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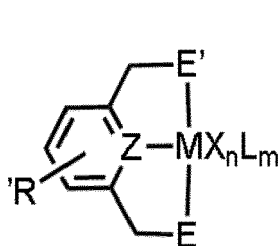
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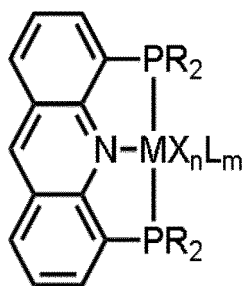
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(54) **ELECTROCATALYTIC OXIDATION OF ALCOHOLS USING ACCEPTOR-LESS DEHYDROGENATION CATALYSTS**

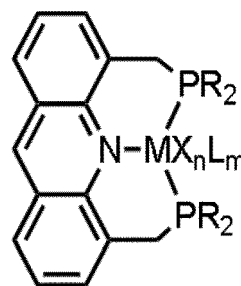
(57) A use of an acceptor-less dehydrogenation catalyst for an electrocatalytic oxidation of an alcohol to an ester or/and an acid under electrochemical conditions, the acceptor-less dehydrogenation catalyst being represented by the structure of any one of the formulae F1, F2, or F3:



F1



F2



F3

M being selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Os, Pt, Ir, Mn;
L and X being ligands; X is an anionic ligand, L is a neutral ligand,
Z being selected from the group consisting of C, N;
R' being an organic substituent of the aromatic ring;
E' is selected in the group consisting of N, P, C, O and/or S-donors;
R being an organic substituent, typically selected from the group consisting of ⁱPr, ^tBu, Ph, Et, Me, Bn, H.

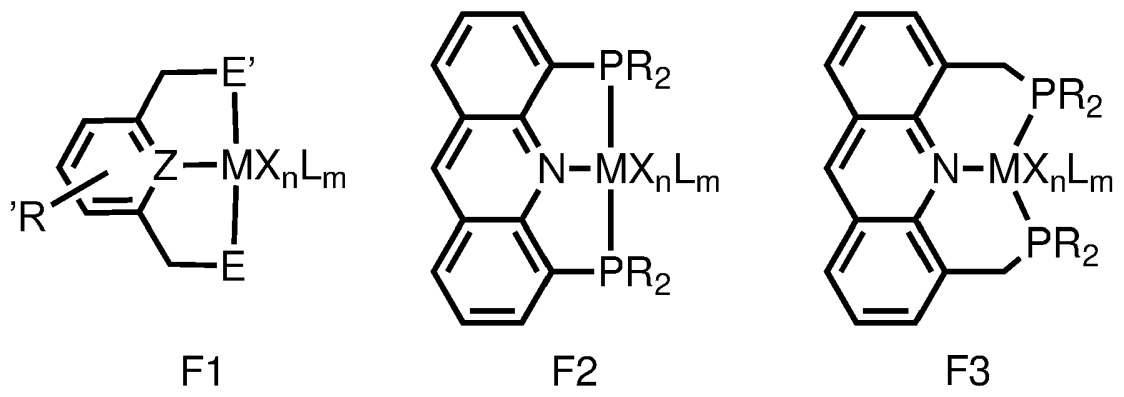


Fig. 1

Description

TECHNICAL FIELD

5 **[0001]** The invention relates to the dehydrogenation process of alcohols in the presence of acceptor-less dehydrogenation catalysts under electrochemical conditions.

BACKGROUND ART

10 **[0002]** Various thermal methods are known for the dehydrogenation/oxidation of alcohols to aldehydes/ketones, acids and esters.

[0003] Dehydrogenation/oxidation of alcohols can be performed in the presence of an oxidant/hydrogen-acceptor *via* transfer hydrogenation. Catalytic transfer hydrogenation reactions is well-known using molecular catalysts. These processes mainly use acetone as both the solvent and the hydrogen-acceptor, mainly focusing on the oxidation of secondary alcohols that undergo facile transfer hydrogenation. Other co-oxidants/hydrogen-acceptors might be suitable olefins. For example, using Rh-based transfer hydrogenation catalysts, the Grützmacher group showed that ethanol can be oxidized and reformed to ethyl acetate in the presence of ketones or alkenes (Angew. Chem. Int. 2008, 47, 3245-3249).

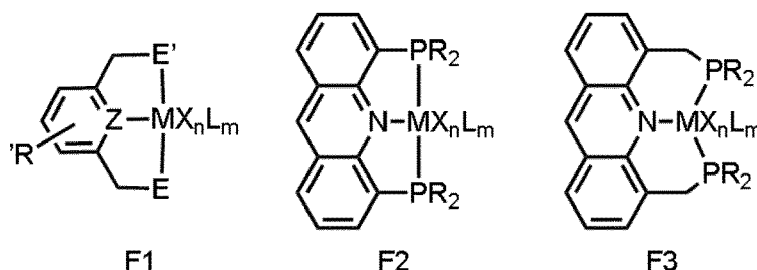
15 **[0004]** In recent years, transfer hydrogenation catalysts were proposed as possible catalyst candidates for the electrochemical oxidation of alcohols. In 2010, *Grützmacher et al* have described a fuel cell operating in a strongly basic media (2M KOH) for the oxidation of ethanol to acetate (CH_3COO^-), using as the anode catalyst a molecular $[\text{Rh}(\text{OTf})(\text{trop}_2\text{NH})(\text{PPh}_3)]$ complex, deposited on a conductive carbon support (Angewandte Chemie International Edition 2010, 49 (40), 7229-7233). In a 2020 review paper, *Cook et al* have presented the current State-of-the-Art for molecular electrocatalysis capable of alcohol oxidation, illustrated by three case studies; namely a copper/nitroxyl radical cooperative catalyst system (case 1), noble metal-hydrides with proximal amine group (case 2) for transfer hydrogenation, nickel hydrides with P_2N_2 ligands (case 3) (Molecular Electrocatalysts for Alcohol Oxidation: Insights and Challenges for Catalyst Design, ACS Appl. Energy Mater. 2020, 3 (1), 38-46).

20 **[0005]** Nevertheless, published results for the molecular electrocatalytic oxidation of alcohols is limited to low turnover numbers (<5), substrates that undergo facile transfer hydrogenation (e.g. isopropanol and secondary alcohols in general) and at unknown or high overpotential (>1.2 V). Hence, the reactivity is in general limited to products obtainable via transfer hydrogenation (2-electron oxidation products), or activated alcohols (e.g. benzyl alcohol) without the possibility to oxidize reform simple aliphatic alcohols, e.g. to their corresponding esters under electrocatalytic conditions.

SUMMARY OF THE INVENTION

35 **[0006]** Various embodiments are directed to addressing the effects of one or more of the problems set forth above. The following presents a simplified summary of embodiments in order to provide a basic understanding of some aspects of the various embodiments. This summary is not an exhaustive overview of these various embodiments. It is not intended to identify key/critical elements or to delineate the scope of these various embodiments. Its sole purpose is to present some concepts in a simplified form as a prelude to the more detailed description that is discussed later.

40 **[0007]** The present invention provides the use of an acceptor-less dehydrogenation catalyst for an electrocatalytic oxidation of an alcohol to an ester or/and an acid under electrochemical conditions, the acceptor-less dehydrogenation catalyst being represented by the structure of any one of the formulae F1, F2 or F3:



M being selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Os, Pt, Ir, Mn;

L and X being ligands;

Z being selected from the group consisting of C, N;

R' being an organic substituent of the aromatic ring;

E' is selected in the group consisting of N, P, C, O and/or S-donors;

R being an organic substituent, typically selected from the group consisting of *i*Pr, *t*Bu, Ph, Et, Me, Bn, H.

[0008] In particular embodiments, the alcohol is electrocatalytic oxidized at least to an ester.

[0009] In particular embodiments, the electrocatalytic oxidation is carried out in a homogeneous phase.

[0010] In other particular embodiments, the acceptor-less dehydrogenation catalyst is solubilized in the alcohol which is oxidized, the oxidation being realized without additional organic solvent.

[0011] In other particular embodiments, the acceptor-less dehydrogenation catalyst is solubilized in an additional organic solvent.

[0012] In particular embodiments, the use is carried out in a heterogeneous phase, and the acceptor-less dehydrogenation catalyst is immobilized on a conductive support.

[0013] In particular embodiments, the use is carried out under heterogeneous conditions and in that the alcohol is oxidized at least to ester.

[0014] Under heterogenous conditions, advantageously, the solvent is water and the pH between 7 and 14.

[0015] In some particular embodiments, X is an anionic ligand.

[0016] In some embodiments, L is a neutral ligand.

[0017] In some particular embodiments, the alcohol is advantageously oxidized at least to 30 FE% (Faradaic Efficiency) to an ester with these conditions: 0.1 M LiCl, 0.1 M LiOH in EtOH, 1 mM catalyst, 0.3 V vs Ag/AgNO₃ (0.01 M in 0.1M TBAPF₆ in CH₃CN), glassy carbon working electrode, separated counter electrode compartment.

[0018] In some particular embodiments, the alcohol is advantageously oxidized at least to 50 FE% (Faradaic Efficiency) to an ester with these conditions: 0.1 M LiOH in 10 % w/w EtOH in H₂O, catalytic ink comprised of 0.2 mg/cm² catalyst, 1 mg/cm² carbon black (xc72r), 5 μL/cm² Nafion[®] (5 % w/w) deposited on Toray paper, 0.3 V vs Ag/AgCl, cathode compartment separated by an anion exchange membrane (Sustanion).

[0019] In some particular embodiments, the alcohol is advantageously oxidized at least to 25 FE% (Faradaic Efficiency) to an ester with these conditions: 0.2 M LiBF₄ in 10 % w/w EtOH in H₂O, catalytic ink comprised of 0.2 mg/cm² catalyst, 1 mg/cm² carbon black (xc72r), 5 μL/cm² Nafion[®] (5 % w/w) deposited on a conducting support (Toray paper), 3 mA constant current electrolysis, separated cathode compartment.

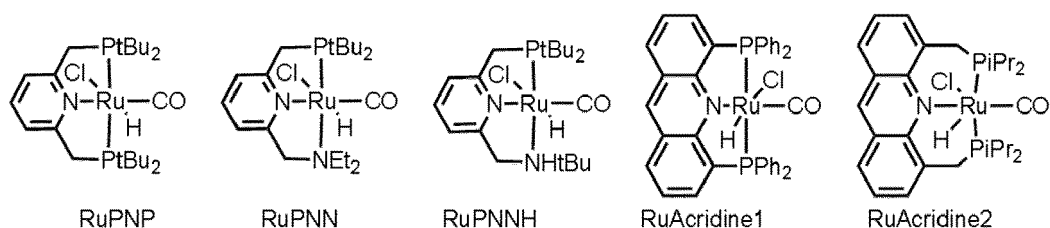
[0020] In some embodiments, in the formulae F1:

$$E' = ER_2;$$

E being selected from the group consisting of P, N;

R being selected from the group consisting of *i*Pr, *t*Bu, Ph, Et, Me, Bn H.

[0021] In some particular embodiments, the catalyst is represented by the structure of any one of the formulae RuPNP, RuPNP, RuPNNH, RuAcridine1, or RuAcridine2:



[0022] In some embodiments, alcohol is ethanol and ethanol is oxidized to ethyl acetate.

[0023] In some particular embodiments, the electrocatalytic oxidation is conducted:

- at ambient temperature, without heating, or
- at temperature inferior to 60°C.

[0024] In some embodiments, the organometallic catalyst is in contact with a working solution comprising the alcohol and comprising a base chosen in the group comprising MOH, MOR (R = alkyl, benzyl), MOtBu (with M = Li, Na, K), or neutral organic bases such as lutidine, pyridine, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene), TBD (Triazabicyclodecene) or other guanidine bases, trialkyl amines, or strong phosphorous bases, such as Verkade's proazaphosphatranes and phosphazenes.

[0025] In some particular embodiments, the organometallic catalyst is PNN, the base being KOH or LiOH, 1 mM of

organometallic catalyst being solubilized in the working solution comprising 0.1M of the base.

[0026] In some embodiments, a constant current of 3 mA is applied.

[0027] In some particular embodiments, an anodic half-cell reaction is coupled with a cathodic half-cell reaction, the cathodic half-cell reaction being an electrochemical reduction of CO_2 to CO.

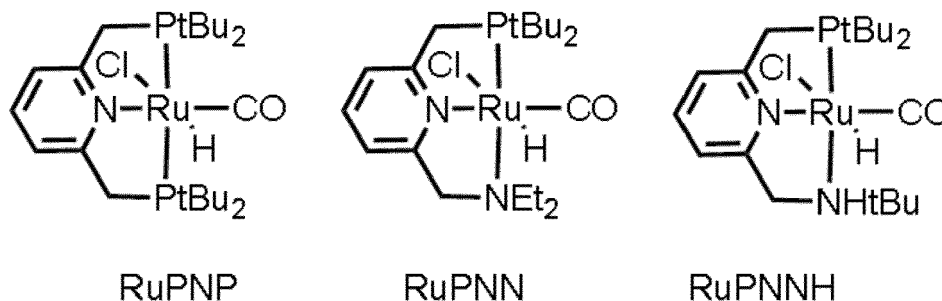
[0028] Advantageously, the electrocatalytic oxidation takes place in a flow cell.

[0029] The present invention will be understood and appreciated more fully from the following detailed description. In this description:

- Figure 1 shows the structure of three acceptor-less dehydrogenation catalyst for an electrocatalytic oxidation of an alcohol to an ester or/and an acid under electrochemical conditions;
- Figure 2 shows the structure of five Ruthenium acceptor-less dehydrogenation catalyst for an electrocatalytic oxidation of an alcohol to an ester or/and an acid under electrochemical conditions;
- Figure 3 shows the principles of electrochemical activation of acceptor-less dehydrogenation catalysts, in homogeneous system (separate cell);
- Figure 4 is ^1H -NMR of electrolytic solution, experimental conditions being 0.1M LiOH in pure EtOH, 1-5 mM catalyst, $T = 25^\circ\text{C}$, $V_{\text{applied}} = 0.3 \text{ V vs SCE}$;
- Figure 5 shows the principles of electrochemical activation of acceptor-less dehydrogenation catalysts, in heterogeneous system (flow-cell);
- Figure 6 is a charge versus time curve obtained in a flow cell, the experimental conditions being 0.1M LiOH in 10 wt% EtOH in H_2O , 0.2 mg.cm^{-2} catalysts, $T = 25^\circ\text{C}$, $V_{\text{applied}} = 0.3 \text{ V vs SCE}$;
- Figure 7 is ^1H -NMR (D_2O) after reaction using the conditions 0.1M LiOH, EtOH, 0.3V vs SCE, 1mM cat, $T = 25^\circ\text{C}$, homogenous conditions, AD catalysts being RuPNN;
- Figure 8 is a charged passed elapsed diagram under conditions of Figure 7, $\text{TON} = 17$, $\text{TOF} = 3,4 \text{ h}^{-1}$;
- Figure 9 is a charged passed diagram using the conditions 0.2 mg.cm^{-2} cat, 0.3 V vs SCE, 10 wt% EtOH in H_2O , 0.1M LiOH, heterogeneous conditions, $\text{TON} = 160$, $\text{TOF} = 60 \text{ h}^{-1}$, $\text{TON}_{\text{EtOAc}} = 47$, $\text{TON}_{\text{OAc}} = 113$, AD catalyst being RuPNN.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0030] A group of ruthenium pincer complexes such as

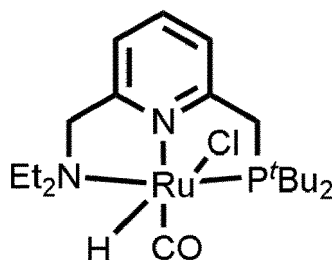


are shown to be active in the electrochemical oxidation of ethanol.

[0031] The reaction set-up used is a three-electrode assembly comprising of an inert glassy carbon working electrode, a platinum mesh counter-electrode separated from working compartments by a ceramic frit, and either a SCE (sat. Calomel) or an Ag/AgNO_3 (0.01M AgNO_3 , 0.1 M TBAP in CH_3CN) reference electrode. In this homogeneous three-electrode set-up, the molecular catalyst (in general 1 mM) is directly solubilized in the working solution. The working solution generally comprises the alcohol (ethanol) and 0.1 M of base (e.g. KOH, LiOH, NaOH), both as electrolyte and co-substrate.

[0032] The products formed are analyzed by ionic chromatography, GC/MS and ^1H -NMR.

[0033] As an example, using the PNN-complex



in 0.1M KOH at 0.3 V vs. SCE, 6.2 mM acetate can be formed after 3h, corresponding to turnovers > 6.

[0034] To the knowledge of the inventors, this is the first example for the electrochemical activation of AD-dehydrogenation catalysts for primary aliphatic alcohols. Nevertheless, the product formed (acetate) is reminiscent to reaction pathways also accessible via transfer-hydrogenation catalysts. Tuning the conditions (e.g. 0.1M LiOH), the unique reactivity of AD-catalysts can be explored. Under these conditions (still 0.3 V vs. SCE), > 7mM of ethyl acetate can be formed (together with 11 mM acetate). To the knowledge of the inventors, this is the first example of molecular electrochemical reforming of ethanol to ethyl acetate with an AD-catalysts.

[0035] Although homogenous conditions are advantageous in terms of few necessary infrastructure needed, as well as the possibility to analyze the reaction (mechanism) in detail, for practical applications, immobilizing the catalyst on an electrode surface might be more desirable.

[0036] A catalytic ink was fabricated by mixing the catalyst with a conducting support (e.g. carbon black, carbon nanotubes, graphene) and a binder (e.g. Nafion®), suspended in a solvent (e.g. acetone, THF, ethanol).

[0037] The mixture is sonicated shortly and then deposited on an electrode support (e.g. Freudenberg paper, Toray paper, carbon cloth) via hot drop casting (in general, 10 °C below the boiling point of the employed solvent).

[0038] Catalysts loadings on the final electrode are 0.2 mg/cm².

[0039] A 10 cm² electrode (Freudenberg paper as support) was fabricated and inserted into an electrochemical flow cell.

[0040] The anolyte (and catholyte) compartment including tubings had a volume of 100 mL.

[0041] A Sustanion® anion exchange membrane was used to separate catholyte and anolyte compartments.

[0042] A 10 cm² commercial Pt/Ti alloy was used as the cathode.

[0043] The anolyte solution was recycled and flown through the flow cell at a rate of 1L/h.

[0044] Electrolysis was conducted in 0.1 M LiOH in 10wt% ethanol in water at 0.3 V vs. Ag/AgCl (cell potential of. 1.74 V) for 3 h at 25 °C.

[0045] GC/MS and IC confirmed the formation of 2 mM ethylacetate (turnovernumber > 47) and 4.6 mM acetate (turnovernumber > 110) with faradaic efficiencies around >90% under un-optimized conditions.

[0046] Importantly, the low cell potential has to be noted as well as a low overpotential at the anode of approximately 520 mV.

[0047] These results demonstrate the possibility of immobilizing the catalysts successfully, increasing catalyst lifetime and upscaling the reaction conditions.

[0048] The invention demonstrates that for the first time acceptor-less dehydrogenation catalysts can be activated electrochemically and that, moreover, their thermal chemistry can be directly translated into electrochemical schemes, i.e. the same products can be obtained under thermal and electrochemical set-ups.

[0049] Compared to the few examples of heterogenous ethanol reforming to ethyl acetate for example, catalyst loading is extremely low (as well as the transition metal content). In addition, given that AD-catalysts can be activated electrochemically, their broad range of applications can be electrified.

[0050] Finding suitable molecular electrocatalysts for alcohol reformation is a remarkable challenge. Most reported cases of molecular electrocatalytic alcohol oxidation are limited to non-preparative studies, secondary alcohols known to be good transfer hydrogenation targets and or low turnover number <5. An example of performing molecular electrocatalytic alcohol oxidation by the Grützmaier group using a transfer hydrogenation catalyst, is not able to access the same chemical space than under thermal activation schemes.

[0051] Using electrochemistry instead of thermal activation has several advantages including, cheap reagents (electrons), safety (avoidance of high temperature and pressure, as well as explosive/highly reactive reagents), control and scalability (flow-application and cell-stacks). Hence, being able to translate a field of classical thermal chemistry (hydrogenation/dehydrogenation chemistry) into electrochemistry is highly advantageous for all applications of that field.

[0052] Using catalytic electrochemistry for the oxidation of ethanol to ethyl acetate allows the production under highly atom and energy efficient conditions. Indeed, using ethanol as the starting material, the only byproduct formed is formally H₂ in the form of protons and electrons. It could thus replace common oxidation procedures using stoichiometric amounts of oxidants or procedures that liberate H₂ under refluxing conditions.

[0053] If the stability and activity of the employed catalysts can be increased, the present method might be interesting

to synthesize a variety of esters from readily available alcohol feedstock under controlled and safe conditions.

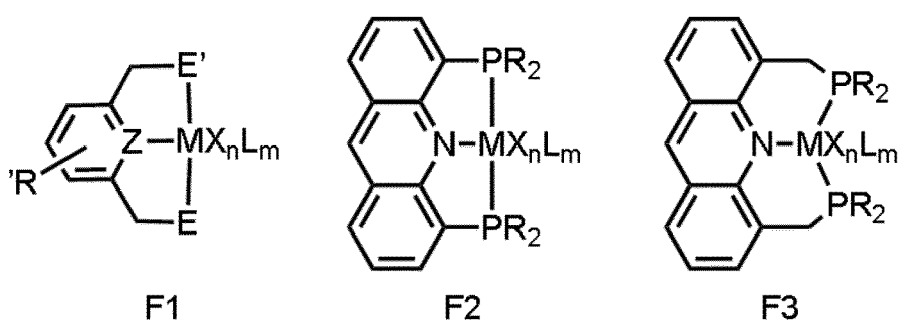
[0054] A commercial electrolyzer for organic synthesis might be fabricated that would allow the preparation of oxidized compounds under highly energy efficient and safe conditions. Adopting a flow cell approach, such an electrolyzer could range from lab scale production for synthetic purposes to large scale acid/ester production from cheap primary resources.

[0055] The possibility to apply the proposed technology to hydrogen storage/release applications has tremendous potential.

[0056] The chemical industry is responsible for around 25% of global industrial energy consumption and thus for around 12.5% of total energy consumption today. Replacing thermal activation schemes in chemistry with electrocatalytic methodologies pledges to bring a long several advantages, such as safety, scalability, atom efficiency, reaction control and finally energy efficiency. Indeed, in electrochemical transformations the energy input for a given reaction can be controlled and monitored finely, offering the opportunity to make electrochemistry a key player in a sustainable economy of the future. Finding potent molecular electrocatalysts for the reversible oxidation/reduction of alcohol/carbonyl substrates is thus a remarkable challenge.

Claims

1. A use of an acceptor-less dehydrogenation catalyst for an electrocatalytic oxidation of an alcohol to an ester or/and an acid under electrochemical conditions, the acceptor-less dehydrogenation catalyst being represented by the structure of any one of the formulae F1, F2, or F3:



M being selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Os, Pt, Ir, Mn;

L and X being ligands; X is an anionic ligand, L is a neutral ligand,

Z being selected from the group consisting of C, N;

R' being an organic substituent of the aromatic ring;

E' is selected in the group consisting of N, P, C, O and/or S-donors;

R being an organic substituent, typically selected from the group consisting of ^tPr, ^tBu, Ph, Et, Me, Bn, H.

2. The use according to claim 1, wherein in that the alcohol is electrocatalytic oxidized at least to an ester.
3. The use according to claims 1-2, wherein in that the electrocatalytic oxidation is carried out in a homogeneous phase.
4. The use according to claim 3, wherein in that the acceptor-less dehydrogenation catalyst is solubilized in the alcohol which is oxidized, the oxidation being realized without additional organic solvent.
5. The use according to claim 3, wherein in that the acceptor-less dehydrogenation catalyst is solubilized in an additional organic solvent.
6. The use according to claims 1-2, wherein in that the use is carried out in a heterogeneous phase, and in that the acceptor-less dehydrogenation catalyst is fixed on a conductive support.
7. The use according to claim 6, wherein in that the use is carried out under heterogeneous conditions and in that the alcohol is oxidized at least to ester.
8. The use according to claims 6-7, wherein solvent is water and the pH is between 7 and 14.

9. The use according to claims 1 to 8, wherein in that the alcohol is oxidized at least to 30 FE% (Faradaic efficiency) to an ester with these conditions: 0.1 M LiCl, 0.1 M LiOH in EtOH, 1 mM catalyst, 0.3 V vs Ag/AgNO₃ (0.01 M in 0.1M TBAPF₆ in CH₃CN), glassy carbon working electrode, separated counter electrode compartment.

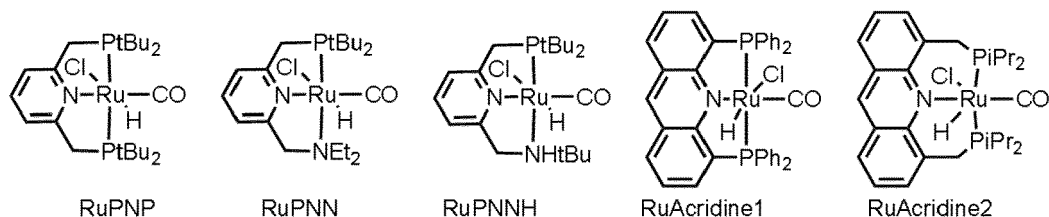
10. The use according to claims 1 to 9, wherein in that in the formulae F1:

$$E' = ER_2;$$

E being selected from the group consisting of P, N;

R being selected from the group consisting of ⁱPr, ^tBu, Ph, Et, Me, Bn H.

11. The use according to claims 1-10, wherein in that the catalyst is represented by the structure of any one of the formulae RuPNN, RuPNP, RuPNNH, RuAcridine1, or RuAcridine2:



12. The use according to claims 1 to 11, wherein in that alcohol is ethanol and that ethanol is oxidized to ethyl acetate.

13. The use according to claims 1 to 12, wherein in that the electrocatalytic oxidation is conducted:

- at ambient temperature, without heating, or
- at temperature inferior to 60°C.

14. The use according to claims 1 to 13, wherein in that the organometallic catalyst is in contact with a working solution comprising the alcohol and comprising a base chosen in the group comprising MOH, MOR (R = alkyl, benzyl), MO^tBu (with M = Li, Na, K), or neutral organic bases such as lutidine, pyridine, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene), TBD (Triazabicyclodecene) or other guanidine bases, trialkyl amines, or phosphorous bases, such as Verkade's proazaphosphatranes, or phosphazenes.

15. The use according to claim 14, wherein in that a constant current between 1 and 10 mA is applied.

16. The use according to claim 1 to 15, wherein in that an anodic half-cell reaction is coupled with a cathodic half-cell reaction, the cathodic half-cell reaction being an electrochemical reduction of CO₂ to CO.

17. The use according to claims 1 to 16, wherein in that the electrocatalytic oxidation takes place in a flow cell.

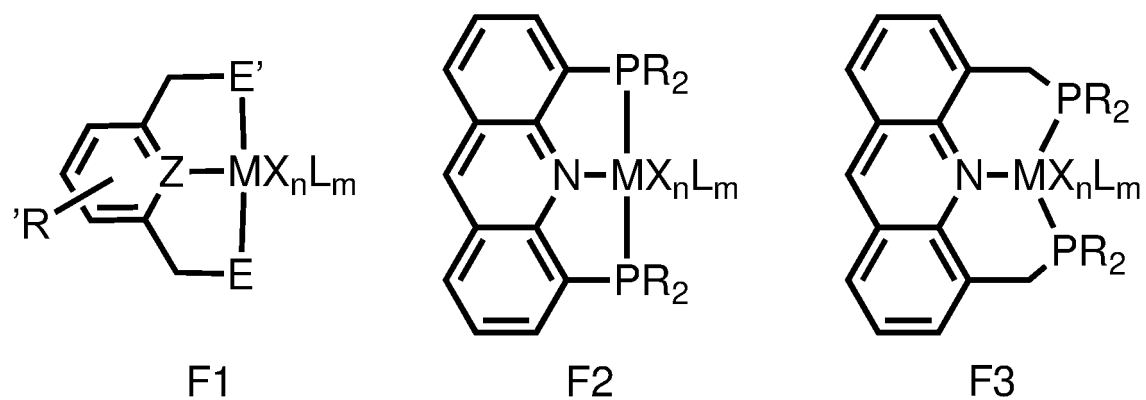


Fig. 1

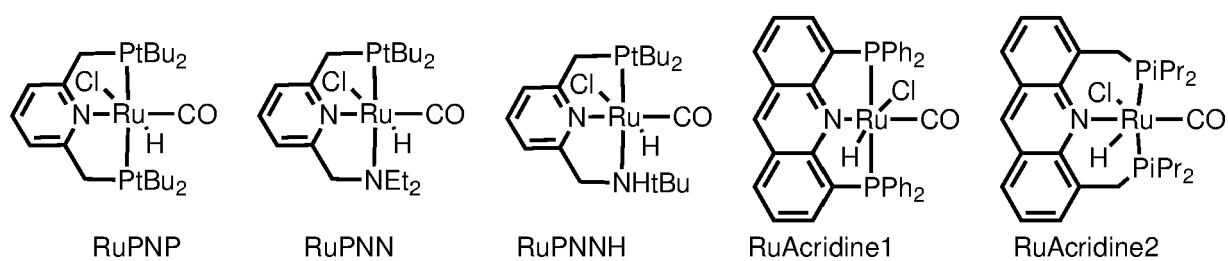


Fig. 2

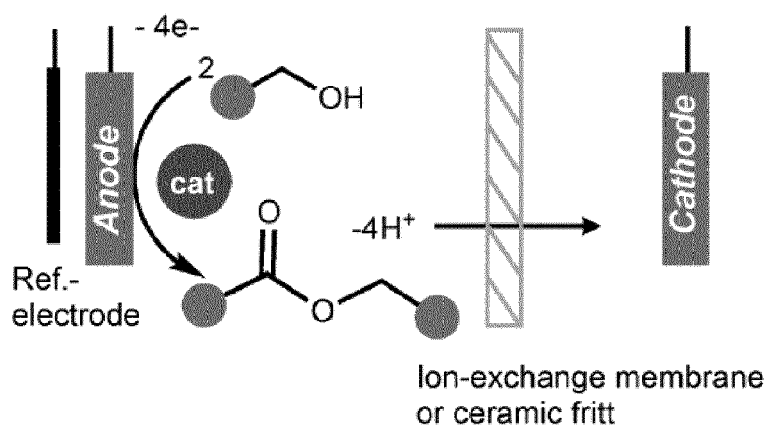


Fig. 3

^1H -NMR of electrolyte solution:

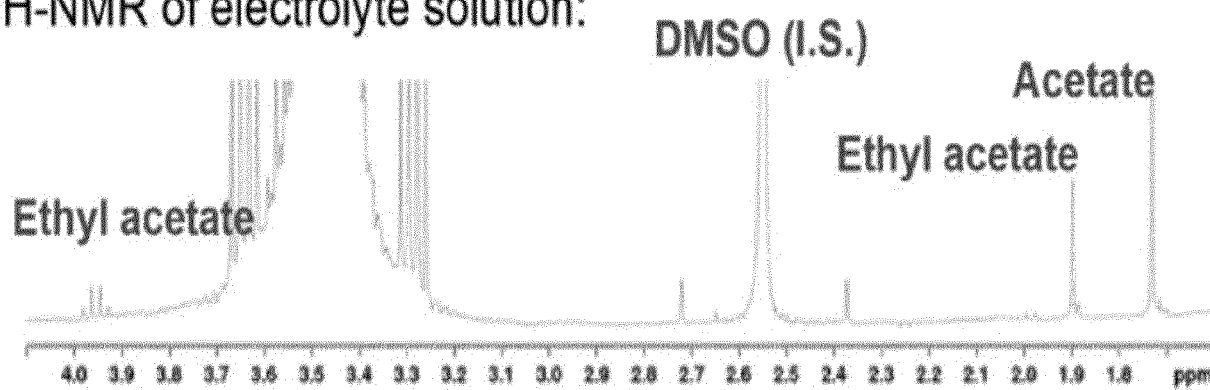


Fig. 4

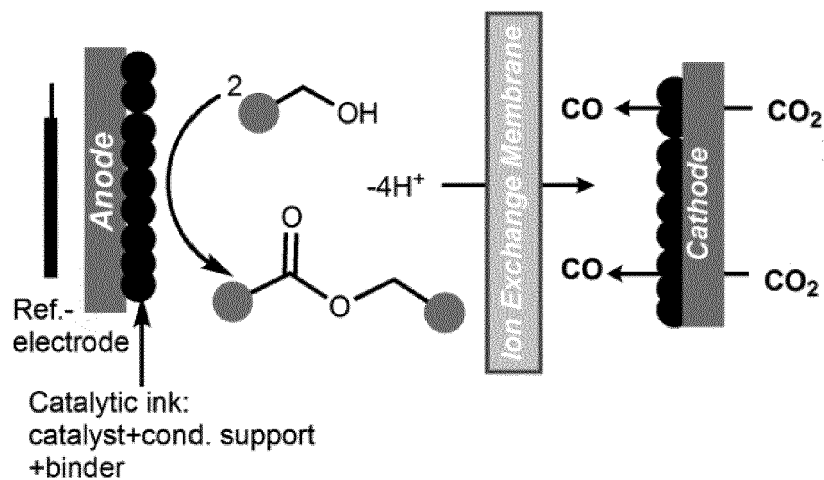


Fig. 5

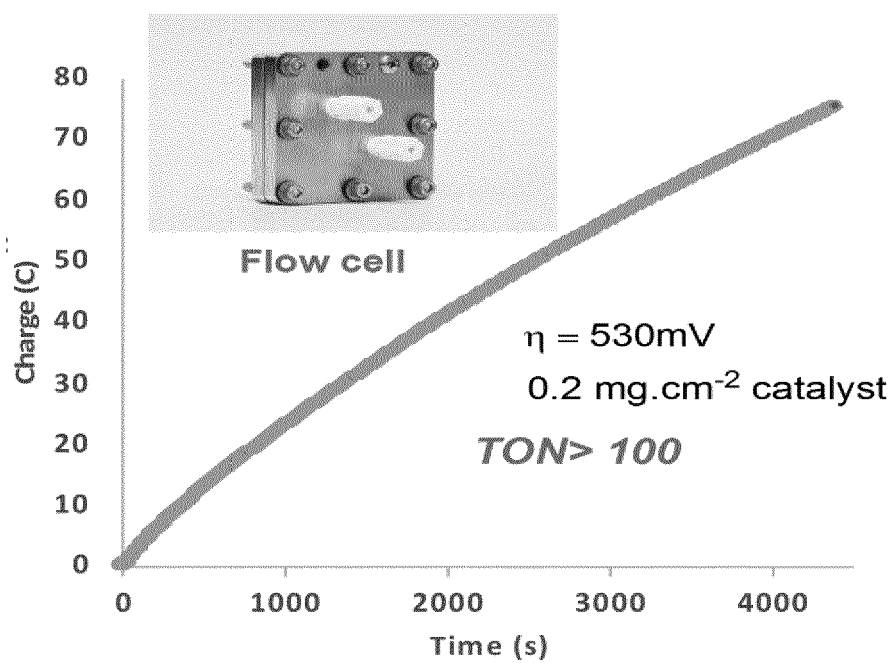


Fig. 6

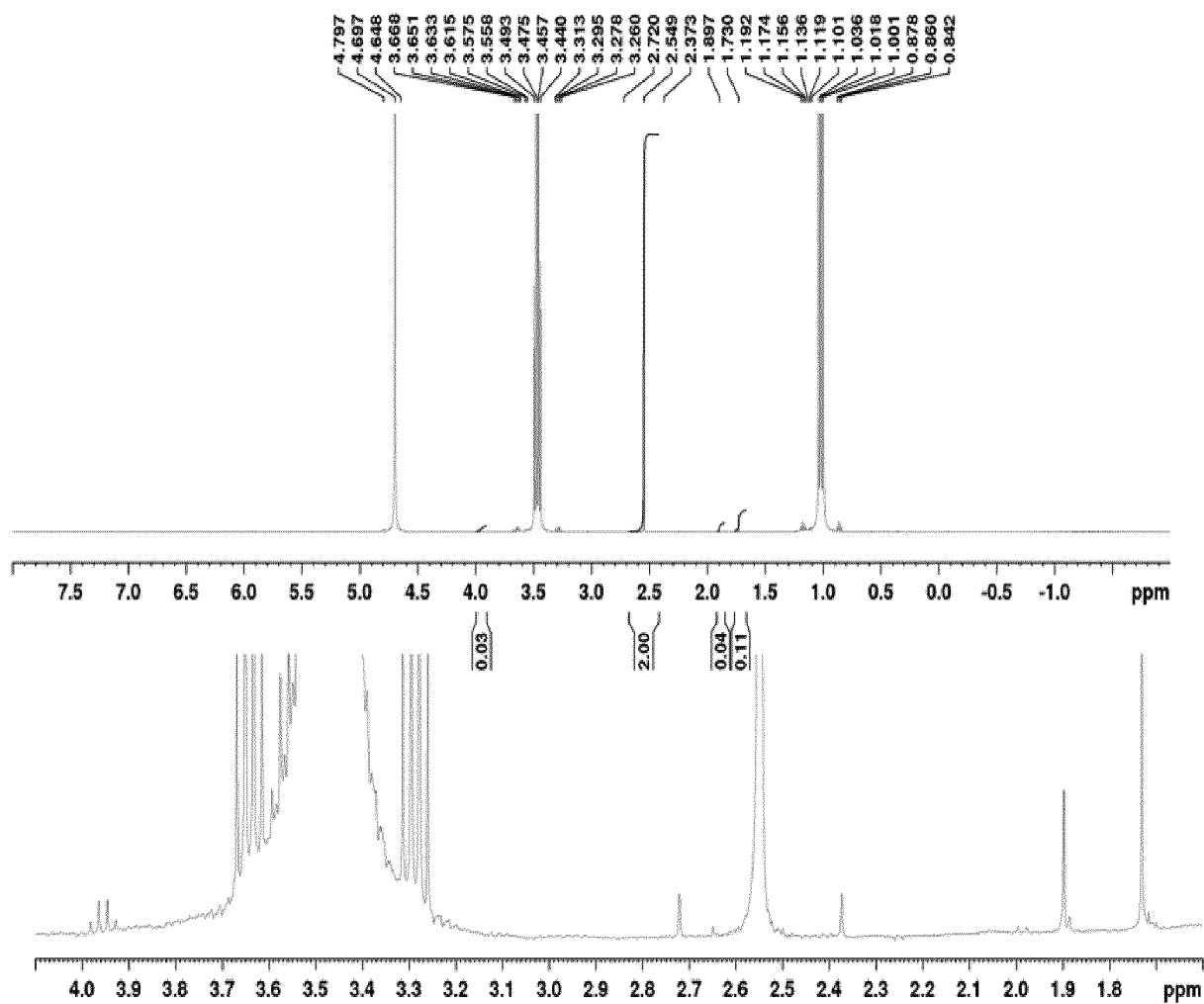


Fig. 7

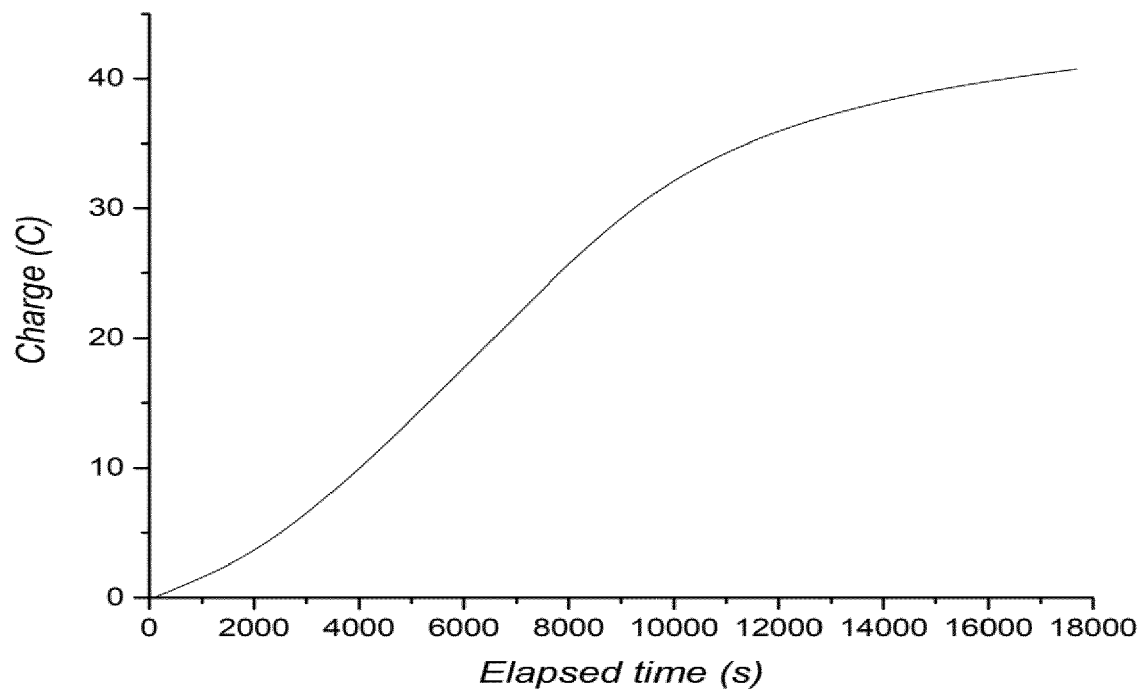


Fig. 8

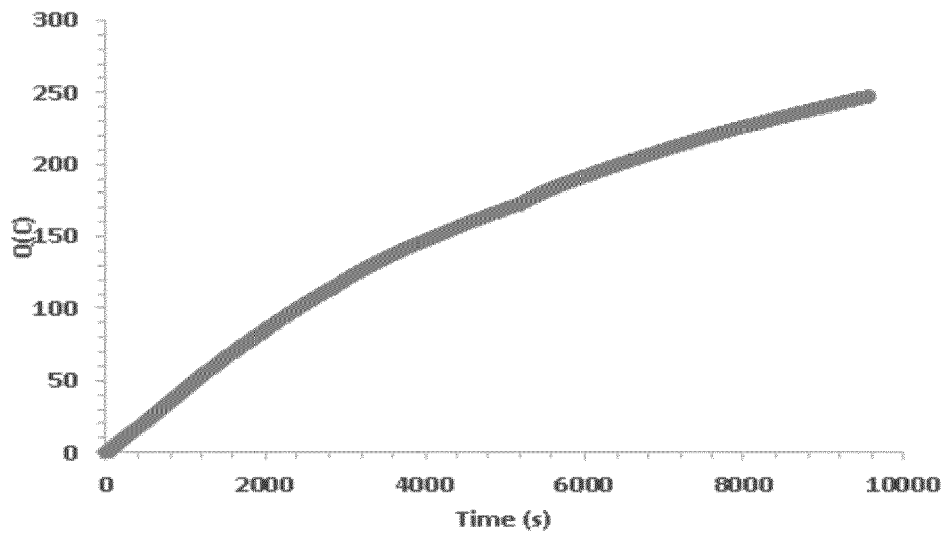


Fig. 9

**PARTIAL EUROPEAN SEARCH REPORT**

Application Number

under Rule 62a and/or 63 of the European Patent Convention.
This report shall be considered, for the purposes of
subsequent proceedings, as the European search report

EP 20 21 6238

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2017/283447 A1 (MILSTEIN DAVID [IL] ET AL) 5 October 2017 (2017-10-05) * the whole document *	1-17	INV. C25B1/02 C25B1/23 C25B3/07
A,P	TRINCADO MONICA ET AL: "Homogeneously catalyzed acceptorless dehydrogenation of alcohols: A progress report", COORDINATION CHEMISTRY REVIEWS, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 443, 24 May 2021 (2021-05-24), XP086603986, ISSN: 0010-8545, DOI: 10.1016/J.CCR.2021.213967 * Abstract, Section 2 *	1-17	C25B3/23 C25B9/15 C25B11/054 C25B11/065 C25B11/085
			TECHNICAL FIELDS SEARCHED (IPC)
			C25B

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC so that only a partial search (R.62a, 63) has been carried out.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

1

Place of search	Date of completion of the search	Examiner
Munich	16 August 2021	Ritter, Thomas
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		

EPO FORM 1503 03.82 (P04E07)



**INCOMPLETE SEARCH
SHEET C**

Application Number
EP 20 21 6238

5

10

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Claim(s) completely searchable:

-

Claim(s) searched incompletely:

1-17

Reason for the limitation of the search:

See the reasoning in point 2 of the accompanying search opinion.

16-08-2021

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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