

**Short thesis for the degree of doctor of Philosophy
(PhD)**

**Efficient chemical hydrogen storage using Ir(I)-NHC-
phosphine complex catalysts in a flow reactor**

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List of abbreviations

bmim:	1-butyl-3-methylimidazolium-2-ylidene
bpy:	2,2'-bipyridine
cod:	1,5-cyclooctadiene
Cp*:	pentamethylcyclopentadienyl
emim:	1-ethyl-3-methylimidazolium-2-ylidene
HPLC:	high pressure liquid chromatography
GC:	gas chromatography
IMes:	1,3-bis-(2,4,6-trimethylphenyl)-imidazol-2-ylidene
L1:	2,2'-bi-2-imidazoline
mtppts-Na₃:	sodium salt of monosulfonated triphenylphosphine
mtppps-Na:	sodium salt of trisulfonated triphenylphosphine
NHC:	N-heterocyclic carbene
NMR:	Nuclear Magnetic Resonance
OTf:	methyl trifluoromethanesulfonate
PCy₃:	tricyclohexylphosphine
ppy:	polypyrrole
pta:	1,3,5-triaza-7-phosphaadamantane
py:	pyridine
TH₂BPM:	4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine
TOF:	turnover frequency: (mol reacted substrate) / (mol catalyst × time), h ⁻¹
TON:	turnover number: (mol reacted substrate) / (mol catalyst)

I. Introduction and objectives

The rise of the world's population and the developing countries' pursuit for a higher standard of living and economy are both the causes of the constant increase of energy demand, which is one of the greatest challenges of the 21st century.

Fossil fuels have many and various good qualities, however, their limited availability and uneven geographical locations lead to dependence on imports in many countries. Carbon dioxide and other toxic chemicals resulting from their combustion also present a major issue. All these requirements might be resolved by a different type of energy source: hydrogen. Hydrogen is an excellent fuel: it has outstanding heat of combustion, and its combustion only produces energy and pure water. It has unlimited availability in its compounds on the planet.

Chemical hydrogen storage is the catalytic insertion and removal of hydrogen from compounds. The process is simplified, if both reactions are performed by the same catalyst, only changing the temperature and / or the pressure: this is called a hydrogen battery. One of the methods for chemical hydrogen storage utilizes formic acid and its salt derivatives. A very promising prospect is dehydrogenation carried out in the aqueous solution of formate salts, and then the hydrogenation of the resulting bicarbonate ions, which yields the starting material, formate (*Figure 1*).

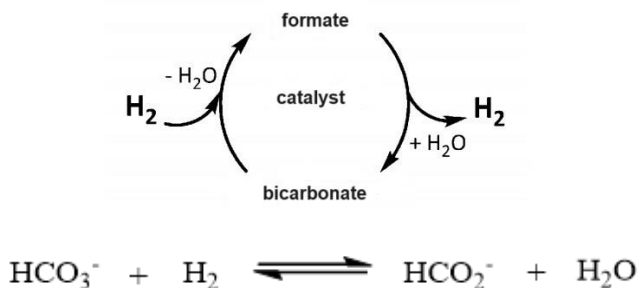


Figure 1. Formate based hydrogen storage cycle.

The Homogeneous Catalysis Research Group, located in the Physical Chemistry Department of the University of Debrecen, has been investigating the practical viability of the formate-bicarbonate based hydrogen storage for years. Joining the research group, my aim was to explore hydrogenation reactions, hydrogen evolution and hydrogen storage reactions catalyzed by Ir(I)-complexes containing N-heterocyclic carbene and water-soluble phosphine ligands, namely $[\text{Ir}(\text{cod})(\text{emim})(\text{mtppps})]$ and $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$. My further intention was to immobilise these catalysts on commercially available ion-exchange materials, and test the resulting heterogenized catalysts in the hydrogen storage cycle.

II. Experimental methods

[Ir(cod)(emim)(mtppts)] (**1**) and Na₂[Ir(cod)(emim)(mtppts)] (**2**) were synthesized according to published procedures. The complexes are sensitive to air, so all reactions were performed under oxygen-free conditions using standard Schlenk techniques. Their purity was checked by ¹H-NMR, ¹³C-NMR, ³¹P-NMR spectroscopic methods.

Hydrogenation reactions were carried out in high-pressure glass reactors (batch method), or in a hydrogenation microreactor (flow method). Flow reactions were implemented in a H-Cube[®] continuous flow hydrogenation reactor. The reaction takes place in a catalyst tube (CatCart[®]). In case of homogeneous catalytic reactions, an empty, inert catalyst tube was used, the catalyst was dissolved in the solvent. In case of heterogeneous catalytic reactions, the anchored catalyst was loaded into catalyst tubes, closed on both sides, and placed in the reactor.

The evolution of hydrogen from aqueous phase dehydrogenation of cesium formate was followed by gasvolumetry method, the gas burette was connected to the H-Cube[®] reactor.

Aqueous phase samples were analyzed by an AGILENT 1220 INFINITY type HPLC instrument, using a Supelcogel 610H column for separation. Organic compounds with a C≡C bond were analyzed by a AGILENT 7890A gaschromatography instrument, with an OPTIMA-1 column.

The 1,5-cyclooctadiene exiting from **1** was detected with a Skyray 6800 type GC-MS instrument, by Dr. Attila Kiss (Organic Chemistry Department, University of Debrecen).

The heterogenization of **2** was performed on ion exchange materials of various structure and particle size. The tests were carried out under argon atmosphere, and followed by a Shimadzu UV-1700 type spectrophotometer. Stability tests were executed in a DITABIS MHR 13 type heating thermo-mixer.

The structure and surface of the heterogenized catalysts were investigated by IR and RAMAN spectroscopic methods, and images were recorded with an optical microscop. The RAMAN and optical microscopic experiments were performed by Dr. István Csarnovics (Physics Department, University of Debrecen), and Dr. István Szabó (Physics Department, University of Debrecen).

Infrared spectra were recorded on a PerkinElmer, Spectrum Two FT-IR Spectrometer in ATR mode.

III. New scientific results

1. Formate-bicarbonate hydrogen storage cycle was successfully carried out in a flow reactor, using a homogeneous phase Ir(I)-complex.

During my PhD work my aim was the investigation of both directions of the formate-bicarbonate hydrogen storage cycle, and the execution of the whole cycle under flow conditions. First, the dehydrogenation of cesium formate was studied, under various temperature, flow rate and substrate concentration parameters (*Figure 2*).

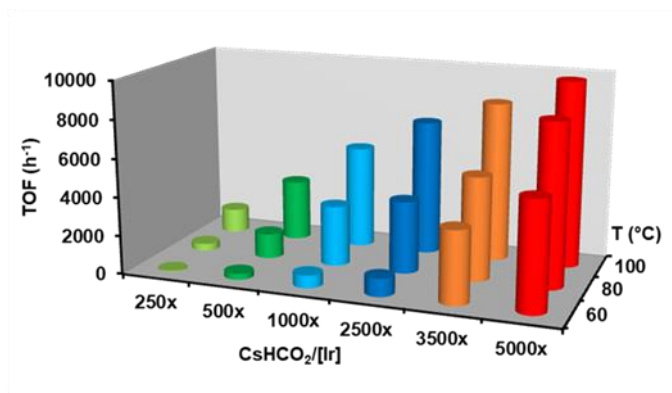


Figure 2. The temperature and substrate concentration dependence of dehydrogenation of aqueous cesium formate in a flow reactor.

[1] = ■ 0,025; ■ 0,05; ■ 0,1; ■ 0,25; ■ 0,35; ■ 0,5 mM;
[mtpts] = ■ 0,05; ■ 0,1; ■ 0,2; ■ 0,5; ■ 0,7; ■ 1,0 mM;
[CsHCO₂] = 0,1 M; V(H₂O) = 50 mL.

Reactions were performed under atmospheric pressure. Complex **1** in the presence of 2 equivalent of *mtppts*-Na₃ was an efficient catalyst of dehydrogenation in a flow reactor. TOF value of 10.000 was reached under 100°C temperature and in the presence of 5000x substrate excess.

The reactor was connected to a gas burette, the solution of cesium formate was circulated in the reactor, and the hydrogen gas developing in the reaction was captured in the gas burette, thus following the time course of the reaction.

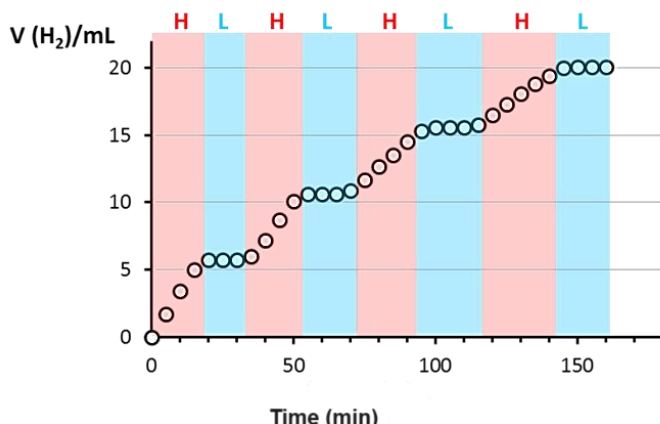


Figure 3. Hydrogen evolution under high (100°C, **H**) and low (25°C, **L**) temperature intervals, in dehydrogenation of cesium formate controlled by temperature.

[CsHCO₂] = 0,081 M; [**1**] = 0,1 mM; [*mtppts*-Na₃]/[Ir] = 2; V(H₂O) = 25 mL;

$v = 2,0 \text{ mL} \times \text{min}^{-1}$, $T = 100^\circ\text{C}$ (**H**) or 25°C (**L**).

It was found that the reaction proceeds quickly in a 100°C reactor, however, hydrogen evolution immediately stopped, when the reactor was cooled down to 25°C temperature, the entering cold reaction mixture is

enough to cool down the reactor in the matter of seconds (*Figure 3*). This way, switching the temperature of the reactor between 100 and 25°C made it possible to start and stop the evolution of hydrogen on demand.

The other side of the hydrogen storage catalytic cycle, the hydrogenation of cesium bicarbonate was also studied. Similar to the dehydrogenation of formate, the effect of various parameters were examined: temperature, flow rate and substrate concentration (*Figure 4*).

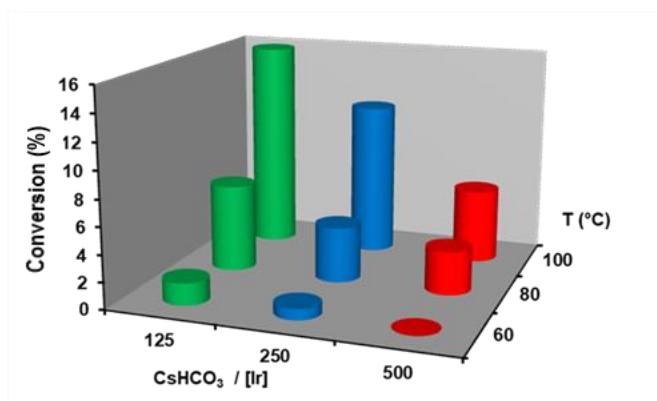


Figure 4. The temperature dependence of dehydrogenation of aqueous cesium bicarbonate in a flow reactor.

$[1] = \text{■ } 0.4; \text{■ } 0.1; \text{■ } 0.067 \text{ mM};$

$[mtpts] = \text{■ } 0.8; \text{■ } 0.2; \text{■ } 0.134 \text{ mM};$

$[\text{CsHCO}_3] = 0.05 \text{ M}, p(\text{H}_2) = 90 \text{ bar}; V(\text{H}_2\text{O}) = 50 \text{ mL}.$

As expected, the increase in temperature favors the reaction, although the hydrogenation proceeds significantly slower than the dehydrogenation of formate under atmospheric pressure.

After investigating the reactions separately, the implementation of the formate-bicarbonate hydrogen storage cycle was attempted in one mutual experiment.

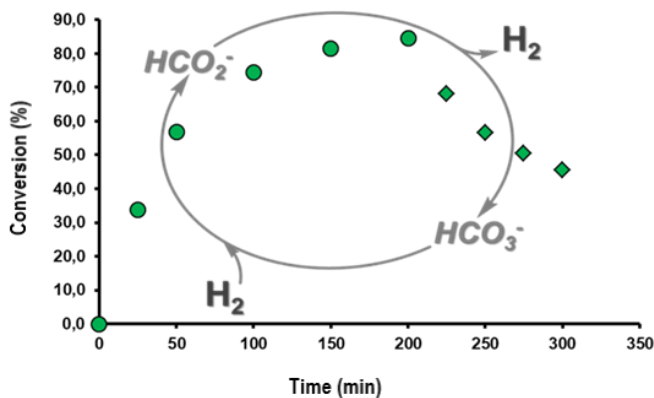


Figure 5. Hydrogenation of bicarbonate to formate, and dehydrogenation of formate to bicarbonate in an open system, under flow conditions.

$[\text{CsHCO}_3]/[\mathbf{1}] = 75$; $[\text{mtpts-Na}_3]/[\mathbf{1}] = 2$; $V(\text{H}_2\text{O}) = 25 \text{ mL}$; $P(\text{H}_2) = 90 \text{ bar}$ (0-200 min) or 1 bar (200-300 min), $T = 100 \text{ }^\circ\text{C}$; $v = 1,0 \text{ mL} \times \text{min}^{-1}$.

The experiment was successfully carried out in the flow reactor (*Figure 5*), where the reaction mixture was continuously circulated in the heated hydrogenation reactor. Under the presented circumstances, the bicarbonate was gradually hydrogenated to formate, the conversion reached 85% in 3 and a half hours. At this point, hydrogen pressure was decreased from 90 bar to 1 bar, and the solution was further circulated in the system. The reduction of pressure resulted in the dehydrogenation of formate, reaching 50% conversion in 100 minutes.

2. Heterogenisation of $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ complex was successfully performed on commercially available ion exchange type supports.

One of the methods for anchoring a metal complex bearing an ionic charge is the reaction with a solid ion exchange support. During my PhD work, I performed the immobilization of $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ on six, commercially available ion exchange supports. The solid supports have various differences between them based on their structure: they have different particle sizes, basicity, ion exchange capacity, which all contribute to the properties of the final heterogenized catalyst.

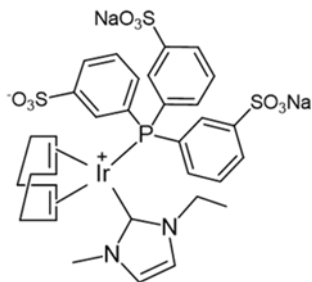


Figure 6. $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ (**2**)

All six selected ion exchange materials were capable of anchoring the iridium complex, however, there were significant difference in the duration of the heterogenisation process, and the stability of the resulting catalyst under acidic and basic conditions. *Figure 7* represents the gradual decrease in absorbance during the interaction between **2** and Lewatit Monoplus MP 500 support.

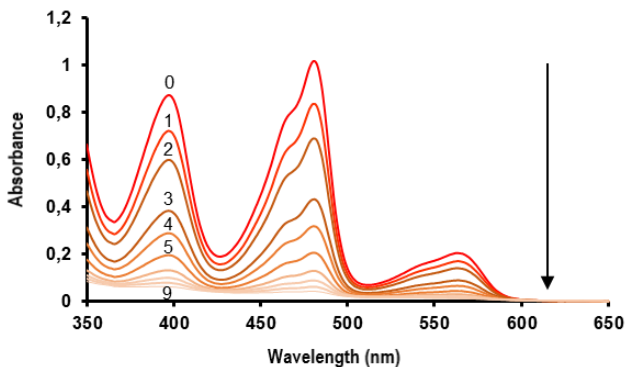


Figure 7. Spectrophotometric study of heterogenisation of **2** on Lewatit MonoPlus MP 500 support.

$m(\mathbf{2}) = 1,5$ mg, $m(\text{support}) = 50$ mg, $V(0,01 \text{ M HCl}) = 1$ mL, $t_{\text{total}} = 32$ min, $T = \text{RT}$.

Spectra: 0. – complex; 1.- complex + support, immediately; 2-9. – every 4 minutes.

Table 1 shows the description of the ion exchange supports, and the data of anchoring and leaching experiments. Supports with cellulose or dextrane base structure are able to anchor the complex quickly, however, the resulting catalysts did not perform well in the leaching tests. Synthetic polymer based support materials, especially the one with a polystyrene matrix, heterogenized the complex less readily, but successfully. The macroporous Lewatit MonoPlus MP 500 ion exchange support displayed outstanding stability under acidic and basic conditions.

Table 1. Spectrophotometric study of heterogenization of **2**, and leaching under acidic and basic conditions.

Support structure	Name	Anchoring	Leaching (%)	
		Duration (min)	0,1 M H ₃ PO ₄	0,1 M Na ₃ PO ₄
Cellulose	DEAE-Cellulose	4	36	45
Dextrane	Molselect DEAE-25	4	15	27
Polymethacrylate	Relisorb QA405/EB	8	16	23
PS/DVB	DIAION HPA25	12	4	8
PS/DVB	Amberlite IRA-900	20	5	4
PS/DVB	Lewatit MonoPlus MP 500	32	1	4

Anchoring: $m(\mathbf{2}) = 5$ mg, $m(\text{support}) = 50$ mg, $V(\text{H}_2\text{O}) = 2$ ml, $T = \text{RT}$.

Leaching: $m(\mathbf{2} \times \text{support}) = 30$ mg, $V(\text{solution}) = 2,5$ ml, $t = 1$ hour, $T = \text{RT}$.

The immobilization of the red coloured **2** on Lewatit MonoPlus MP 500 support resulted in red catalyst beads, which slowly turn yellow under hydrogen pressure. The same colour change can be observed in the reaction of solid **2** and 1 bar hydrogen as well, which was investigated by infrared spectroscopic method. The increase of the absorbance peak at 2249 cm^{-1} was observed in the IR spectra, which is a characteristic vibration of Ir-H terminal hydrides.

The creation of the yellow hydride complex could be a consequence of hydrogenation, during which the 1,5-cyclooctane ligand dissociates from the coordination sphere. This presumption is confirmed by the GC-MS analysis of the reaction mixture after homogeneous and heterogeneous phase hydrogenation: the hydrogenated product, cyclooctane appeared in the chromatogram of the mixture.

3. Hydrogenating activity and stability of heterogenized $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ was demonstrated with organic unsaturated compounds, in a flow reactor.

Hydrogenation of phenylacetylene, diphenylacetylene and 1-hexyne was investigated in methanol with heterogenized $2 \times \text{Lewatit MonoPlus MP 500}$ catalyst in a H-Cube[®] microfluidic hydrogenating reactor.

Hydrogenating reactions of phenylacetylene in methanol solvent showed that the heterogenized complex is an efficient catalyst of the reaction in a flow reactor. It is notable that the reaction proceeded even at 20°C temperature, with 4% conversion. The rate of the conversion increased with elevating temperature, resulting in 61% conversion at 90°C temperature (Figure 8).

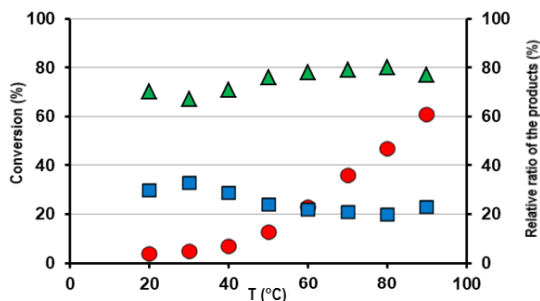


Figure 8. Temperature dependence of hydrogenation of phenylacetylene (●), and the relative ratio of styrene (▲) and ethylbenzene (■), catalyzed by heterogenised $2 \times \text{Lewatit MonoPlus MP 500}$ in a flow reactor.

$[\text{phenylacetylene}] = 0,05 \text{ M}$, $m = (2 \times \text{Lewatit MonoPlus MP500}) = 200 \text{ mg}$, $p(\text{H}_2) = 20 \text{ bar}$,

$T = 20\text{-}90^\circ\text{C}$, $v = 1,0 \text{ ml/min}$, solvent = methanol.

These results are excellent, given that the substrate solution spends less than a minute on the anchored catalyst due to the structure of a flow reactor.

The same reaction was carried out after two weeks of regular use, and six months after the first use, in order to assess the recyclability of the anchored catalyst (*Figure 9*). The excellent stability of the catalyst was demonstrated, it retained a significant portion of its catalytic activity after two weeks, and was able to perform hydrogenation even after six months.

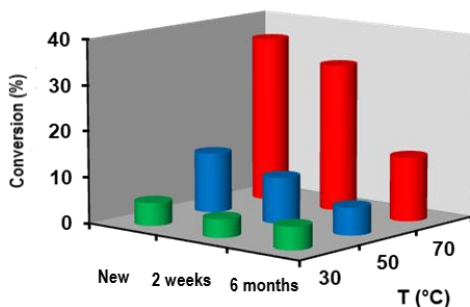


Figure 9: Catalytic hydrogenation of phenylacetylene with new $2 \times$ Lewatit MonoPlus MP 500 catalyst, after 2 weeks and after 6 months, in a flow reactor.

[phenylacetylene] = 0,05M, $m((2) \times \text{Lewatit MonoPlus MP500}) = 200\text{mg}$,
 $p(\text{H}_2) = 20 \text{ bar}$, $v = 1,0 \text{ ml/min}$, solvent = methanol.

The outstanding stability of the heterogeneous $2 \times$ Lewatit MonoPlus MP 500 is an advantageous feature, compared with the dissolved **2**.

The anchored catalyst was efficient at the hydrogenation of diphenylacetylene as well. Conversions were more moderate, compared with the reactions of phenylacetylene, however, this is a general phenomenon observed with internal alkynes, compared with terminal alkynes. Diphenylethane, the fully saturated product was not detectable in the final reaction mixture; only *cis*-stilbene and *trans*-stilbene were present. 90% selectivity was feasible for *cis*-stilbene, under 20 bar hydrogen pressure and 90°C temperature. Reaction conditions for eliminating the small amount of *trans*-stilbene present have not been identified yet.

Aliphatic unsaturated compound, 1-hexyne was also chosen for investigating the catalytic activity of heterogenised **2** × Lewatit MonoPlus MP 500. Under moderate temperature conditions, 1-hexene and hexane was formed nearly in equal amount. Increasing temperature favoured the formation of 1-hexene.

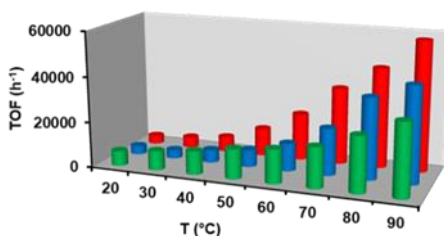


Figure 10.: TOF values for hydrogenation of diphenylacetylene (■), 1-hexyne (■) and phenylacetylene (■) catalyzed by **2** × Lewatit MonoPlus MP 500 in H-Cube reactor.

[substrate] = 0,05 M, m(**2** × Lewatit MonoPlus MP500) = 200 mg, $p(\text{H}_2)$ = 20 bar,
 T = 20 – 90 °C, v = 1,0 ml/min.

The significant stability of the heterogenized catalyst compensates for the slight loss of activity compared with the homogeneous phase reactions. TOF values calculated for heterogeneous phase reactions were remarkable, reaching as high as 57330 h^{-1} under 90°C temperature.

4. Formate-bicarbonate hydrogen storage cycle was accomplished with heterogenized $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ complex in a flow reactor.

The previously described formate-bicarbonate cycle was successfully carried out with the heterogenized complex, in flow reactor (*Figure 11*). The same catalyst beads were used for three cycles after storing them under argon atmosphere, only slight loss of activity was observed in these consecutive cycles.

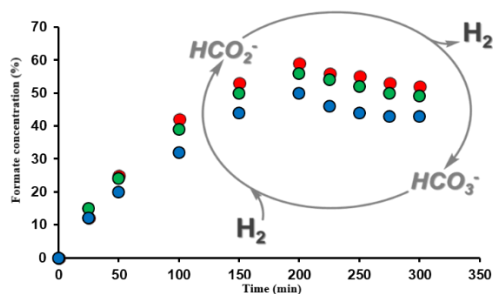


Figure 11. Formate-bicarbonate hydrogen storage catalytic cycle using $2 \times$ Lewatit MonoPlus MP 500 catalyst in H-Cube reactor.

First day (●) second day (●) third day (●).

[substrate] = 0,1 M, $m(2 \times \text{Lewatit MonoPlus MP500}) = 180 \text{ mg}$, $[\text{cat}] / [\text{substrate}] = 1:20$,
 $p(\text{H}_2) = 1 \text{ bar or } 50 \text{ bar}$, $T = 80^\circ\text{C}$, $v = 1 \text{ ml/min}$, solvent = water.

IV. Possible applications of the results

The research presented in my thesis is basic research in the field of homogeneous catalysis and catalytic hydrogen storage, in addition to catalyst development. My results demonstrate that *N*-heterocyclic carbenes and various phosphine ligands form stable complexes with iridium. The complexes prepared are active catalysts in hydrogenation of ketones and in transfer hydrogenation and dehydrogenation of secondary alcohols. The 1-phenylethanol/acetophenone hydrogenation catalytic cycle was realized at atmospheric pressure without the use of high pressure. The two processes were controlled by the controlled addition of H₂ gas.

The practical application of the results is expected to be mainly in the field of energy storage in hydrogen. The hydrogenation of ketones is also important because the reaction products are alcohols, which are the building blocks of pharmaceuticals, flavours, fragrances and pesticides.

V. List of publications

Publications related to the dissertation

English articles in international journals:

Henrietta Horváth, Gábor Papp, Henrietta Kovács, Ágnes Kathó, Ferenc Joó: **Ir(I)-NHC- phosphine complex-catalyzed hydrogen generation and storage in aqueous formate/bicarbonate solutions with use of a tubular flow reactor - effective response to changes in hydrogen demand.** *International Journal of Hydrogen Energy*, **2019**, 44, 28527-28532.

Henrietta Kovács, Krisztina Orosz, Gábor Papp, Ferenc Joó, Henrietta Horváth: **Immobilization of an Iridium(I)-NHC-Phosphine Catalyst for Hydrogenation Reactions under Batch and Flow Conditions.** *Catalysts*. **2021**, 11 (6), 1-11.

List of other publications

English articles in international journals:

Csilla Enikő Czégéni, Henrietta Kovács, Gábor Papp, Ágnes Kathó, Ferenc Joó: **Ion-exchange resin-supported palladium catalysts for hydrodehalogenation of aryl halides under batch and continuous flow conditions.** *Inorg. Chim. Acta*. **2023**, 556, 121613.



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Registry number: DEENK/292/2024.PL
Subject: PhD Publication List

Candidate: Henrietta Kovács
Doctoral School: Doctoral School of Chemistry
MTMT ID: 10066110

List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

1. Kovács, H., Orosz, K. A., Papp, G., Joó, F., Horváth, H.: Immobilization of an Iridium(I)-NHC-Phosphine Catalyst for Hydrogenation Reactions under Batch and Flow Conditions. *Catalysts*. 11 (6), 1-11, 2021. EISSN: 2073-4344.
DOI: <http://dx.doi.org/10.3390/catal11060656>
IF: 4.501
2. Horváth, H., Papp, G., Kovács, H., Kathó, Á., Joó, F.: Iridium(I) NHC-phosphine complex-catalyzed hydrogen generation and storage in aqueous formate/bicarbonate solutions using a flow reactor - Effective response to changes in hydrogen demand. *Int. J. Hydrog. Energy*. 44 (53), 28527-28532, 2019. ISSN: 0360-3199.
DOI: <http://dx.doi.org/10.1016/j.ijhydene.2018.12.119>
IF: 4.939





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List of other publications

Foreign language scientific articles in international journals (1)

3. Czégéni, C. E., Kovács, H., Papp, G., Kathó, Á., Joó, F.: Ion-exchange resin-supported palladium catalysts for hydrodehalogenation of aryl halides under batch and continuous flow conditions. *Inorg. Chim. Acta.* 556, 1-9, 2023. ISSN: 0020-1693.
DOI: <http://dx.doi.org/10.1016/j.ica.2023.121613>
IF: 2.8 (2022)

Total IF of journals (all publications): 12,24

Total IF of journals (publications related to the dissertation): 9,44

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

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