Iridium-Catalyzed Dehydrogenation in a Continuous Flow Reactor for Practical On-Board Hydrogen Generation From Liquid Organic Hydrogen Carriers

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To enable the large-scale use of hydrogen fuel cells for mobility applications, convenient methods for on-board hydrogen storage and release are required. A promising approach is liquid organic hydrogen carriers (LOHCs), since these are safe, available on a large scale, and compatible with existing refueling infrastructure. Usually, LOHC dehydrogenation is carried out in batch-type reactors by transition metals and their complexes and suffers from slow H₂ release kinetics and/or inability to reach high energy density by weight, owing to low conversion or the need to dilute the reaction mixture. In this study, a continuous flow reactor is used in combination with a heterogenized iridium pincer complex, which enables a tremendous increase in LOHC dehydrogenation rates. Thus, dehydrogenation of isopropanol is performed in a regime that, in terms of gravimetric energy density, hydrogen generation rate, and precious metal content, is potentially compatible with applications in a fuel-cell powered car.

Introduction

One of the seventeen UN sustainable development goals for 2030 is affordable and clean energy,[1] and an important part of that goal is to make energy generation, storage and delivery carbon-neutral. One suggested future energy management concept is the so-called hydrogen economy, where the use of hydrogen as an energy carrier is implied, which in turn can feed fuel cells for on-demand electricity generation. The concept involves the storage of energy from fluctuating renewable energy sources like solar and wind in the form of hydrogen, from which energy can be released on demand by an end-user. However, a key problem is hydrogen storage. With the highest energy density by weight, gaseous hydrogen is at the same time characterized by a low energy density by volume. While cryogenic, high-pressure and other storage systems have been developed, perhaps the most promising in terms of safety, on-board storage and compatibility with the existing infrastructure are liquid organic hydrogen carriers (LOHCs).[2,3] Dehydrogenation of LOHCs has been extensively studied in recent years, but any practical application remains challenging. Common problems include slow H₂ extrusion kinetics and/or the inability to reach a high energy density by weight. One type of LOHCs are cycloalkanes and their derivatives (Figure 1), which are typically hydrogen rich (> 6 wt% of hydrogen), yet have high enthalpies of dehydrogenation (> 14 kcal per mol of H₂) accompanied by high reaction barriers. This leads to slow hydrogen release even at high temperatures, and the need to supply high heat fluxes, which makes reactor design more complicated. Elementary noble metals are used as catalysts since other species often cannot tolerate the temperatures required. A popular cycloalkane-based LOHC is perhydro dibenzyltoluene.[4] A variation uses N-substituted analogues of cycloalkanes, for example perhydro-N-ethylcarbazole,[5] which so far holds the highest reported productivity of hydrogen with 10.9 gH₂ g⁻¹ min⁻¹, albeit at a low amount of extracted H₂ of 1.2 wt%.[6]

Another type of LOHCs are acyclic heteroatom-rich molecules that are characterized by much lower enthalpies of dehydrogenation, such as formic acid[6] or alcohols.[7] Milder operation conditions are thus enabled, sometimes at a cost of lower hydrogen content. Homogeneous transition metal complexes are often used as dehydrogenation catalysts for this type of LOHCs. Commonly, dehydrogenation is carried out in batch-type reactors and reaction temperatures cannot exceed substrate boiling points; this is often combined with comparatively low thermal stability of catalysts. Another limitation especially expressed for dehydrogenative coupling reactions is the formation of products that are solids or viscous liquids. This makes rapid and complete dehydrogenation in neat substrates...
virtually impossible and requires the dilution by inert solvents. This in turn is reducing the practical amount of released hydrogen by an order of magnitude or more. Representative examples include dehydrogenation of isopropanol over PNP-ligated ruthenium pincer complex (low temperature/stability), as well as dehydrogenative formation of amides from alcohols and amines or dehydrogenative homo-coupling of ethyleneglycol (dilution is needed). As a result, the overall performance of transition metal complexes in LOHC dehydrogenation is currently far from the desired practical conditions (Figure 1).

Here we describe the use of heterogenized transition metal complexes for dehydrogenation of an acyclic heteroatom-rich LOHC in a continuous flow reactor. Previously, iridium pincer complexes of the type of (POCOP)Ir (POCOP = 2,6-(tBu2PO)2C6H3) were shown to be productive catalysts for acceptorless dehydrogenation of neat alcohols that are compatible with operation temperatures around 200 °C. The heterogenized versions of (POCOP)Ir are even more thermally stable. In combination with a continuous flow reactor, which is free from substrate boiling point limitations, very high temperatures were enabled, combined with the accurate control of reaction conditions and the easy separation of reaction products from the catalyst. We thus combine excellent selectivity and activity of transition metal complexes in dehydrogenation of heteroatom-rich LOHCs with the high operation temperatures and the stability of traditional heterogeneous catalysts. As a substrate we use isopropanol, which is non-toxic, safe, readily available and forms a liquid and robust single dehydrogenation product; in addition, isopropanol recently attracted considerable interest as a hydrogen-lean molecule for use in direct fuel cells, not the least because it is less prone to CO2 formation compared to primary alcohols. Our approach allowed unprecedented and industrially relevant turnover numbers (TONs up to 1600000) and turnover frequencies (TOFs, up to 160000 h−1), which translates to a productivity of up to 25 g H2 g−1 Ir min−1. When productivity and conversion are simultaneously optimized, 3.1 wt % of the theoretical stored 3.3 wt % of hydrogen can be extracted.

Results and Discussion

Synthesis and characterization of catalysts

For use in a continuous flow setup a heterogenized catalyst is needed. A suitable (POCOP)Ir complex should therefore possess a functional group that does not interfere with catalysis, and at the same time is capable of reacting with a heterogeneous support. Synthetic routes to such compounds can be quite complex and labor-intensive, and perhaps the most successful and easy approach reported to date involves complex 1, which has an additional phosphinite moiety in the para position. Complex 1 readily undergoes P–O bond rupture
when treated with mesoporous calcined silica (Scheme 1a). A new Si–O bond is then formed between silica and the pincer complex, and complex 1 is turned into pinkish 1@SiO₂, where the complex is covalently attached to the silica. We also prepared the new complex 2 containing a free carboxylic acid moiety, which was obtained through a benzyl group deprotection from the corresponding ester (Scheme 1b). The use of a carboxyl group to support an iridium pincer complex on a MOF protection from the corresponding ester (Scheme 1b). The use of a carboxyl group to support an iridium pincer complex on a MOF has been described previously, but the synthetic route was much more complicated compared to the synthesis of 2; in addition, unlike 1, complex 2 is air-stable and allows convenient handling.

Complex 2 was supported on alumina calcined at 550 °C (2@Al₂O₃-calcined) and also on non-calcined alumina (2@Al₂O₃-non-calcined) for comparison. To immobilize 2, it was heated in a suspension of alumina in isopropanol in the presence of a base (to generate the active dihydride form of the catalyst). After 2 h, the solution turned almost colorless, while the alumina acquired an orange-red color, implying immobilization of the complex is covalently attached to the silica. We also prepared the new complex 2 containing a free carboxylic acid moiety, which was obtained through a benzyl group deprotection from the corresponding ester (Scheme 1b). The use of a carboxyl group to support an iridium pincer complex on a MOF protection from the corresponding ester (Scheme 1b). The use of a carboxyl group to support an iridium pincer complex on a MOF has been described previously, but the synthetic route was much more complicated compared to the synthesis of 2; in addition, unlike 1, complex 2 is air-stable and allows convenient handling.

Acceptance of dehydrogenation of isopropanol

The supported catalysts were placed in a tubular reactor (inner d = 5 mm) equipped with a metal frit on the outlet side, and the reactor was heated using an aluminum block with the alcohol feed provided via an HPLC pump. When liquid alcohols were passed over 1@SiO₂ in the flow reactor, a pinkish solution containing pincer complexes was collected, indicating severe leaching. With gaseous substrate, however, the supported catalysts were robust, allowing multiple-hour studies.

Batch dehydrogenation of alcohols with POCOP iridium pincer complexes have typically used PhCH(OH)CH₃ as a substrate but we chose isopropanol, which is a more attractive LOHC, being cheaper and having a higher hydrogen content. After passing through the flow reactor, the products were condensed and analyzed by ¹H NMR spectroscopy. At operating temperatures below 300 °C only isopropanol and acetone were observed. At temperatures above 300 °C additional acetone condensation products were detected. Possible impurities in hydrogen were analyzed with the help of GC-FID, GC-MS and IR spectroscopy (see the Supporting Information for details).

Scheme 1. (a) Immobilizing complex 1 on silica to give 1@SiO₂. (b) Immobilizing complex 2 on alumina to give 2@Al₂O₃. (c) Molecular structures (from XRD) of p-BnOOC(POCOP)IrHCl (3) and of p-HOOC(POCOP)IrHCl (2). Hydrogen atoms are omitted for clarity.
In a flow reactor, the dehydrogenation rate for a given amount of catalyst is a function of temperature and flow rate. The lower the flow rate, the higher is the contact time between a catalyst and a substrate, usually resulting in higher conversion and a lower TOF (see below). TOFs at the high flow rate limit at various temperatures are given in Table 1. In an open batch reactor, refluxing isopropanol can be dehydrogenated by the homogeneous catalyst \( \text{POCOP}{\text{IrHCl}} \) at 83°C with several tens of turnovers per hour.\(^{[11]} \)

In the flow reactor, it is possible to take full advantage of the heterogeneous nature of \( 1@\text{SiO}_2 \) by performing dehydrogenations well above the boiling point of the alcohol thereby significantly increasing the reaction rate. For instance, at 350°C, the catalyst \( 1@\text{SiO}_2 \) gave an unprecedentedly high TOF of 99936 h\(^{-1}\), which is almost two orders of magnitude higher than TOFs that can be reached with \( \text{POCOP}{\text{IrHCl}} \) in a batch system. At the same time, conversion was around 45%. Even higher values were observed at 375°C (163866 h\(^{-1}\) and 70.2% conversion, which turn into a 25 g\(_{\text{H}_2}\) g\(_{\text{Ir}}\)\(^{-1}\) productivities and 2.1 wt% of H\(_2\) release). The effect of the flow rate on the dehydrogenation of isopropanol by \( 1@\text{SiO}_2 \) at 350°C is depicted in Figure 2. As expected, high flow rates, or, in other words, shorter space times (the time a given fluid parcel spends inside a reactor) results in higher TOFs, but overall lower conversion and yields. Extrapolation of the flow-rate-TOF dependence allows an estimation of the maximum TOF at 350°C of approximately 120000 h\(^{-1}\). The highest conversion observed at slow flow rates (0.03 mL min\(^{-1}\)) was 99%, in agreement with the equilibrium composition of an isopropanol, acetone and H\(_2\) mixture, calculated using literature data.\(^{[20]} \) The 99% conversion is retained upon increase of the flow rate until a TOF of approximately 22000 h\(^{-1}\) is reached. Similar observations for different temperatures and catalysts are given in the Supporting Information. When the desired flow rates were instrumentally accessible, the predicted conversions were usually reached. Importantly, since the equilibrium is reached quickly, \( 1@\text{SiO}_2 \) and \( 2@\text{Al}_2\text{O}_3 \) are very effective catalysts for the reverse reaction as well, which means that hydrogenation and dehydrogenation can both be done using the same catalyst. Although our equipment does not allow a control experiment in a flow setup, hydrogenation of acetone to isopropanol in a batch reactor under 40 atm of H\(_2\) proceeds with a good rate (see the Supporting Information, Table S1). It is also worth noting that in a flow reactor under an equilibrium pressure of 1 atm of H\(_2\) the theoretical conversion would not exceed 90% up to 260°C, which emphasizes that to dehydrogenate LOHCs, high temperatures are needed not only from a kinetic but also from a thermodynamic point of view.

Despite the high temperatures used, the dehydrogenation was found to be very selective. Only above 300°C and at slow flow rates small amounts of acetone condensation products and traces of diisopropyl ether were detected, which is most likely a result of a prolonged exposure of the acetone towards the acidic sites on the SiO\(_2\) support. After condensation of the volatiles, the gas phase of the 350°C reaction contains only hydrogen and propane (0.1–0.5%; see the Supporting Information for details). To elucidate how propane is formed, isopropanol was passed over the support without the iridium complex in a control experiment and formation of small amounts of propylene was detected. Under catalytic conditions the latter is hydrogenated to propane. Since no fuel-cell or Pd-poisonous compounds\(^{[21]} \) are present, further purification could easily be achieved through the use of hydrogen-selective membranes if needed. Importantly, and as a proof of principle, the hydrogen formed was used to support the operation of a

**Table 1.** Continuous flow dehydrogenation at different temperatures. Since the flow system dehydrogenation rate is dependent on flow rate, experimentally observed upper limits are usually given.

| T [°C] | TOF [h\(^{-1}\)] 1@SiO\(_2\) | 2@Al\(_2\)O\(_3\)-calcined | 2@Al\(_2\)O\(_3\)-noncalcined |
|--------|-----------------|------------------|------------------|
| 135    | 147             | –                | –                |
| 150    | 321             | 324              | –                |
| 175    | 1218            | –                | –                |
| 190    | 2250            | –                | –                |
| 200    | 2922            | 2001             | –                |
| 260    | 16405           | 10512            | 2300             |
| 300    | 34908           | 24366            | –                |
| 350    | 99936           | 56060            | 24018            |
| 375    | 163866          | –                | –                |

**Figure 2.** Left: space-time dependence of TOF and conversion for dehydrogenation of iPrOH by \( 1@\text{SiO}_2 \) at 350°C. Space-time is here defined as \( \nu(\text{cat})/\text{flow rate (ml min}^{-1}) \). Right: Eyring plot for acceptorless dehydrogenation of iPrOH by \( 1@\text{SiO}_2 \) in a flow reactor. Initial dehydrogenation rates were used, temperature span 135–350°C.
small fuel cell that did not reveal any decrease in power over a period of 6 h (see the Supporting Information for details).

It is likely that dehydrogenation is a first order reaction at the iridium sites; indeed, when a standard packed bed-reactor model for a first-order reaction was used, linearized plots of conversion versus reaction time were observed except for the highest rates where the reverse reaction becomes non-negligible (see the Supporting Information for details). The resulting rate constants (in mol s⁻¹) give rise to a linear Eyring plot over the temperature span of 135–350 °C (Figure 2, right). Apparent activation parameters are ΔH° = 14.0 ± 0.3 kcal mol⁻¹ and ΔS° = -49.6 ± 0.7 cal mol⁻¹ K⁻¹ for 1@SiO₂ and ΔH° = 12.3 ± 0.2 kcal mol⁻¹ and ΔS° = -53.6 ± 0.3 cal mol⁻¹ K⁻¹ for 2@Al₂O₃-calcined.

Of the three catalyst formulations tested, 1@SiO₂ was found to have the highest activity. Thus, at 260 °C, TOFs of 16405, 10512, and 2300 h⁻¹ were observed for 1@SiO₂, 2@Al₂O₃-calcined and 2@Al₂O₃-non-calcined, respectively. The superior activity of 1@SiO₂ over 2@Al₂O₃-calcined is retained for the whole range of temperatures studied, and the stability tests were mostly performed using 1@SiO₂ for this reason. A typical activity decay plot is shown in Figure 3. For 1@SiO₂ at 350 °C, the activity loss was around 28% over 18.5 h, which allowed to observe a TON as high as 160000 and converted more than two liters of isopropanol with just 5 mg of iridium pincer complex. Decay patterns were usually close to linear during the first 72 h. Interestingly, if normalization to the amount of iridium sites; indeed, when a standard packed bed-reactor model for a first-order reaction was used, linearized plots of conversion versus reaction time were observed except for the highest rates where the reverse reaction becomes non-negligible (see the Supporting Information for details). The resulting rate constants (in mol s⁻¹) give rise to a linear Eyring plot over the temperature span of 135–350 °C (Figure 2, right). Apparent activation parameters are ΔH° = 14.0 ± 0.3 kcal mol⁻¹ and ΔS° = -49.6 ± 0.7 cal mol⁻¹ K⁻¹ for 1@SiO₂ and ΔH° = 12.3 ± 0.2 kcal mol⁻¹ and ΔS° = -53.6 ± 0.3 cal mol⁻¹ K⁻¹ for 2@Al₂O₃-calcined.

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Catalyst resting state and deactivation

The first few milliliters of dehydrogenation product usually have a pale yellow color indicating the presence of leached catalyst. This initial loss accounts for approximately 1.7–1.9 mg of pincer complex out of 5 mg loaded (for 1@SiO₂, and 2@Al₂O₃-calcined) as shown by ICP-MS, and predominately happens in the form of (POCH₃)Ir–CO according to NMR spectroscopy with an internal standard. Subsequent portions are clear and contain negligible amounts of Ir. Thus, when normalized to pincer complex, less than 0.01 mg was found in 1.0 l of product produced at 350 °C. Accordingly, iridium corresponding to 2.9 mg of complex was found in the used catalyst after 8 h and to 2.5 mg after 24 h. Unlike 1@SiO₂ and 2@Al₂O₃-calcined, 2@Al₂O₃-non-calcined revealed virtually no leaching at 260 °C and comparatively slow one at 350 °C (1.0 mg of complex over 8 h).

³¹P MAS NMR and IR spectra of batches of 1@SiO₂ after 1 h of reaction are consistent with the presence of 1-CO@SiO₂ [12] as the major species (Figure 4). The batches of Al₂O₃-based catalysts used for 1–2 h reveal a resonance at 198.4 ppm in ³¹P MAS NMR spectra (Figure S8) and an IR band at 1946 cm⁻¹, which are very characteristic of the 16e complex 2-CO@Al₂O₃. The IR spectrum also contains a weak band at 2026 cm⁻¹ (Figure S10), for which the respective ³¹P NMR signal was not observed due to low concentration. This region is common for 18e compounds of the type (POCH₃)IrH(X)CO, [11,22] and thus was attributed to the structure 2-H(CO)OAl@Al₂O₃ in Figure 4. It is known that Ir–CO adducts of the type 1-CO@SiO₂ and 2-CO@Al₂O₃ are dead-ends for batch dehydrogenations even at 200 °C, [11] but at the conditions of the flow system they can serve as viable catalyst precursors. [12] Too much Ir–CO formation will still slow down the catalyst, as shown by addition of primary alcohols, which are good CO sources under conditions of interest, to isopropanol. We thus reason that the non-calcined Al₂O₃ support, which bears many more surface –OH groups than the calcined supports, is likely inhibiting the catalyst by providing a mechanism for increased Ir–CO formation, but this at the same time offers opportunities to reduce leaching.

TEM images and XEDS spectra of as-prepared 1@SiO₂ and 2@Al₂O₃ were consistent with an even distribution of Ir over the support (Figure 5a). At temperatures as high as 350 °C, some Ir nanoparticles formation was observed in the used 1@SiO₂ (Figure 5b), which plausibly reveals one of the deactivation pathways. Since Ir nanoparticles derived from (POCH₃)Ir pincer complex were recently shown to be catalytically relevant to polyol deoxygenation reactions, [23] we performed a control experiment aiming at measuring nanoparticle activity. For that
purpose, a sample of $\text{Ir} @ \text{SiO}_2$ was heated at 550°C for 2 h under a stream of Ar, which led to pincer complex decomposition and extensive nanoparticle formation (Figure 5c). This decomposed sample revealed a TOF of only $432 \text{ h}^{-1}$ at 350°C, indicating that although nanoparticles are catalytically active, they are substantially less productive compared to the molecular catalysts under the same conditions. Interestingly, no nanoparticles were observed in a sample of used $\text{Ir} @ \text{Al}_2\text{O}_3$ (Figure 5d).

Hence, decomposition of $\text{Ir} @ \text{Al}_2\text{O}_3$ proceeds in a way where Ir remains dispersed over the support. Further support of the decomposition route is provided by iridium L-edge XANES spectra of as-prepared and used $\text{Ir} @ \text{SiO}_2$ and $\text{Ir} @ \text{Al}_2\text{O}_3$ in Figure 6. The XANES spectrum of fresh $\text{Ir} @ \text{SiO}_2$ shifts towards lower binding energy after catalysis, indicating a reduction. The spectra of the as-prepared catalysts were modeled using FEFF 9.6,[12] with full multiple scattering and self-consistent field calculations to 7 Å. The calculated spectra reproduce the position and the finer features of the spectra and thus verify presence of the proposed molecular compounds on both supports.

The potential reduction of $\text{Ir} @ \text{SiO}_2$ is consistent with the observed nanoparticles. Noteworthy is the sharpness of the spectrum, indicative of a complete conversion into the reduced state. Further in situ investigations are in preparation. The $\text{Ir} @ \text{Al}_2\text{O}_3$ on the calcined support shown in the right panel of Figure 6 does not show any major differences before and after catalysis, supporting the predominate presence of iridium in the form of molecular species.

Comparison between flow and batch reactors

It is interesting to compare flow dehydrogenation with batch dehydrogenation in open (H$_2$ released during dehydrogenation is allowed to escape) and closed (H$_2$ remains in the sealed reactor) systems. Previously we elucidated the mechanism of dehydrogenation of secondary alcohols by homogeneous (POCOP)Ir type systems and found that the reaction is very sensitive to hydrogen mass transfer. For that reason, TOFs vary with concentration of catalysts from a few hundred to a few thousand per hour,[11b] and ultimately, when a hydrogen acceptor is added, the concentration dependence disappears and TOFs reach approximately 15 000 h$^{-1}$ for iPrOH at 190°C, which represents a lower (due to some inhibition by hydrogen acceptor) estimate of a theoretical rate limit that is determined by β-elimination in the respective alcohol.[11b]

In a sealed batch reactor $\text{Ir} @ \text{SiO}_2$ reveals an activity comparable to the one of the homogeneous catalyst (POCOP)IrHCl, and in line with the above mentioned strong rate retardation in the presence of hydrogen formed[11b] TOFs at these conditions are comparatively low (Table 2). In an open batch reactor, data for an alcohol with a higher boiling point, PhCH(OH)CH$_3$, is given for comparison.[11b] It can be seen that flow reactor TOFs observed at high flow rates are roughly comparable to the TOFs observed at high dilutions using (POCOP)IrHCl in an open batch reactor. This indicates that at high flow rates the flow reactor operates in a regime that

![Figure 5. TEM images of (A) as-prepared $\text{Ir} @ \text{SiO}_2$, (B) $\text{Ir} @ \text{SiO}_2$ after 8 h reaction at 350°C, (C) $\text{Ir} @ \text{SiO}_2$ after 2 h of heating at 550°C and (D) $\text{Ir} @ \text{Al}_2\text{O}_3$ after 8 h reaction at 350°C.](image)

![Figure 6. XANES spectra of fresh and used $\text{Ir} @ \text{SiO}_2$ and $\text{Ir} @ \text{Al}_2\text{O}_3$ together with a FEFF 9.6-simulated XANES spectrum using the molecular structure.](image)
resembles an open batch reactor rather than a sealed one and is similarly less prone to hydrogen inhibition. This is further supported by apparent activation enthalpies (6.3 kcal mol$^{-1}$ for batch reactor$^{[15]}$ vs 14.0 kcal mol$^{-1}$ for flow reactor) indicating less contribution of mass transfer and higher contribution of bond-breaking in the $\beta$-elimination step in the flow reactor case, and also by a reaction order of one in iridium centers in the flow reactor compared to 0.5 in the batch reactor. Plausibly, support effects, such as differential interaction of the supports with acetone and isopropanol (that are adsorbed) and hydrogen (that is not adsorbed)$^{[26–27]}$ may give rise to the observed effects, but further studies are needed to confirm or disprove this hypothesis.

Overall, the use of a flow reactor and supported iridium pincer complexes demonstrated a very high activity in acceptorless dehydrogenation of isopropanol. For comparison, selected examples of homogeneous and heterogeneous catalysts for the same reaction are given in Table 3.

The highest TOFs recorded to date in dehydrogenation of secondary alcohols for a transition metal complex was 14145 h$^{-1}$, with a TON of 40000 observed in total.$^{[16]}$ We also made a comparison with one of the standard heterogeneous catalysts, palladium on charcoal (Table S5), with the molar amount of Pd equal to Ir; this comparison also clearly favors the supported pincer complex (TOF 780 vs 99936 h$^{-1}$ at 350°C). This is in line with the Arrhenius activation energy in alcohol dehydrogenation for Pd/C, which was reported as 23.6 kcal mol$^{-1}$ under conditions where mass-transfer problems were carefully excluded, which can be compared to 15.0 kcal mol$^{-1}$ for 1@SiO$_2$. Additionally, a somewhat related recent paper$^{[17]}$ published after this work was completed, reports hydrogen production from a methanol-water mixture over an immobilized iridium complex catalysts and reports much lower activity compared to the present system.

Relating dehydrogenation activity performance to practical applications, modern hydrogen-powered cars consume around 1 kg of hydrogen per 100 km. Assuming that a car travels that distance in 1 h, the catalyst needed to feed a fuel cell with hydrogen has to contain approximately 2 g of Ir in roughly 0.3 L reactor volume (350°C, dehydrogenation regime with 94% conversion and TOF of 46000 h$^{-1}$, or 17.4 g$_{\text{Ir}}$ g$^{-1}$ min$^{-1}$ with 3.1 wt% of hydrogen released). While iridium is a precious metal with limited supply, this quantity is, in fact, comparable to the amount of platinum, palladium and rhodium used in the catalytic converter of a standard car and much lower than the platinum used in the fuel cell of the same car. Therefore, iridium pincer complex catalyzed dehydrogenation is, in principle, compatible with practical applications, provided that the stability of the catalysts can be improved. Importantly, the hydrogen produced has sufficient purity and does not contain compounds that are expected to decrease the performance of fuel cells and hydrogen-selective membranes. The same catalysts can be used to recover the hydrogen-rich form of the LOHC and could potentially become part of a cycle. Although the H$_2$ wt% in isopropanol is less than the US DOE target,$^{[18]}$ this is so far the best approximation to that value with acceptable H$_2$ release kinetics.

### Conclusions

In summary, we have described a new approach towards practical hydrogen generation from LOHCs. A key improvement over state-of-the-art is the use of a continuous flow reactor in combination with a heterogenized transition metal complex as a catalyst. This enabled dehydrogenation of one of the acyclic heteroatom containing LOHCs (isopropanol), for which transition metal complexes often reveal high activity and selectivity. Operation at temperatures more common for traditional heterogeneous catalysts resulted in hydrogen generation productivity exceeding systems previously reported by a factor of two both for H$_2$ generation rate and wt% H$_2$ released (Figure 1) and approaching values reasonable for vehicle propulsion. The generated hydrogen has a high purity with only uncritical impurities and there is a potential to perform the reverse reaction in the same reactor. We therefore believe that

### Table 3. Selected catalysts for isopropanol dehydrogenation and their activity.

| Catalyst       | T [°C] | Conditions                  | Productivity | Ref.   |
|----------------|-------|-----------------------------|--------------|--------|
| Pt/C           | 160   | Gas phase, heterogeneous    | 0.2 g$_{\text{H}_2}$ g$^{-1}$ min$^{-1}$ | [28]   |
| Cu/MCM-41      | 350   | Gas phase, heterogeneous    | 0.05 g$_{\text{H}_2}$ g$^{-1}$ cm$^{-2}$ h$^{-1}$ | [29]   |
| Raney nickel   | 82    | Liquid phase, heterogeneous | 0.0025 g$_{\text{H}_2}$ g$^{-1}$ cm$^{-2}$ min$^{-1}$ | [30]   |
| Cu/C           | 175   | Gas phase, heterogeneous    | 0.014 g$_{\text{H}_2}$ g$^{-1}$ cm$^{-2}$ min$^{-1}$ | [31]   |
| Ru-pincer      | 90    | Liquid phase, heterogeneous | 1.1 g$_{\text{H}_2}$ g$^{-1}$ cm$^{-2}$ h$^{-1}$ (12 h), 4.7 g$_{\text{H}_2}$ g$^{-1}$ cm$^{-2}$ min$^{-1}$ (0.3 h) | [8]    |
| Supported Ir pincer | 350   | Gas phase, heterogeneous    | 25 g$_{\text{H}_2}$ g$^{-1}$ min$^{-1}$ | this work |

$^{[a]}$ Substrate/catalyst ratio = 16000:1.
the approach described herein can form a basis for a large family of related processes for hydrogen generation using different alcohols or amines, for example, and provided improvement in catalysts-support binding strength, can lead to development of practical systems for hydrogen generation from LOHCs.

Experimental Section

General considerations

All manipulations were carried out under an inert gas atmosphere using standard Schlenk, high vacuum line and glovebox techniques, unless otherwise stated. Toluene and THF were distilled under vacuum from Na/benzophenone. POCH was distilled under argon from calcium hydride. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. CP MAS spectra were recorded on Bruker Avance II 500 MHz spectrometer. 1H and 13C NMR chemical shifts are reported in parts per million and referenced to the signals of deuterated solvents. 31P{1H} NMR chemical shifts are reported relative to an external 85% solution of phosphoric acid. IR spectra were recorded on a Bruker Alpha spectrometer. Gas chromatograms were obtained on a Bruker 430- GC chromatograph, using BRS-MS 30 m × 0.25 mm column with film thickness 0.50 μm, carrier gas - nitrogen, flow 5 ml min⁻¹, injection volume 10.0 μl; initial column temperature of 40°C was held for 2 min, and then gradually raised to 80°C with a ramp of 10°C min⁻¹. Elemental analyses were done by the H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Complexes (P(But)PO-POCOP)Ir(C₇H₆) (1) and 1HClO₃ as well as 3,5-dihydroxybenzoic acid benzyl ester were prepared according to literature procedures.[36]

Syntheses

POCOP ligand L1: A procedure similar to that reported by Brookhart and co-workers for related phosphinates was used.[36] A Straus flask was charged with 3,5-dihydroxybenzoic acid benzyl ester (0.506 g, 2.072 mmol) and NaH (0.109 g, 4.542 mmol, 2.2 eq) inside a nitrogen atmosphere glovebox, followed by vacuum-transfer of 20 mL of THF on the vacuum line. The mixture was refluxed for 1 h, brought to room temperature, di-tert-butylchlorophosphine (0.98 mL, 5.159 mmol, 2.5 eq) was added by syringe, and the mixture was refluxed for an additional 1 h. After evaporation of the solvent in vacuum, the residue was extracted with pentane, and the extract was filtered through a pad of Celite. The residue was dried under high vacuum for 3 h at 50°C to give a colorless viscous oil, which turned into a crystalline-like material upon standing overnight. Yield 0.998 g (90%). 31P{1H} NMR (162 MHz, CDCl₃): δ = 154.84 ppm (s); 1H NMR (400 MHz, CDCl₃): δ = 8.05–0.83 (m, 2H, Ar-H), 7.78 (apparent pentet, J = 2.5 Hz, 1H, Ar-H), 7.11–7.18 (m, 2H, Ar-H), 7.06–7.00 (m, 3H, Ar-H), 5.05 (s, 1H, CH₂-PH), 1.08 ppm (d, JPH = 11.7 Hz, 3H, 4 C(CH₃)₃); 13C{1H} NMR (101 MHz, CDCl₃): δ = 165.91 (7-C), 161.57 (dd, JPC = 10.1 Hz, JPH = 1.0 Hz, 2C and 6-C), 136.78 (s, 9-C), 133.17 (13-C), 128.40 (12-C, 12.14 (s, 10-C and 14-C), 113.43 (dd, JPH = 10.2 Hz, JPH = 0.9 Hz, 3-C and 5-C), 13.27 (t, JPC = 12.8 Hz, 1-C), 66.76 (s, 8-C), 35.76 (d, JPC = 26.8 Hz, 4 C(CH₃)₃), 27.43 ppm (d, JPC = 15.6 Hz, 6 C(CH₃)₃).

Complex 3: A Straus flask was charged with POCOP ligand L1 (0.998 g, 1.874 mmol) and [Ir(COD)Cl] (0.630 g, 0.938 mmol) inside a nitrogen atmosphere glovebox, followed by vacuum transfer of 30 mL of toluene on the vacuum line. The flask was sealed, immersed into an oil bath and heated at 120°C overnight. The volatiles were removed in vacuum, and the residue was purified by column chromatography (under air) on silica using a hexane-CH₂Cl₂, 3:1–1:1 mixture as eluent. A red-orange fraction was collected, evaporated, and the residue was washed with a small amount of hexane. After drying under vacuum, 3 was obtained as a red microcrystalline powder. Yield 1.174 g (82%). 31P{1H} NMR (162 MHz, CDCl₃): δ = 176.6 ppm (s); 1H NMR (400 MHz, CD₂Cl₂): δ = 7.84–7.44 (m, 2H, 10-H and 14-H), 7.42–7.37 (m, 2H, 11-H and 13-H), 7.36–7.33 (m, 1H, 12-H), 7.25 (s, 2H, 3-H and 5-H), 5.32 (s, 2H, 8-H), 1.38–1.34 (m, 36H, 4 C(CH₃)₃), −0.473 ppm (t, JPH = 12.9 Hz, 1H, Ir-H); 13C{1H} NMR (101 MHz, CDCl₃): δ = 167.17 (vt, J = 5.9 Hz, 2-C and 6-C), 166.79 (s, 4-C), 136.44 (s, 9-C), 128.70 (s, 11-C and 13-C), 128.58 (t, JPH = 3.5 Hz, 1-C), 128.32 (s, 10-C and 14-C), 127.66 (s, 4-C), 106.14 (vt, J = 5.3 Hz, 3-C and 5-C), 66.66 (s, 8-C), 43.35 (vt, J = 11.4 Hz, 2 C(CH₂)₃), 39.79 (vt, J = 12.6 Hz, 2 C(CH₂)₃), 27.76 (vt, J = 3.1 Hz, 2 C(CH₂)₃), anal. calc for C₂₆H₂₂IrO₂P₂; C 47.39, H 6.10; found C 47.31, H 6.07.

Complex 2: A Straus flask was charged with complex 3 (0.150 g, 0.197 mmol), 5% Pd/C (0.045 g), as well as 10 mL of THF and 10 mL of MeOH. The solution was freeze-pump-thaw degassed, refilled with H₂, at −196°C and stirred for 2 h at room temperature. The reaction mixture was filtered through a pad of Celite, the volatiles were evaporated and the residue was washed with a small amount of hexane. After drying under vacuum, 2 was obtained as a red microcrystalline powder. Yield 0.128 g (97%). 31P{1H} NMR (162 MHz, CD₂Cl₂): δ = 174.3 ppm (s); 1H NMR (400 MHz, CD₂Cl₂): δ = 10.98 (br s, 1H, COOH), 7.17 (s, 2H, Ar-H), 1.40–1.35 (m, 36H, 4 C(CH₃)₃), −0.433 ppm (t, JPH = 12.9 Hz, 1H, Ir-H); 13C{1H} NMR (101 MHz, CD₂Cl₂): δ = 167.56 (vt, J = 5.9 Hz, C-O), 127.36 (s, C- COOH), 127.96 (t, JPH = 3.5 Hz, C₆H₅), 106.70 (vt, J = 5.3 Hz, Ar-C), 43.58 (vt, J = 11.5 Hz, 2 C(CH₂)₃), 40.09 (vt, J = 12.5 Hz, C(CH₂)₃), 27.67–27.61 ppm (m, overlapping, 4 C(CH₂)₃), IR (ATR, solid); v ≈ 2800 cm⁻¹, (center of gravity, very broad, s, –OH), 1674 cm⁻¹ (s, –O); anal. calc for C₂₆H₂₂IrO₂P₂; C 41.22, H 6.02; found C 41.72, H 6.21.

2@Al₂O₃: In a typical experiment, alumina (0.400 g) was dried under high vacuum for 0.5 h at 50°C in a Straus flask. Complex 2 (0.020 g, 0.030 mmol), BuO-D (0.005 g, 0.045 mmol) and 10 mL of iPrOH were added, the flask was fully immersed into an oil bath and heated at 100°C for 1 h. The flask was brought to room temperature, the solution was decanted, and the solid residue was washed with iPrOH (2×2 mL) and dried under vacuum.

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In a sealed batch reactor: In a typical experiment, in a nitrogen atmosphere glovebox, the catalyst (0.0050 g of (POCOP)IrHCl (d = 5 mm, l = 200 mm), equipped with a porous metal plug at one end to prevent catalyst escape. The catalyst was sealed, taken out of a glovebox, placed inside an aluminum block heater and connected to a flask with the substrate via an HPLC pump. The reactor was pre-heated to the specified temperatures and the flow of substrate was switched on. Cooling of an outlet tubing and collection flask was used to ensure that products of the reaction will not be partially evaporated by the hydrogen stream. For experiments with the continuous flow reactor, the data scattering was around ±10% for repeated experiments and was associated mainly with fluctuations of the hydrogen stream. For experiments with the continuous flow reactor, the data scattering was around ±10% for repeated experiments and was associated mainly with fluctuations of the hydrogen stream. The latter was determined using the volume of the samples collected. The consumption of substrate was also measured in a few experiments to confirm proper mass balance.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: dehydrogenation · flow chemistry · iridium · pincer complexes · liquid organic hydrogen carriers

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