHCO_3 had to be reduced, which resulted in a much faster decrease in pH (and thus a faster increase in the formate concentration) than if the carbon dioxide gas pressure had been increased at a constant HCO_3^- concentration. There is also an example of the latter experimental arrangement (in fact, it is the more general one).

The authors of the above-mentioned publications ([2]-[4]) clearly state that the real substrate of bicarbonate hydrogenation is the HCO_3^- anion, even in the presence of CO_2 . In this context, it is necessary to define what is considered a substrate in a chemical transformation. In our opinion, a substrate is the type of starting material on which the chemical transformation takes place, and which appears in a changed form in the product of the reaction. Determining this is not always easy if various exchange processes take place during the reaction. (Substrate and

reactant are not 100% synonymous with each other, because a reactant can also be an auxiliary substance, e.g. a proton-binding base, etc.). During the hydrogenation of bicarbonate in the presence of CO₂, CO₂ can (also) be a substrate if it is itself directly hydrogenated to formate. However, if its role is limited only to pH adjustment (forming an acidic environment), then it is considered a simple auxiliary material. From the point of view of the present invention, the measurement results that have been published so far in the literature are not sufficient to decide the question.

The following considerations are based on the work of *J. N. Butler* "Carbon Dioxide Equilibria and Their Applications" (Lewis Publishers, Chelsea, USA, 1991) [5] and *X. Li et al.* (Fluid Phase Equilibria 2018, 458, 253-263) [6] and use the data available there. The reference to approximations refers to the fact that the activity coefficients were considered to be 1 in the calculations, and e.g. the effect of ionic strength was not taken into account.

Henry's law applies to the dissolution of carbon dioxide in water: $[\text{CO}_2] = K_H \times P(\text{CO}_2)$, i.e. increasing the pressure of carbon dioxide linearly increases the concentration of dissolved (hydrated) CO₂. If the concentration of dissolved carbon dioxide is given in mol/liter (M) units, and the pressure of gaseous carbon dioxide is given in atm (with a good approximation in bar units), then the value of Henry's constant for pure water at 25 °C is $K_H = 10^{-1.5} = 0,0316$; and at 35 °C, $K_H = 10^{-1.7} = 0,0200$. This value decreases with increasing temperature and also changes with ionic strength, but this does not significantly affect the following considerations. As the CO₂ pressure increases, the dissolved CO₂ concentration also increases, and at 25 °C it is approximately 0.0316 M (1 bar), 0.316 M (10 bar), and 3.16 M (100 bar). The acid dissociation constant of the dissociation equilibrium $\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+$ is $\text{p}K_{a1} = 6,35$ (25 °C) and 6.309 (35 °C), respectively. For a given pH, the relationship between bicarbonate anion concentration and CO₂ pressure can be given by the following formula:

$$\log [\text{HCO}_3^-] = \text{p}K_{a1} + \text{p}K_H + \log P(\text{CO}_2) + \text{pH}$$

Accordingly, and as can be read from the formula, the equilibrium bicarbonate concentrations also increase due to the larger amounts of CO₂ dissolved under higher pressure. According to the *measurement* data published in *Butler's* mentioned publication [5], in NaHCO₃ solutions with a solvent concentration of $m = 1$ mol/kg, at 35 °C, under different $P(\text{CO}_2)$ pressures, the equilibrium pHs shown in the table below are formed (column 2), from which the equilibrium HCO₃⁻ concentrations in column 3 can be calculated.

Reference table 1

$P(\text{CO}_2)$ (bar)	pH	$[\text{HCO}_3^-]$ (M)
9.2	6.99	1.13
20.0	6.86	1.83
92.8	6.33	2.50

As the solution placed under CO_2 pressure initially contained NaHCO_3 at a concentration of 1 M (at this temperature and concentration, the concentration of the NaHCO_3 solution expressed in molality and molarity is practically the same), the increase in $[\text{HCO}_3^-]$ concentration under the influence of 9.2 bar CO_2 is only 13% and even at 20 bar CO_2 is only 83%. It can also be seen that the concentration of the bicarbonate ion changes *non-linearly* with the increase in CO_2 pressure, the more than 10-fold increase of which (from 9.2 bar to 92.8 bar) entails only a little more than a two-fold increase in the bicarbonate concentration. The reason for this phenomenon is that H_2CO_3 and HCO_3^- formed from dissolved carbon dioxide form a buffer solution. From these considerations, it follows that if the catalytic hydrogenation is first order with respect to the substrate, then the initial rate of hydrogenation should vary linearly with the pressure of CO_2 if dissolved CO_2 itself were the substrate. If, on the other hand, the substrate of the hydrogenation is the bicarbonate anion, then increasing the CO_2 pressure is followed by an increase in the reaction rate to a lesser extent. Some of the experiments really showed this, but there are also different experiences. Such e.g. the already mentioned decrease in the rate of hydrogenation when the CO_2 pressure is increased ([2] and [3]).

It is interesting that although the equilibrium (i.e. actually existing in the reaction mixture) HCO_3^- concentration can be much higher under CO_2 pressure than in the absence of CO_2 , according to the data published in the literature, this is rarely reflected in the experimentally achieved final formate concentrations, which usually do not exceed the *measured* HCO_3^- concentration. In some cases, however, in the presence of CO_2 , the formation of more formate (specifically formic acid, HCO_2H) than the amount of bicarbonate (HCO_3^-) taken in was detected, the amount of which rarely exceeded 30-40% of the taken bicarbonate. The formation of HCO_2H can only be interpreted as the hydrogenation of dissolved (hydrated) CO_2 in addition to or instead of bicarbonate. The logical question arises as to whether the higher formate concentration found in the acidic medium during the given time, compared to the yields achieved with pure H_2 , comes from the higher hydrogenation of the CO_2 added to the gas space or the HCO_3^- already present in the solution. In other words: which substrate does the reaction mechanism prefer, i.e. how much proportion of the product comes from bicarbonate, or how much of the dissolved CO_2 . (Of course, in the case of various catalysts, the mechanism of

hydrogenation of bicarbonate and hydrated carbon dioxide, especially when both substrates are present together, can be significantly different.)

The situation is complicated if, under the given conditions, a rapid exchange process takes place between the dissolved CO_2 (or the resulting H_2CO_3) and HCO_3^- . In that case, it is not possible to decide whether, in addition to the hydrogen carbonate, the (hydrated) CO_2 dissolved in the reaction mixture also reacts independently or whether the reactant is only the HCO_3^- formed during the rapid exchange. Most of the literature reports do not even pay attention to this possibility: they consider the process as "CO₂-hydrogenation" even when the originally introduced NaHCO_3 did not react to 100%, i.e. all of the formed formate could have come from hydrogen carbonate without that hydrated CO_2 would have reacted with hydrogen. However, if 100% of the originally introduced HCO_3^- is converted into formate, then the amount of formate (formic acid) that exceeds this is necessarily formed from the CO_2 that was originally in the gas phase. Of course, in the presence of basic auxiliary materials, e.g. amines, the CO_2 in the gas phase is also reduced, since it gives a bicarbonate (possibly carbonate) salt with the base, which is known to be hydrogenable. In such cases, however, according to experimental experience, the amount of the base present determines the maximum achievable formate concentration.

The inventors of the present invention believe that for a clear answer, the exchange process indicated in the previous paragraph, or - with isotopic labeling - the examination of the isotope ratio formed in the formate obtained as a product, primarily with mass spectrometry methods, would be necessary. However, the following observations deserve consideration.

a) In the publications [2]-[4] mentioned several times above, the reactions were carried out in high-pressure NMR tubes, and was followed by ^1H or ^{13}C NMR spectroscopy using $\text{NaH}^{13}\text{CO}_3$, an isotopically labeled Na-bicarbonate starting material. During the reaction, the ^1H and ^{13}C measurements clearly showed the increase in formate concentration over time, which was determined quantitatively from the ratio of the formate HCO_2^- proton signal intensity to the corresponding internal standard (DSS) proton signal intensity. The conversion of the starting material and the final formate concentration were calculated based on these data. With this method, it is not possible to distinguish whether the detected formate was formed from bicarbonate or hydrated CO_2 .

In other cases (such as in the above-mentioned publication [1]), the formate concentration formed was determined by HPLC measurements, using elution with an acidic medium. The latter method does not differentiate between formate and formic acid, either, because formate is also protonated in the eluent used and can be detected as formic acid.

b) The HCO_3^- anion can also be hydrogenated without CO_2 in an aqueous solution. On the other hand, knowing that in the absence of HCO_3^- , i.e. when the aqueous solution containing only the catalyst is placed under a H_2/CO_2 gas mixture, even at high pressure and temperature, only a negligible amount of formic acid is formed (see e.g. [1]), it seems obvious to assume that
5 the HCO_3^- hydrogenates at a much higher rate than hydrated CO_2 (ie, bicarbonate is the substrate for hydrogenation).

c) We mentioned earlier that in the presence of bases, CO_2 introduced in the gas phase is also hydrogenated, since with the base it gives a bicarbonate (possibly carbonate) salt, which is known to be hydrogenable. In such cases, however, according to experimental experience, the
10 amount of base present (KOH, NaOH, dimethylamine, etc.) determines the maximum achievable formate concentration.

d) Some catalysts break formic acid (HCO_2H) into hydrogen and carbon dioxide at an extremely high rate. Of course, this process only takes place in an acidic medium where the formic acid *does not* predominantly dissociate, because otherwise it would be dehydrogenation of
15 the formate anion. In purely aqueous solutions (i.e. in the absence of NaHCO_3), the low final concentration of the formic acid formed in the reaction $\text{CO}_2 + \text{H}_2 = \text{HCO}_2\text{H}$ may also be the result of the fact that the catalyst also breaks down the product and the balance is strongly shifted in the direction of the starting materials.

Based on the data published in the already mentioned publication [4] by *Laurenczy et al.*, the
20 final formate concentrations contain significant concentration data (1.53 M and 1.70 M), but in no reaction did the concentration of the formed HCO_2^- exceed the measured NaHCO_3 or KHCO_3 concentration in the used 1-50 bar CO_2 pressure range. Assuming that formate was formed solely by hydrogenation of the input KHCO_3 , the maximum bicarbonate conversion was 85%. These observations clearly indicate that the CO_2 present in the H_2/CO_2 mixtures has
25 primarily a *kinetic effect* on the hydrogenation of hydrogen carbonate. The details of this have not been revealed in the studies so far, but the decrease in the pH of bicarbonate solutions due to the effect of dissolved CO_2 may influence the formation of catalytically active metal complex particles (almost certainly hydrido-complexes). However, there are limits to the pH reduction, as can be seen from reference table 1 above. However, the direct self-hydrogenation of dissolved
30 CO_2 does not significantly contribute to the amount of formate formed. In this sense, it is not a *reactant (substrate)* of hydrogenation, and the Le Chatelier-Braun principle cannot be applied to it, according to which increasing the concentration of the reactant(s) favors the formation of products. It is well known that the Le Chatelier-Braun principle is a clearly formulated thermodynamic law, but it does not say anything about the *kinetics* of the given reaction.

US4067958 patent discloses a process for producing hydrogen from fuel gas containing carbon monoxide and other components. The fuel gas is passed through an aqueous solution containing sodium and potassium carbonate and/or bicarbonate while the corresponding formate is formed. The formate solution is then catalytically decomposed to produce hydrogen and carbonate and/or bicarbonate. The cited patent document also presents the equipment implementing the procedure. The catalysts used can be transition metals, their oxides or sulfides on a support resistant to alkalis.

Laurency *et al.* (Inorg. Chem. Comm. 2007, 10, 558-562) published a Ru(II) complex, namely the $[\text{RuCl}_2(\text{PTA})([\text{9}] \text{aneS}_3)]$ complex (where PTA is 1,3, 5-triaza-7-phosphadamantane and $[\text{9}] \text{aneS}_3$ is 1,4,7-trithiacyclononane), which can catalyze the hydrogenation of carbon dioxide and bicarbonates in an aqueous medium. In the publication, it is stated that although the catalytic activity is very modest, the presence of intermediate products appearing during the reaction, suggested by previous theoretical and practical results, has been undoubtedly proven.

In US20120321550 patent document, Fukuzumi *et al.* disclose in great detail mononuclear transition metal complexes (including stereoisomers) that can be used in hydrogen storage processes (starting from Y. Himeda's previous work). In their case, hydrogen is produced from alcohols, and then the starting alcohol is recovered from the formed aldehyde by hydrogenation with a similar catalyst. Furthermore, the $\text{HCOOH}/\text{HCOO}^-/\text{CO}_2/\text{HCO}_3^-$ balance is successfully used in these systems. In their case, the pH in the given system is also a key issue, also in connection with the pH sensitivity of the ligand. Although the formate/hydrocarbonate cycle plays a role in the systems described in the referenced patent document, the family of catalysts used has a different structure than that disclosed in the present invention, and does not contain either N-heterocyclic (hereafter sometimes: NHC) carbene or phosphine.

Mahajan summarizes his experiments in formate decomposition (sodium, potassium, lithium and cesium formate) catalyzed by transition metal complexes in US6596423 patent document. Conducting the reaction according to the described procedure (at a temperature in the range of 80-150 °C), the reaction product also contains traces of carbon monoxide (less than 50 ppm). The patent document mentions several possible complexing metals, including iridium. Possible catalysts can be transition metal carbonyl complexes or ligand-coordinating complexes containing an N-donor group (for example, a 2,2'-dipyridyl group). It also provides several options for the reaction medium, such as water or methanol.

In patent application No. DE102006030449, a device suitable for reversible hydrogen storage is disclosed. The basis of the operation of the equipment is the binding of hydrogen and its release. Hydrogen is bound by reducing potassium carbonate and/or potassium bicarbonate in

aqueous solution to potassium formate with an electric current in the presence of hydrogen gas and a ZnO or ZnO/TiO₂ catalyst. Hydrogen is released from an aqueous solution of potassium formate, formic acid or their mixture using platinum or palladium catalysts. Note that not the same catalyst is used for hydrogen storage and hydrogen release.

5 Patent application No. *US7939461* discloses metal complexes that catalyze the decomposition of formic acid with hydrogen formation. The application also discloses the theoretical possibility of a device that enables the storage and recovery of hydrogen produced during the decomposition of formic acid. The disclosed metal complexes contain two transition metal ions (binuclear complexes), which may be identical or different. In the description of the
10 invention, iridium is included among the possible metal atoms. Possible ligands in substituted or unsubstituted form are cyclopentadiene, N-atom-containing heterocyclic aromatic compounds, such as bipyridine, phenanthroline, bipyrimidine. In the given examples, the production of a water-soluble iridium-ruthenium complex and the decomposition of formic acid with the formation of hydrogen and carbon dioxide under various conditions (different temperatures and
15 pH) are presented. The description also presents complexes (for example containing iridium) that catalyze the formation of formic acid from hydrogen and carbon dioxide. The catalysts disclosed in the referenced patent document have a different structure than the complex catalysts disclosed in the present invention, so for example they do not contain phosphine ligands.

In a publication by *Beller* and his research group (Tetrahedron Lett. 2009, 50, 1603-1606), it
20 was described how hydrogen production from formic acid with a Ru-containing catalyst can be influenced by adding organic bases and inorganic salts to the catalyst system. It has been demonstrated that the presence of amidine compounds increases hydrogen production, and under optimal conditions, hydrogen can be efficiently produced from a formic acid/amine mixture. The catalyst system proved to be most effective in the presence of 1,2-bis-
25 (diphenylphosphino)ethane (dppe) and N,N-dimethyl-n-hexylamine in the case of [RuCl₂(benzene)]₂ precursor.

Patent document No. *WO2012143372* presents a process by which hydrogen can be produced from formic acid by selective dehydration using a catalyst system containing transition metal complexes coordinating at least one tetradentate ligand. Although iridium is also mentioned
30 among the possible transition metals, ruthenium, cobalt and iron are included in the disclosed preferred embodiments of the invention. The description mentions phosphine ligands, but carbene complexes of transition metals are not mentioned as precursors.

Joó et al. [Angew. Chem. Int. Ed. 2011, 50, 10433-10435 (hereinafter: own research results)] also investigated the possibilities of using the formate/hydrocarbonate cycle. The catalyst

described here is the Ru(II)-*m*tppps -complex, from which Ru-formate dihydride is formed during the reaction, which specifically performs the decomposition. The chemical storage of H₂ in formate was achieved within one system, since at the applied temperature, in the presence of the Ru(II)-*m*tppps catalyst, the formate decomposes (no CO₂ emissions), while after the decomposition is completed, the initial formate solution can be recovered by filling the formed HCO₃⁻ and catalyst solution with relatively high pressure H₂. It was possible to complete the cycle several times in a row. Although the formate/hydrocarbonate cycle plays a role in the systems described in the publications, the catalyst is a Ru(II) complex, and complexes of iridium or other transition metals are not mentioned, and the use of NHC carbene as a ligand does not arise.

Himeda (Green Chem. 2009, 11, 2018-2022) investigated the decomposition of formic acid in an aqueous medium in the presence of an iridium catalyst. The resulting hydrogen did not contain carbon monoxide. 4,4'-dihydroxy-2,2'-bipyridine was present as a ligand. Based on the results, the Ir-bipyridyl complexes proved to be very active catalysts. At 90 °C, the catalytic activity was TOF=14000 h⁻¹. The author also investigated the effect of formate on the decomposition of formic acid. He found that this catalyst is also active in the decomposition of HCOOH/HCOO⁻ mixtures. Furthermore, on a theoretical-principle level, he predicted that the aqueous solution of the CO₂ formed (HCO₃⁻ solution) can be rehydrogenated and that formic acid is formed again by lowering the pH. He also proposed the mechanism of the reaction taking place, in which he identified the catalytically active intermediate as Ir-hydride.

Using a similar Ir catalyst, also *Himeda et al* solved the rehydrogenation of CO₂ formed from the decomposition of formic acid by changing its pH within a single system (Nature Chem. 2012, 4, 383-388). The catalyst they use (through the pH sensitivity of the ligand) catalyzes the decomposition of formic acid in an acidic pH range, while the reduction of CO₂ comes to the fore in alkaline solutions. According to their suggestion, H₂ can be stored reversibly in formate solutions.

Although the formate/hydrocarbonate cycle also appears in the two aforementioned publications, but the catalyst used does not contain either NHC carbene or phosphine, during the decomposition the pH is in the acidic range, i.e. the formic acid decomposes (CO₂ is also formed), and the pH must be increased in order for the reduction process to start, in contrast to our system, where the pH does not change significantly.

Nolan et al. in US6774274 patent document disclose complexes of formula [Ir(cod)(N)(L)]X, which were prepared by reaction of [Ir(cod)(py)₂](PF₆) (where cod is 1,5-cyclooctadiene, py and meaning pyridine) and L or together with N and L ligands. The use of said catalysts in the hydrogenation of olefins is also disclosed. The preparation of the complex

according to formula $[\text{Ir}(\text{cod})(\text{py})(\text{SIMes})]\text{PF}_6$ (where SIMes is 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene or a related N-heterocyclic carbene) and its main features are demonstrated. In the referenced patent document, nucleophile-type N-heterocyclic carbenes are mentioned as an alternative to phosphine ligands, which are widespread in homogeneous catalysis, emphasizing the general experimental experience that using N-heterocyclic carbene ligands with more favorable steric and/or electronic characteristics instead of phosphine ligands, a significant catalytic performance increase can be achieved in the case of olefins. The patent document does not disclose catalysts containing a mixture of NHC carbene and phosphine ligands, and in addition offers a solution to a fundamentally different technical problem.

In their publication (Angew. Chem. Int. Ed. 2008, 47, 3966-3968), *Laurenczy et al.* present an efficient, selective system suitable for hydrogen evolution from an aqueous solution of formic acid in the presence of a water-soluble, *in situ* produced catalyst. $[\text{Ru}(\text{II})(\text{H}_2\text{O})_6](\text{tos})_2$ -complex, where tos means tosyl-4-sulfonate and RuCl_3 , were used as precursors, and meta-trisulfonated triphenylphosphine (*m*tppts) as ligand. Sodium formate was added to the solution to activate the catalyst.

In another publication (ChemCatChem 2013), *Laurenczy et al.* investigated the catalytic decomposition of a $\text{HCOOH}/\text{HCOO}^-$ mixture in the presence of a water-soluble catalyst containing Ru-ions, where the ligands forming the complex were cationic triarylphosphine derivatives substituted with one or more trimethylammonium groups. Optimization experiments were also carried out with the most promising precursor, during which, among other things, the effect of pH, temperature, catalyst concentration and ligand/Ru ratio were investigated. The catalytic cycle number achieved under optimal conditions was $\text{TOF} = 1950 \text{ h}^{-1}$.

In the publications listed above, the catalyst system is ruthenium-based and contains though various phosphine ligands, but there is no mention of NHC carbenes as possible ligands.

Patent document WO2008047312 by *Laurenczy et al.* refers to a process by which hydrogen and carbon dioxide can be produced in an aqueous medium from formic acid by a catalytic method, without the generation of carbon monoxide. The catalyzed process takes place in a wide temperature range and at room temperature ($T = 25 \text{ }^\circ\text{C}$). The patent document also mentions iridium as a transition metal, the complexes of which may be suitable as catalysts in the investigated processes, but no relevant experimental results are presented. In preferred embodiments of the invention, iridium is not included. Among the possible ligands of transition metal complex catalysts, it mentions phosphines, preferably aromatic phosphines, specifically *m*tppts and *m*tppts ligands, and carbenes. However, the document does not give a specific example of the latter. The patent document does not state that the carbon dioxide or HCO_3^-

solution formed during decomposition would be converted back into formic acid or formate solution.

US8133464 patent document by *Laurency et al.* also relates to the decomposition of various formic acid/formate mixtures into hydrogen and carbon dioxide. Compared to their previous patent (WO2008047312), the range of catalysts used has been widened. The patent document discloses a complex with the composition $M(L)_n$, where M is preferably Ru and Rh, but can also be Ir. Several variations of L as a ligand are claimed, where L can be a sulfonated phosphine and/or carbene and/or a hydrophilic group and combinations thereof. However, this patent document does not provide a clear range of possible carbenes as ligands either.

U.S. Patent *US10944119B2* discloses a process that enables the storage and release of hydrogen. Although the document mentions the bicarbonate-formate cycle in relation to the storage and release of hydrogen, however, during the release of hydrogen, the used transition metal catalyst (ruthenium-containing complex) is dissolved in an organic solvent or solvent mixture, and the resulting bicarbonate is formed in the aqueous phase separated from the organic solution containing the catalyst. So much has been revealed about the hydrogenation of bicarbonate that this step can also be facilitated by the same catalyst system as the decomposition of formate.

Chinese patent document No. *CN105283436B* discloses a process for producing formic acid from hydrogen gas and carbon dioxide in the presence of a catalyst. The process is carried out in an acidic medium containing a polar solvent (e.g. water or DMSO) and no base, carbonate, bicarbonate or formate is added.

US patent document *US20150105571A1* discloses a process for converting carbon dioxide or bicarbonate into a formic acid derivative (e.g. formate salt, formate ester and formamide) using a catalyst system containing molecular hydrogen and cobalt complex.

Based on the state of the art, it can be established that the effect of CO_2 on the hydrogenation of bicarbonate with various catalysts can be either speed-increasing or speed-decreasing, and the extent cannot be determined based on prior knowledge. Based on the research results and experience summarized above, the creators of the present invention believe that the actual substrate of CO_2 hydrogenation is the HCO_3^- anion. Its concentration naturally increases with CO_2 pressure, but not linearly, as Henry's law would require (even in small pressure ranges).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: A catalytic cycle suitable for storing and releasing hydrogen, where the hydrogenation of hydrogen carbonate (HCO_3^-) is carried out in the presence of carbon dioxide (CO_2) in the gas space.

5 Figure 2: The change in pH with increasing CO_2 pressure in 0.1 M NaHCO_3 solution at 80°C .

Figure 3: The change of the catalytic cycle number (TurnOver Number, hereinafter: TON) depending on the applied CO_2 pressure using $[\text{Ir}(\text{emim})(\text{cod})(\text{mtpms})] + \text{mtppts}$ catalyst in a batch reactor with a total volume of 100 ml.

10 Figure 4: The change of the catalytic cycle number (TON) values as a function of pH using $[\text{Ir}(\text{emim})(\text{cod})(\text{mtpms})] + \text{mtppts}$ catalyst in a batch reactor with a total volume of 100 ml.

Figure 5: The change of the catalytic cycle number (TON) values as a function of the applied CO_2 pressure – using $[\text{Ir}(\text{emim})(\text{cod})(\text{mtpms})] + \text{mtppts}$ catalyst in a batch reactor with a total volume of 600 ml.

15 Figure 6: The change of the catalytic cycle number (TON) values as a function of pH using $[\text{Ir}(\text{emim})(\text{cod})(\text{mtpms})] + \text{mtppts}$ catalyst in a batch reactor with a total volume of 600 ml.

Figure 7: Comparison of catalytic cycle number (TON) values obtained in Examples 4-7.

THE PROBLEM TO BE SOLVED BY THE INVENTION

The technical problem to be solved with the invention is to provide a reaction system
20 suitable for the reversible storage of hydrogen gas that can be used in fuel cells or other
equipment requiring H_2 , which enables the production of hydrogen gas (H_2) free of CO_x by-
products by breaking down formates in an aqueous reaction system, as well as the hydrogenation
of hydrogen carbonates produced in the same reaction system using the same catalyst in such a
way, that the activity of the catalyst in the hydrogenation step of hydrogen carbonates is greater
25 than the activity of the catalysts in the previously known hydrogenation process of hydrogen
carbonates.

DISCOVERY ACCORDING TO THE INVENTION

Our invention achieves the mentioned goals with a solution based on the surprising
discovery that if the hydrogenation of hydrogen carbonates is carried out in an aqueous reaction
30 system with carbon dioxide present in the gas space, the activity of the catalyst according to the
invention will be up to six times higher - the depending on the conditions used (properly chosen

pressure and temperature) – as in the case of hydrogenation of hydrogen carbonates in an aqueous reaction system with pure hydrogen.

BRIEF DESCRIPTION OF THE INVENTION

1. A process for the hydrogenation of hydrogen carbonate (HCO_3^-), in an aqueous reaction system, preferably said hydrogen carbonate being selected from sodium hydrogen carbonate (NaHCO_3), lithium hydrogen carbonate (LiHCO_3), cesium hydrogen carbonate (CsHCO_3) and potassium hydrogen carbonate (KHCO_3) and for the production of formate, preferably formate selected from the group of sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) and potassium formate (HCOOK),

10 said process comprising bringing said hydrogen carbonate and a catalyst into contact with each other at an elevated temperature, preferably at $60\text{--}100^\circ\text{C}$, more preferably at 80°C , at a pressure of 1-1200 bar, preferably 10-100 bar;

where the catalyst is a catalyst with the general formula $[\text{Ir}(\text{cod})(\text{NHC})\text{P}_a] + n\text{P}_b$,

where in the formula

15 Ir is iridium;

cod is 1,5-cyclooctadiene;

NHC is an N-heterocyclic carbene, preferably 1-R-3-methylimidazol-2-ylidene, where R is C1-C6 alkyl or benzyl;

n is an integer from 1 to 4; and

20 P_a and P_b are independently 1,3,5-triaza-7-phosphadamantane (pta), monosulfonated triphenylphosphine (*mtpms*) or trisulfonated triphenylphosphine (*mtppts*);

wherein the hydrogenation of hydrogen carbonate is carried out in such a way that carbon dioxide is present in the gas space.

2. The process according to Point 1, wherein the catalyst used is selected from the following:

25 a) a catalyst according to the formula $[\text{Ir}(\text{emim})(\text{cod})(\text{mtpms})] + \text{mtppts}$, wherein emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *mtpms* is monosulfonated triphenylphosphine and *mtppts* is trisulfonated triphenylphosphine;

b) a catalyst according to the formula $[\text{Ir}(\text{bmim})(\text{cod})(\text{mtpms})] + \text{mtppts}$, wherein bmim is 1-butyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *mtpms* is monosulfonated triphenylphosphine and *mtppts* is trisulfonated triphenylphosphine;

30 c) a catalyst according to the formula $[\text{Ir}(\text{hexmim})(\text{cod})(\text{mtpms})] + \text{mtppts}$, wherein hexmim is 1-hexyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *mtpms* is monosulfonated triphenylphosphine and *mtppts* is trisulfonated triphenylphosphine;

d) a catalyst according to the formula $[\text{Ir}(\text{2mim})(\text{cod})(\text{mtppts})] + \text{mtppts}$, wherein 2mim is 1,3-dimethyl-imidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and mtppts is trisulfonated triphenylphosphine;

e) a catalyst according to the formula $[\text{Ir}(\text{Bnmim})(\text{cod})(\text{mtppts})] + \text{mtppts}$, wherein Bnmim is 1-benzyl-3-methylimidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and mtppts is trisulfonated triphenylphosphine;

f) a catalyst according to the formula $[\text{Ir}(\text{emim})(\text{cod})(\text{mtppts})] + \text{pta}$, wherein emim is 1-ethyl-3-methylimidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and pta is 1,3,5-triaza-7-phosphadamantane; and

g) a catalyst according to the formula $[\text{Ir}(\text{emin})(\text{cod})(\text{mtppts})] + \text{mtppts}$, wherein emim is 1-ethyl-3-methylimidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine.

3. A process for decomposing a formate, preferably a formate selected from sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) and potassium formate (HCOOK) in an aqueous reaction system and for producing hydrogen gas (H_2) free of CO_x by-products, and in the same reaction system, for the hydrogenation of the resulting hydrogen carbonate (HCO_3^-), preferably a hydrogen carbonate selected from the group of sodium hydrogen carbonate (NaHCO_3), lithium hydrogen carbonate (LiHCO_3), cesium hydrogen carbonate (CsHCO_3) and potassium hydrogen carbonate (KHCO_3) in an aqueous reaction system, thus for the production of a formate, preferably a formate selected from the group of sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) and potassium formate (HCOOK);

where the reactants and the reaction products are formed in a reversible reaction cycle by using the reaction system of the formate decomposition step and the bicarbonate hydrogenation step and by choosing the values of temperature, pressure and pH within the ranges specified below, and this reaction cycle is repeated the required number of times;

where the formate decomposition step includes bringing the formate into contact with the catalyst in an aqueous reaction system, at an elevated temperature, preferably at 60-100 °C, preferably at 80 °C, preferably at a pH greater than 8, preferably at a $\text{pH}=8.3 \pm 0.2$, in an Ar gas atmosphere;

where the hydrogenation step of the hydrogen carbonate includes bringing the hydrogen carbonate and a catalyst into contact with each other, at an elevated temperature, preferably at 60-100°C, more preferably at 80°C, under pressure of 1-1200 bar, preferably 10-100 bar;

where the catalyst is a catalyst with the general formula $[\text{Ir}(\text{cod})(\text{NHC})\text{P}_a] + n\text{P}_b$,

where in the formula

Ir is iridium;

cod is 1,5-cyclooctadiene;

NHC is an N-heterocyclic carbene, preferably 1-R-3-methylimidazol-2-ylidene, where R is
5 C1-C6 alkyl or benzyl;

n is an integer from 1 to 4; and

P_a and P_b mean independently a 1,3,5-triaza-7-phosphadamantane (pta), monosulfonated triphenylphosphine (*m*tppms) or trisulfonated triphenylphosphine (*m*tppts);

according to which the hydrogenation of hydrogen carbonate is carried out in such a way that
10 carbon dioxide is present in the gas space.

4. The process according to Point 3, *according to which* the catalyst used is selected from the following:

a) a catalyst according to the general formula [Ir(emim)(cod)(*m*tppms)] + *m*tppts, where
emim is 1-ethyl-3-methylimidazol-2-ylidene, cod means 1,5-cyclooctadiene, *m*tppms is
15 monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

b) a catalyst according to the general formula [Ir(bmim)(cod)(*m*tppms)] + *m*tppts, where
bmim is 1-butyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppms is
monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

c) a catalyst according to the general formula [Ir(hexmim)(cod)(*m*tppms)] + *m*tppts, where
20 hexmim is 1-hexyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppms is
monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

d) a catalyst according to the general formula [Ir(2mim)(cod)(*m*tppms)] + *m*tppts, where
2mim is 1,3-dimethyl-imidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppms is monosulfonated
triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

25 e) a catalyst according to the general formula [Ir(Bnmim)(cod)(*m*tppms)] + *m*tppts, where
Bnmim is 1-benzyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppms is
monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

f) a catalyst according to the general formula [Ir(emim)(cod)(*m*tppms)] + pta, where emim is
1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppms is monosulfonated
30 triphenylphosphine and pta is 1,3,5-triaza-7-phosphadamantane; and

g) a catalyst according to the general formula [Ir(emim)(cod)(*m*tppms)] + *m*tppms, where
emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppms is
monosulfonated triphenylphosphine.

5. Use of the process according to Point 3 for a hydrogen storage system.

6. The hydrogen storage system according to Point 4, which is a hydrogen battery.

7. Use of the hydrogen storage system according to Point 5 or 6 for storing the hydrogen required to operate a fuel cell or other equipment requiring H_2 , and optionally for releasing thereof to the extent of necessary.

5 DETAILED DESCRIPTION OF THE INVENTION

In the course of our work, we developed a process for the hydrogenation of hydrogen carbonate (HCO_3^-) in an aqueous reaction system in the presence of a catalyst, where the process includes bringing the aforementioned hydrogen carbonate, hydrogen and catalyst into contact with each other in such a way that carbon dioxide is present in the gas space, thus formate ($HCOO^-$) is produced.

In the course of our work, we came to the surprising discovery that if the hydrogenation of hydrogen carbonate in an aqueous reaction system is carried out in such a way that carbon dioxide is present in the gas space, then the activity of the catalyst according to the invention will be up to six times higher – depending on the applied pressure and temperature –, than in the case of hydrogenation of hydrogen carbonate in an aqueous reaction system with pure hydrogen.

Based on the above, the first aspect of our invention is to provide a process for the hydrogenation of a hydrogen carbonate (HCO_3^-), preferably sodium hydrogencarbonate ($NaHCO_3$), lithium hydrogencarbonate ($LiHCO_3$), cesium hydrogencarbonate ($CsHCO_3$) or potassium hydrogencarbonate ($KHCO_3$) in an aqueous reaction system in the presence of carbon dioxide in the gas space, and for the production of a formate, preferably sodium formate ($HCOONa$), lithium formate ($HCOOLi$), cesium formate ($HCOOCs$) or potassium formate ($HCOOK$), where the hydrogen carbonate and the catalyst are brought into contact with each other at an elevated temperature, preferably at 60-100°C, more preferably at 80°C, at a pressure of 1-1200 bar, preferably 10-100 bar.

In one embodiment of the invention, the amount of CO_2 present in the gas space during the contact between said hydrogen carbonate and the catalyst is: $p(CO_2) > 0$ bar and $p(CO_2) \leq 50$ bar.

The mentioned catalyst is a catalyst of the general formula $[Ir(cod)(NHC)P_a] + nP_b$, which is suitable for the decomposition of formates in an aqueous reaction system and the production of hydrogen gas (H_2) free of CO_x by-products, or for the hydrogenation of hydrogen carbonates (HCO_3^-), where in the formula Ir is iridium, cod is 1,5-cyclooctadiene and NHC is an N-heterocyclic carbene, preferably 1-R-3-methylimidazol-2-ylidene, where R is C1-C6 alkyl or benzyl, P_a and P_b independently of each other are 1,3,5-triaza-7-phosphadamantane (pta),

monosulfonated triphenylphosphine (*m*tppts) or trisulfonated triphenylphosphine (*m*tppts), and *n* is an integer from 1 to 4.

If the catalytic hydrogenation of bicarbonate into formate according to the invention and the catalytic decomposition of formate into bicarbonate are combined in such a way that the mentioned steps are carried out in the same reaction system, in an aqueous medium, in the presence of a water-soluble catalyst, i.e. the reactants and reaction products are formed in a reversible reaction cycle, then we can create a hydrogen storage system.

Based on the above, a further aspect of our invention is to provide a process for the decomposition of formate, preferably sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) or potassium formate (HCOOK) in an aqueous reaction system and for the production of hydrogen gas (H₂) free of CO_x by-products, and for the hydrogenation of a hydrogen carbonate (HCO₃), preferably sodium hydrogen carbonate (NaHCO₃), lithium hydrogen carbonate (LiHCO₃), cesium hydrogen carbonate (CsHCO₃) or potassium hydrogen carbonate (KHCO₃), produced in the same reaction system, in an aqueous reaction system in the presence of carbon dioxide in the gas space to produce formate, preferably sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) or potassium formate (HCOOK), where using the reaction system of the process for decomposing of formate and for hydrogenating hydrogen carbonate according to the invention, and by choosing the reaction conditions, such as temperature, pressure and pH, within the ranges given below, the reactants and reaction products are formed in a reversible reaction cycle, and this reaction cycle is repeated in the required number of times.

In the mentioned process, the formate decomposition step is carried out by bringing the formate, preferably sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) or potassium formate (HCOOK) into contact with the catalyst in an aqueous reaction system at an elevated temperature, preferably at 60-100°C, preferably at 80°C, preferably at a pH greater than 8, preferably at a pH=8.3±0.2, in an Ar gas atmosphere.

A further aspect of our invention is a hydrogen storage system that includes the components described above in the invention. The hydrogen storage system according to the invention is preferably a hydrogen accumulator.

Another aspect of the invention is the use of the hydrogen storage system according to the invention to store the hydrogen required for the operation of a fuel cell (or other equipment requiring H₂) and, where applicable, to release it as needed.

In the following, our invention is illustrated with examples for a better understanding, which, however, we do not intend to interpret as a limitation of the invention.

EXAMPLES

Example 1: Examining the change in pH in NaHCO₃ solution as a function of CO₂ pressure.

5 We investigated the change of pH in a 0.1 M NaHCO₃ solution at a temperature of 80°C as a function of the applied CO₂ pressure (*Xiaolu Li, Cheng Peng, John P. Crawshaw, Geoffrey C. Maitland, J.P. Martin Trnsler, Fluid Phase Equilibria, 2018, 458, 253 -263*).

The change in pH as a function of the CO₂ pressure can be seen in Figure 2, from which it can be clearly read that the pH of the solution shifts in an acidic direction as the CO₂ pressure increases, however, the change is not linear – even a small amount of carbon dioxide causes a significant degree of acidification. It can be concluded that by using the highest CO₂ pressure (50 bar) that we used, the pH practically drops from 8.2 to 5.7.

Example 2: Investigation of the effect of CO₂ on the activity of the [Ir(emim)(cod)(*m*tppts) + *m*tppts catalyst.

15 The general formula of the tested catalyst is [Ir(emim)(cod)(*m*tppts) + *m*tppts, where emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is monosulfonated triphenylphosphine and *m*tppts is triple sulfonated triphenylphosphine.

Reaction mixture: in a 100.0 mL constant temperature batch reactor (100 mL Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20 - 20.0 ml solution volume,
- 80°C,
- [Ir] = 0,0005 mol/dm³,
- [*m*tppts] = [Ir],
- [*m*tppts] = 0,001 mol/dm³,
- 25 - [HCO₃Na] = 0,1 mol/dm³,
- p(H₂) = 50 bar,
- p(CO₂) = varied in the range of 0-50 bar,
- reaction time = 1 hour.

In summary, we found that by varying the CO₂ pressure between 0 and 50 bar (under the reaction conditions used), the achieved TON value increases from 121 to 213, which means an almost two-fold increase in reaction rate. The formate concentration in the solution obtained after a reaction time of 1 hour without the use of CO₂ is $[\text{HCO}_2^-]_0 = 60.5 \text{ mM}$, and in a 50 bar CO₂ atmosphere $[\text{HCO}_2^-]_{50} = 106.5 \text{ mM}$. From this, a total of 2.13 mmol HCO₂⁻ was formed in an atmosphere of 50 bar CO₂, which is only 6.5% more than the originally measured amount of bicarbonate (2 mmol). The obtained measurement results are shown in Figure 3.

From the data in Figure 3, we determined the change in the catalytic cycle number as a function of pH using the data in Figure 2 presented in Example 1 (change in pH with increasing CO₂ pressure). The obtained results are shown in Figure 4.

Example 3: Investigation of the effect of CO₂ on the activity of the [Ir(emim)(cod)(*m*tppts) + *m*tppts catalyst.

Reaction mixture: in a 600.0 ml constant temperature batch reactor (600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 200,0 ml solution volume,
- 80°C,
- $[\text{Ir}] = 0,00005 \text{ mol/dm}^3$,
- $[\text{mtppts}] = [\text{Ir}]$,
- $[\text{mtppts}] = 0,0001 \text{ mol/dm}^3$,
- $[\text{HCO}_3\text{Na}] = 0,1 \text{ mol/dm}^3$
- $p(\text{H}_2) = 50 \text{ bar}$,
- $p(\text{CO}_2) = \text{varied in the range of 0-50 bar}$,
- reaction time = 1 hour.

In summary, we found that by varying the CO₂ pressure between 0 and 50 bar (under the reaction conditions used), the achieved TON value increases from 260 to 576, which means a more than two-fold increase in speed. The formate concentration in the solution obtained after a reaction time of 1 hour without the use of CO₂ is $[\text{HCO}_2^-]_0 = 13.0 \text{ mM}$, and in a 50 bar CO₂ atmosphere $[\text{HCO}_2^-]_{50} = 28.8 \text{ mM}$. In other words, the resulting formate concentration does not approach the measured bicarbonate concentration (100.0 mM) in any case, the maximum degree of bicarbonate conversion (conversion) is 28.8%. The obtained measurement results are shown in Figure 5.

From the data in Figure 5, we determined the change in the catalytic cycle number as a function of pH by using the data in Figure 2 mentioned in Example 1 (change in pH with increasing CO₂ pressure). The obtained results are shown in Figure 6.

Example 4: Investigation of the effect of CO₂ on the activity of the catalyst [Ir(bmim)(cod)(*m*tppts)] + *m*tppts.

The general formula of the tested catalyst is [[Ir(bmim)(cod)(*m*tppts)] + *m*tppts, where bmim is 1-butyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine.

Reaction mixture: in a 100.0 and 600.0 ml constant temperature batch reactor (100 and 600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20,0 and 200,0 ml solution volume,
 - 80°C,
 - [Ir] = 0,0005 mol/dm³ and 0,00005 mol/dm³,
 - [*m*tppts] = [Ir],
 - [*m*tppts] = 0,001 mol/dm³ and 0,0001 mol/dm³,
 - [HCO₃Na] = 0,1 mol/dm³
 - p(H₂) = 50 bar,
 - p(CO₂) = 0 or 50 bar
- reaction time = 1 hour.

Table 1: The obtained catalytic cycle number (TON) values

TON	50 bar H ₂	50 bar H ₂ + 50 bar CO ₂
100 ml reactor	144	212
600 ml reactor	368	808

In summary, we found that by changing the pressure of CO₂ from 0 to 50 bar (under the reaction conditions used), the achieved TON value increases from 144 to 212 and from 368 to 808, which also in this case is due to the effect of CO₂ means a significant increase in reaction rate.

Example 5: Investigation of the effect of CO₂ on the activity of the [Ir(hexmim)(cod)(*m*tppts)] + *m*tppts catalyst.

The general formula of the investigated catalyst is [Ir(hexmim)(cod)(*m*tppts)] + *m*tppts, where hexmim is 1-hexyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine.

Reaction mixture: in a 100.0 and 600.0 ml constant temperature batch reactor (100 and 600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20,0 and 200,0 ml solution volume,

- 80°C,
- $[\text{Ir}] = 0,0005 \text{ mol/dm}^3$ and $0,00005 \text{ mol/dm}^3$,
- $[\text{mtppts}] = [\text{Ir}]$,
- $[\text{mtppts}] = 0,001 \text{ mol/dm}^3$ and $0,0001 \text{ mol/dm}^3$,
- 5 – $[\text{HCO}_3\text{Na}] = 0,1 \text{ mol/dm}^3$
- $p(\text{H}_2) = 50 \text{ bar}$,
- $p(\text{CO}_2) = 0$ or 50 bar
- reaction time = 1 hour.

Table 2: The obtained catalytic cycle number (TON) values

TON	50 bar H ₂	50 bar H ₂ + 50 bar CO ₂
100 ml reactor	134	204
600 ml reactor	285	522

10

In summary, we found that by changing the CO₂ pressure from 0 to 50 bar (under the reaction conditions used), the achieved TON value increases from 134 to 204 and from 285 to 522, which in this case is also due to the effect of CO₂ means a significant increase in reaction rate.

15 **Example 6:** Investigation of the effect of CO₂ on the activity of the catalyst $[\text{Ir}(\text{2mim})(\text{cod})(\text{mtppts})] + \text{mtppts}$.

The general formula of the tested catalyst is $[\text{Ir}(\text{2mim})(\text{cod})(\text{mtppts})] + \text{mtppts}$, where 2mim is 1,3-dimethylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and mtppts is trisulfonated triphenylphosphine.

20 Reaction mixture: in a 100.0 and 600.0 ml constant temperature batch reactor (100 and 600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20,0 and 200,0 ml solution volume,
- 80°C,
- $[\text{Ir}] = 0,0005 \text{ mol/dm}^3$ and $0,00005 \text{ mol/dm}^3$,
- 25 – $[\text{mtppts}] = [\text{Ir}]$,
- $[\text{mtppts}] = 0,001 \text{ mol/dm}^3$ and $0,0001 \text{ mol/dm}^3$,
- $[\text{HCO}_3\text{Na}] = 0,1 \text{ mol/dm}^3$
- $p(\text{H}_2) = 50 \text{ bar}$,
- $p(\text{CO}_2) = 0$ or 50 bar

reaction time = 1 hour.

Table 3: The obtained catalytic cycle number (TON) values

TON	50 bar H ₂	50 bar H ₂ + 50 bar CO ₂
100 ml reactor	158	256
600 ml reactor	228	786

In summary, we found that by changing the CO₂ pressure from 0 to 50 bar (under the reaction conditions used), the achieved TON value increases from 158 to 256 and from 228 to 786, which is also in this case the effect of CO₂ means a significant increase in reaction rate.

Example 7: Investigation of the effect of CO₂ on the activity of the catalyst [Ir(Bnmim)(cod)(*m*tpms)] + *m*tppts.

The general formula of the tested catalyst is [Ir(Bnmim)(cod)(*m*tpms)] + *m*tppts, where Bnmim is 1-benzyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tpms is monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine.

Reaction mixture: in a 100.0 and 600.0 ml constant temperature batch reactor (100 and 600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20,0 and 200,0 ml solution volume,
 - 80°C,
 - [Ir] = 0,0005 mol/dm³ and 0,00005 mol/dm³,
 - [*m*tpms] = [Ir],
 - [*m*tppts] = 0,001 mol/dm³ and 0,0001 mol/dm³,
 - [HCO₃Na] = 0,1 mol/dm³
 - p(H₂) = 50 bar,
 - p(CO₂) = 0 or 50 bar
- reaction time = 1 hour.

Table 4: The obtained catalytic cycle number (TON) values

TON	50 bar H ₂	50 bar H ₂ + 50 bar CO ₂
100 ml reactor	121	262
600 ml reactor	361	1119

In summary, we found that by changing the CO₂ pressure from 0 to 50 bar (under the reaction conditions used), the achieved TON value increases from 121 to 262 and from 361 to 1119, which is also in this case the effect of CO₂ means a significant increase in reaction rate.

Example 8: Investigation of the effect of CO₂ on the activity of the [Ir(emim)(cod)(*m*tpmps)] + pta catalyst.

The general formula of the tested catalyst is [Ir(emim)(cod)(*m*tpmps)] + pta, where emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tpmps is monosulfonated triphenylphosphine and pta is 1,3,5-triaza-7-phosphadamantane.

Reaction mixture: in a 100.0 and 600.0 ml constant temperature batch reactor (100 and 600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20,0 and 200,0 ml solution volume,
 - 80°C,
 - [Ir] = 0,0005 mol/dm³ and 0,00005 mol/dm³,
 - [*m*tpmps] = [Ir],
 - [pta] = 0,001 mol/dm³ and 0,0001 mol/dm³,
 - [HCO₃Na] = 0,1 mol/dm³
 - p(H₂) = 50 bar,
 - p(CO₂) = 0 or 50 bar
- reaction time = 1 hour.

Table 5: The obtained catalytic cycle number (TON) values

TON	50 bar H ₂	50 bar H ₂ + 50 bar CO ₂
100 ml reactor	67	108
600 ml reactor	260	1084

In summary, we found that by changing the CO₂ pressure from 0 to 50 bar (under the reaction conditions used), the achieved TON value increases from 67 to 108 and from 260 to 1084, which in this case is also due to the effect of CO₂ means a significant increase in reaction rate.

Example 9: Investigation of the effect of CO₂ on the activity of the [Ir(emim)(cod)(*m*tpmps)] + *m*tpmps catalyst.

The general formula of the tested catalyst is [Ir(emim)(cod)(*m*tpmps)] + *m*tpmps, where emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tpmps is monosulfonated triphenylphosphine.

Reaction mixture: in a 100.0 and 600.0 ml constant temperature batch reactor (100 and 600 ml Series 5500 HP Compact Reactor manufactured by Parr Instruments):

- 20,0 and 200,0 ml solution volume,
- 80°C,
- 5 – $[\text{Ir}] = 0,0005 \text{ mol/dm}^3$ and $0,00005 \text{ mol/dm}^3$,
- $[\text{mtpms}] = 0,0015 \text{ mol/dm}^3$ and $0,00015 \text{ mol/dm}^3$,
- $[\text{HCO}_3\text{Na}] = 0,1 \text{ mol/dm}^3$
- $p(\text{H}_2) = 50 \text{ bar}$,
- $p(\text{CO}_2) = 0 \text{ or } 50 \text{ bar}$
- 10 reaction time = 1 hour.

Table 6: The obtained catalytic cycle number (TON) values

TON	50 bar H ₂	50 bar H ₂ + 50 bar CO ₂
100 ml reactor	263	320
600 ml reactor	325	2050

In summary, we found that by changing the CO₂ pressure from 0 to 50 bar (under the applied reaction conditions), the achieved TON value increases from 263 to 320 and from 325 to 15 2050, which in this case is also due to the effect of CO₂ means a significant increase in speed.

Figure 7 provides a visual presentation of the results presented in Examples 4-9. The results clearly prove that both in the case of changing the carbene ligand and the phosphine ligand, it can be proven that in the presence of CO₂ (under the given conditions) the rate of hydrogenation of bicarbonate increases several times (2-6 times).

20 INDUSTRIAL APPLICABILITY

The process for the hydrogenation of hydrogen carbonate, which is the subject of our invention, provides an opportunity to provide a renewable energy source, the basis of which is a process for the catalytic decomposition of formate in an aqueous reaction system and the production of hydrogen gas free of CO_x by-products, and for the catalytic hydrogenation of 25 hydrogen carbonate produced in the same reaction system in an aqueous reaction system in the presence of carbon dioxide in the gas space, and thus to produce the corresponding formate.

WHAT IS CLAIMED IS

1. A process for the hydrogenation of hydrogen carbonate (HCO_3^-), in an aqueous reaction system, preferably said hydrogen carbonate being selected from sodium hydrogen carbonate (NaHCO_3), lithium hydrogen carbonate (LiHCO_3), cesium hydrogen carbonate (CsHCO_3) and potassium hydrogen carbonate (KHCO_3) and for the production of formate, preferably formate selected from the group of sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) and potassium formate (HCOOK),

10 said process comprising bringing said hydrogen carbonate and a catalyst into contact with each other at an elevated temperature, preferably at $60\text{--}100^\circ\text{C}$, more preferably at 80°C , at a pressure of 1-1200 bar, preferably 10-100 bar;

where the catalyst is a catalyst with the general formula $[\text{Ir}(\text{cod})(\text{NHC})\text{P}_a] + n\text{P}_b$,

where in the formula

15 Ir is iridium;

cod is 1,5-cyclooctadiene;

NHC is an N-heterocyclic carbene, preferably 1-R-3-methylimidazol-2-ylidene, where R is C1-C6 alkyl or benzyl;

n is an integer from 1 to 4; and

20 P_a and P_b are independently 1,3,5-triaza-7-phosphadamantane (pta), monosulfonated triphenylphosphine ($m\text{tppps}$) or trisulfonated triphenylphosphine ($m\text{tppts}$);

characterized in that the hydrogenation of hydrogen carbonate is carried out in such a way that carbon dioxide is present in the gas space.

2. The process according to Claim 1, *characterized in that* the catalyst used is selected from the following:

a) a catalyst according to the formula $[\text{Ir}(\text{emim})(\text{cod})(m\text{tppps})] + m\text{tppts}$, wherein emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, $m\text{tppps}$ is monosulfonated triphenylphosphine and $m\text{tppts}$ is trisulfonated triphenylphosphine;

30 b) a catalyst according to the formula $[\text{Ir}(\text{bmim})(\text{cod})(m\text{tppps})] + m\text{tppts}$, wherein bmim is 1-butyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, $m\text{tppps}$ is monosulfonated triphenylphosphine and $m\text{tppts}$ is trisulfonated triphenylphosphine;

c) a catalyst according to the formula $[\text{Ir}(\text{hexmim})(\text{cod})(m\text{tppps})] + m\text{tppts}$, wherein hexmim is 1-hexyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, $m\text{tppps}$ is monosulfonated triphenylphosphine and $m\text{tppts}$ is trisulfonated triphenylphosphine;

d) a catalyst according to the formula $[\text{Ir}(\text{2mim})(\text{cod})(\text{mtppts})] + \text{mtppts}$, wherein 2mim is 1,3-dimethyl-imidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and mtppts is trisulfonated triphenylphosphine;

e) a catalyst according to the formula $[\text{Ir}(\text{Bnmim})(\text{cod})(\text{mtppts})] + \text{mtppts}$, wherein Bnmim is 1-benzyl-3-methylimidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and mtppts is trisulfonated triphenylphosphine;

f) a catalyst according to the formula $[\text{Ir}(\text{emim})(\text{cod})(\text{mtppts})] + \text{pta}$, wherein emim is 1-ethyl-3-methylimidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine and pta is 1,3,5-triaza-7-phosphadamantane; and

g) a catalyst according to the formula $[\text{Ir}(\text{emin})(\text{cod})(\text{mtppts})] + \text{mtppts}$, wherein emim is 1-ethyl-3-methylimidazol-2-ilydene, cod is 1,5-cyclooctadiene, mtppts is monosulfonated triphenylphosphine.

3. A process for decomposing a formate, preferably a formate selected from sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) and potassium formate (HCOOK) in an aqueous reaction system and for producing hydrogen gas (H_2) free of CO_x by-products, and in the same reaction system, for the hydrogenation of the resulting hydrogen carbonate (HCO_3^-), preferably a hydrogen carbonate selected from the group of sodium hydrogen carbonate (NaHCO_3), lithium hydrogen carbonate (LiHCO_3), cesium hydrogen carbonate (CsHCO_3) and potassium hydrogen carbonate (KHCO_3) in an aqueous reaction system, thus for the production of a formate, preferably a formate selected from the group of sodium formate (HCOONa), lithium formate (HCOOLi), cesium formate (HCOOCs) and potassium formate (HCOOK);

where the reactants and the reaction products are formed in a reversible reaction cycle by using the reaction system of the formate decomposition step and the bicarbonate hydrogenation step and by choosing the values of temperature, pressure and pH within the ranges specified below, and this reaction cycle is repeated the required number of times;

where the formate decomposition step includes bringing the formate into contact with the catalyst in an aqueous reaction system, at an elevated temperature, preferably at 60-100 °C, preferably at 80 °C, preferably at a pH greater than 8, preferably at a $\text{pH}=8.3 \pm 0.2$, in an Ar gas atmosphere;

where the hydrogenation step of the hydrogen carbonate includes bringing the hydrogen carbonate and a catalyst into contact with each other, at an elevated temperature, preferably at 60-100°C, more preferably at 80°C, under pressure of 1-1200 bar, preferably 10-100 bar;

where the catalyst is a catalyst with the general formula $[\text{Ir}(\text{cod})(\text{NHC})\text{P}_a] + n\text{P}_b$,

where in the formula

Ir is iridium;

cod is 1,5-cyclooctadiene;

NHC is an N-heterocyclic carbene, preferably 1-R-3-methylimidazol-2-ylidene, where R is
 5 C1-C6 alkyl or benzyl;
 n is an integer from 1 to 4; and

P_a and P_b are independently a 1,3,5-triaza-7-phosphadamantane (pta), monosulfonated triphenylphosphine (*m*tppts) or trisulfonated triphenylphosphine (*m*tppts);

characterized in that the hydrogenation of hydrogen carbonate is carried out in such a way
 10 that carbon dioxide is present in the gas space.

4. The process according to Claim 3, *characterized in that* the catalyst used is selected from the following:

a) a catalyst according to the general formula [Ir(emim)(cod)(*m*tppts)] + *m*tppts, where
 emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is
 15 monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

b) a catalyst according to the general formula [Ir(bmim)(cod)(*m*tppts)] + *m*tppts, where
 bmim is 1-butyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is
 monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

c) a catalyst according to the general formula [Ir(hexmim)(cod)(*m*tppts)] + *m*tppts, where
 20 hexmim is 1-hexyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is
 monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

d) a catalyst according to the general formula [Ir(2mim)(cod)(*m*tppts)] + *m*tppts, where
 2mim is 1,3-dimethyl-imidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is monosulfonated
 triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

25 e) a catalyst according to the general formula [Ir(Bnmim)(cod)(*m*tppts)] + *m*tppts, where
 Bnmim is 1-benzyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is
 monosulfonated triphenylphosphine and *m*tppts is trisulfonated triphenylphosphine;

f) a catalyst according to the general formula [Ir(emim)(cod)(*m*tppts)] + pta, where emim is
 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is monosulfonated
 30 triphenylphosphine and pta is 1,3,5-triaza-7-phosphadamantane; and

g) a catalyst according to the general formula [Ir(emim)(cod)(*m*tppts)] + *m*tppts, where
 emim is 1-ethyl-3-methylimidazol-2-ylidene, cod is 1,5-cyclooctadiene, *m*tppts is
 monosulfonated triphenylphosphine.

5. Use of the process according to Claim 3 for a hydrogen storage system.

6. The hydrogen storage system according to Claim 4, which is a hydrogen battery.

7. Use of the hydrogen storage system according to Claim 5 or 6 for storing the hydrogen required to operate a fuel cell or other equipment requiring H₂, and optionally for releasing thereof to the extent of necessary.