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PAPER

The effect of temperature, catalyst and sterics on the rate of *N*-heterocycle dehydrogenation for hydrogen storage

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Efficient hydrogen storage is one of the critical requirements for the use of hydrogen fuel cells in light-duty vehicles. Our investigation of reversible chemical hydrogen storage systems has led to the development of a mixed endothermic–exothermic carrier system. Herein we further investigate the factors affecting the dehydrogenation rate of these carriers. A range of heterogeneous catalysts was synthesized *via* sol–gel methodology and their activity for indoline dehydrogenation was assessed. Metals used included Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt. SiO_2, Al_2O_3, TiO_2 and ZrO_2 were used as supports and Pd/SiO_2 gave the highest conversion over a fixed time. A marked increase in the rate of indoline dehydrogenation was observed when the temperature was increased between 100 and 180 °C, with measured first order rate constants of 1.8×10^{-4} s^{-1} at 100 °C and 5.9×10^{-4} at 120 °C. Although piperidines dehydrogenate more slowly than indolines, steric hindrance around the nitrogen atom in piperidine increases its dehydrogenation rate significantly.

Introduction

The use of hydrogen as a clean energy carrier has been studied extensively over the past decade as concerns over carbon dioxide emissions from vehicles continue to rise.[1,2] While fuel cells have undergone significant advances over this time,[2,3] one of the major barriers to widespread adoption of this technology is the lack of an adequate hydrogen storage method. The US Department of Energy (DOE) has set specific targets that any potential hydrogen fuel system must meet.[4] For 2015, these targets include a net system gravimetric capacity of 5.5 wt% H_2 and volumetric capacity of 40 g H_2 L^{-1}. As well, start-up, shut-down, refilling time and operating temperature restraints are imposed.

Currently, there are four main categories of hydrogen storage materials being considered for vehicular transportation: pure compressed or liquefied hydrogen, adsorbed hydrogen on carbon or other physisorption media, metal hydrides that can reversibly adsorb hydrogen and chemical hydrides that react to release hydrogen. This final category, chemical hydrides, can be further separated into non-metal hydrides (*e.g.* NH_3BH_3) and organic liquids (*e.g.* indoline, piperidine).[5] Compressed or liquefied hydrogen systems have low hydrogen capacity because of the significant amount of added weight from the high-pressure tanks required to house the hydrogen. The cost of compressing the hydrogen is also of concern. Implementing the use of such systems would also require a complete overhaul of the current fueling infrastructure for public distribution. Adsorbed hydrogen systems require either extremely low temperatures for physisorption or extremely high temperatures for chemisorption release. These are also solids, and usually have low gravimetric storage densities. Metal hydrides, despite their generally high gravimetric density, usually require high temperatures to initiate the exothermic hydrogen release. Also, they are solids, which are not ideal for the current fueling infrastructure, and attempts at their regeneration from spent material have generally met limited success. Non-metal hydrides and organic liquids, however, have shown potential for vehicular hydrogen storage applications.[6,7]

Organic liquids can be dehydrogenated easily on-board, are pumpable, and release H_2 endothermically. Endothermicity not only means that the reaction is more controllable, but also means that energy must be supplied to facilitate the reaction. Organic liquids are also easy to hydrogenate off-board, but they usually exhibit poor hydrogen gravimetric density. In contrast, non-metal hydrides have much higher hydrogen gravimetric densities, and release H_2 exothermically, meaning external energy would not be needed to facilitate the reaction. They are, however, usually solids and are much more difficult to regenerate.

We have previously suggested mixed fuel systems combining two hydrogen carriers, where the combination offers mutual enhancement of certain characteristics.[8] In our mixed fuel, the physical combination of an organic liquid (endothermic

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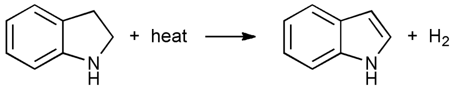
carrier) with a solid, non-metal hydride (exothermic carrier) yields a liquid mixture that is thermodynamically neutral in its H_2 release. A liquid mixture is desirable because a liquid, like gasoline, would be compatible with current fuelling infrastructure and is far easier to pump in on-board systems than a solid fuel. Before that, however, there were limited examples of similar systems reported. In 2006, Gelsey published a similar idea with the hydrolysis of $NaBH_4$ as the exothermic system and a metal hydride as the endothermic system, however the carriers were physically separated from one another so that the advantage of a liquid mixture was not obtained.[9] In 2007, Thorn *et al.* demonstrated the use of a mixed ammonia borane and perhydronaphthalene system at 250–280 °C, although they observed significant degradation, and didn't identify any boron- or nitrogen-containing products.[10] In the same patent, they also discussed the use of non-hydrogen releasing reactions to supply heat for the release of H_2 from an endothermic carrier.

Our mixed hydrogen storage system involved the combination of an amine borane ($R_3N{:}BH_3$) with an organic liquid, indoline. All three amine boranes release three equivalents of H_2 exothermically (eqn (1); $R_3N = NH_3, NHMe_2, NEt_3$; $\Delta H = -156\ \text{kJ mol}^{-1}$)[11,12] upon reaction with H_2O at elevated temperatures, or at room temperature in the presence of a transition metal catalyst (*e.g.* Pt, Pd). Indoline releases one equivalent of H_2 endothermically (eqn (2), $\Delta H = 52\ \text{kJ mol}^{-1}$)[13] at elevated temperatures in the presence of the same or similar catalysts. A 3 : 1 mixture of indoline and borane will therefore, theoretically, give thermally neutral hydrogen release. In practice, however, other factors need to be considered.

$$R_3N{:}BH_3 + 3H_2O \rightarrow R_3N{:}B(OH)_3 + 3H_2 + \text{heat} \quad (1)$$



(2)

A significant concern in this system[8] is the substantial difference in reaction rates between the endothermic and exothermic hydrogen release reactions. The hydrolysis of the amine boranes is very rapid, especially at elevated temperatures in the presence of transition metal catalysts. In contrast, indoline dehydrogenation is much slower. Herein, we report the findings from our investigations of the consequences of this rate disparity and possible methods of overcoming it.

Results and discussion

Consequences of the rate disparity

The rate disparity would threaten the feasibility of the system if the endothermic reaction were too slow to take up the heat generated by the exothermic H_2 release before the heat dissipated into the surroundings. We therefore performed a simple calculation to predict (a) how much of the heat would be lost to the surroundings, and (b) how much catalyst would be necessary to obtain the DOE-mandated rate of H_2 release.

Both reaction rates can be adjusted by modifying the conditions and method. The rate of borane hydrolysis can be controlled by adding the necessary equivalents of water as needed, because the reaction is essentially instantaneous at 100 °C in the presence of a precious metal catalyst. The rate of indoline dehydrogenation is independent of the amount of indoline used (because indoline is the solvent, its concentration is independent of the amount used), but the rate is dependent on the number of available catalyst sites. The rate can be increased by simply increasing the amount of catalyst (*vide infra*).

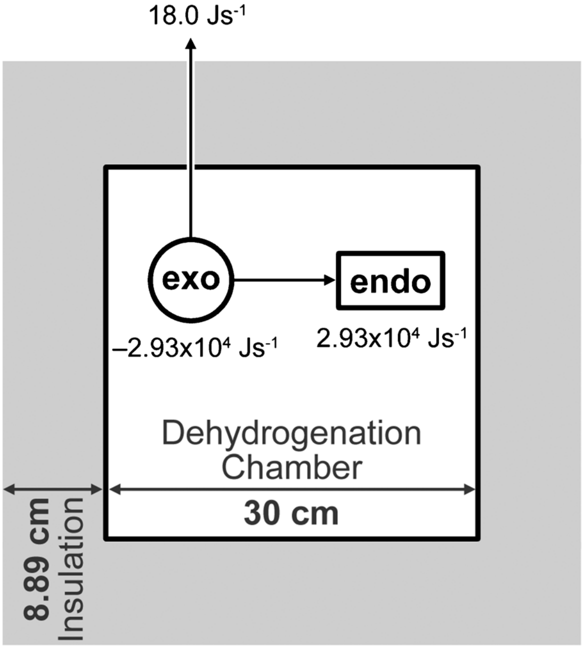


Fig. 1 Schematic of theoretical dehydrogenation chamber and heat exchange based on 30 g Pd.

Increasing the rate of indoline dehydrogenation by increasing the catalyst loading will increase both the financial cost and the energy requirements. The DOE target for H_2 production is $0.02\ \text{g s}^{-1}$ per kW of power needed by the engine.[4] We considered an engine running at 150 horsepower ($\sim$113 kW) for this calculation, meaning a required H_2 production from the system of $2.25\ \text{g s}^{-1}$. A 3 : 1 indoline : amine-borane mix generates half its H_2 from the indoline and half from the amine-borane. In order to generate $1.13\ \text{g s}^{-1}$ of H_2 by indoline dehydrogenation, one would need 30 g of Pd with a heat input of $2.93 \times 10^4\ \text{J s}^{-1}$, based upon the known reaction enthalpy (Fig. 1). That amount of catalyst is too large to be practical, but that amount of heat may not be.

The heat input required by the endothermic reaction ($2.93 \times 10^4\ \text{J s}^{-1}$), plus the heat lost to the surroundings, must be generated by the exothermic reaction (eqn (1)). The radiant heat loss calculation requires a few more assumptions. We assume that (a) the insulation around the reaction chamber is equivalent to the insulating ability of R-13 PINK FIBERGLAS® insulation (thickness = 8.89 cm, R = 13 h ft^2 °F Btu^{-1}, or RSI = 0.42 J K^{-1} m^{-2} s^{-1}), (b) the dehydrogenation chamber measures 30 cm^3 (surface area, σ = 0.54 m^2) and (c) the temperature difference across the chamber wall is 80 K (T_{rxn} = 100 °C, T_{outside} = 20 °C). With these assumptions, radiant heat loss is calculated by eqn (3)[14] to be

18.0 J s^{-1}, which is only a small portion of the heat generated by reaction (2).

$$\text{radiant heat loss} = \mathrm{RSI}\sigma\Delta T \qquad (3)$$

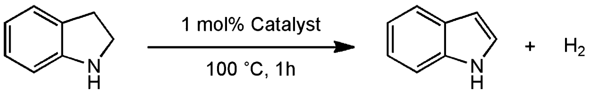
Therefore, although simply increasing the rate of the endothermic system by increasing the amount of catalyst could theoretically generate a thermodynamic balance producing the required amount of H_2, the amount of catalyst required is unreasonable. To this end, adding more catalyst alone is not a sufficient solution, and therefore other ways of increasing the rate of the endothermic dehydrogenation must be found.

Increasing the rate of indoline dehydrogenation

Previously, Cui *et al.* demonstrated rate enhancements of *N*-heterocycle dehydrogenation reactions by the introduction of electron donating or conjugating groups outside the ring.[15] It was shown that there is a correlation between the Hammett parameter (σ_p) of the substituent of a piperidine ring and $\log_{10}(t_{1/2})$ for these reactions. This held true for all substituted piperidines, except for those that had substituents capable of conjugating with the dehydrogenated ring (*e.g.* C(O)NH_2). In this case, the rate was faster than that predicted by the Hammett relationship. There are certainly other modifications that can be done to the *N*-heterocyclic backbone and the reaction conditions in order to increase the rate of dehydrogenation of such endothermic carriers. Herein we discuss the effect of catalyst choice, temperature and sterics on this rate.

Finding the most efficient catalyst for these reactions could lead to a significant rate increase. Our original studies with mixed dehydrogenation systems used Pd exclusively, with either carbon or silica as the support. To evaluate other catalysts, many different metal–support combinations were prepared by the sol–gel procedure of Gonzalez *et al.*[16]

Table 1 Summary of indoline dehydrogenation catalyst screening carried out at 100 °C



Catalyst (5 wt% metal on support)[a]	Conversion[b] (%)
Co/SiO_2	<1
Cu/SiO_2	<1
Fe/SiO_2	<1
Ir/SiO_2	<1
Ni/SiO_2	<1
Pd/Al_2O_3	61 ± 1
Pd/SiO_2	81 ± 1
Pd/SiO_2·Al_2O_3	27 ± 1
Pd/TiO_2	25 ± 3
Pd/ZrO_2[c]	32 ± 3
Pd·Rh/SiO_2[d]	<1
Pt·Pd/SiO_2[d]	<1
Pt/SiO_2	<1
Pt/Al_2O_3	10 ± 1
Rh/SiO_2	6 ± 2
Rh/Al_2O_3	11 ± 1
Ru/SiO_2	3.2 ± 0.6

[a] Based on the amount of metal precursor added during sol–gel procedure. [b] Determined by ^{1}H NMR. [c] 2.5 wt% metal on support. [d] Metal molar ratio of 1 : 1.

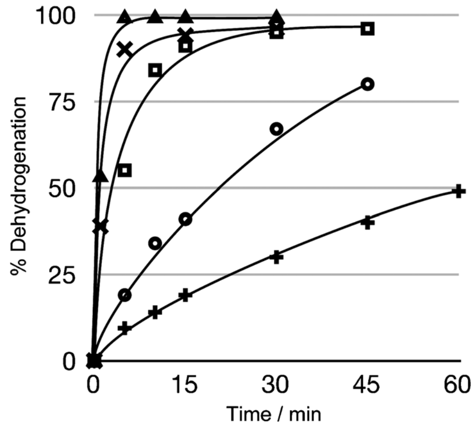


Fig. 2 Indoline dehydrogenation conversion (at 1 mol% loading of a 10 wt% Pd/C) curves (measured by ^{1}H NMR spectroscopy) at 100 °C (+), 120 °C (○), 140 °C (□), 160 °C (×) and 180 °C (▲).

In order to screen the catalysts for their activity, indoline was charged with 1 mol% of the catalyst, and heated to 100 °C. Instead of calculating the rate directly, we determined the conversion after 1 h (Table 1). Although a range of metals and supports was tested, none were more active than our original metal selection of Pd/SiO_2.

The effect of temperature on the rate of indoline dehydrogenation was investigated under the same conditions used in the catalyst study outlined above. Indoline and 1 mol% loading of 10 wt% Pd/C were heated to a number of temperatures ranging from 100 °C to 180 °C. In these tests, Pd/C was used rather than Pd/SiO_2 to enable comparisons with previous experiments in our lab.[8] Small aliquots were removed from the reaction mixture a number of times over the course of an hour, and the yield of H_2 was calculated using ^{1}H NMR spectroscopy presuming only two products: H_2 and indole. The reaction curves are shown in Fig. 2.

The dehydrogenation rate increases with increasing temperature. The first order rate constant of the reaction is 1.8×10^{-4} s^{-1} (or 1.8×10^{-2} s^{-1} per g Pd) at 100 °C and 5.9×10^{-4} s^{-1} at 120 °C, both with 1 mol% Pd loading. At 0.5 mol% Pd and 100 °C, the rate constant was 8.7×10^{-5} s^{-1} (again equivalent to 1.8×10^{-2} s^{-1} per g Pd), showing that the rate is proportional to the mass of Pd used. The reactions at 140 °C and above were too rapid for rate

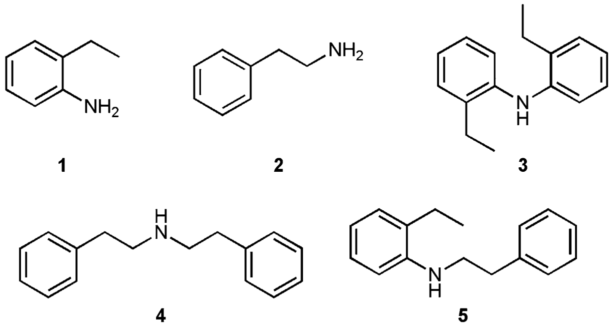
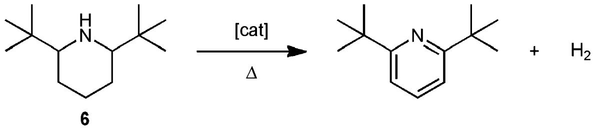


Fig. 3 The identified hydrogenolysis products (**1** and **2**) and the subsequent disproportionation products expected from them (**3**, **4**, and **5**).

constant determination by the methodology employed. While the rate of the reaction increases significantly at temperatures above 140 °C, degradation of the dehydrogenation product is observed. ^1H NMR spectroscopy of the product mixture revealed a number of undesired compounds. Two hydrogenolysis products, 2-ethylaniline (**1**) and 2-phenylethanamine (**2**), were observed by GC/MS. It is known that primary amines such as these tend to undergo Pd-catalyzed disproportionation reactions to give NH_3 and a secondary amine.[17] The three disproportionation products that would be expected from **1** and **2** are structures **3–5**, all of which have a *m*/*z* of 225 (Fig. 3). A peak of that mass was observed by GC/MS.

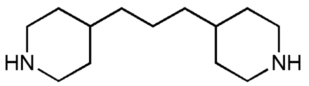
The effect of sterics on heterocycle dehydrogenation

The third strategy to increasing the rate of *N*-heterocycle dehydrogenation was discovered somewhat serendipitously. During previous investigations of mixed dehydrogenation systems, we noted that the lone pair of electrons of the nitrogen atom of the heterocycle was irreversibly binding to the Lewis acidic boron, preventing complete hydrogen release.[18] To prevent this interaction, we looked at sterically encumbered piperidines, such as in 2,6-di-*tert*-butylpiperidine (**6**). During this investigation, we realized that, under similar conditions, **6** undergoes dehydrogenation much faster than the parent piperidine.



(4)

After 1 h at 170 °C, with 1 mol% loading of either Pd/SiO_2 or Pd/Al_2O_3 sol–gel catalysts, the dehydrogenation of **6** yielded 40 ± 4% and 40 ± 3% of 2,6-di-*tert*-butylpyridine, respectively. The extent of dehydrogenation of 1,3-bis-(4-piperidinyl)propane (**7**) under the same conditions was also determined. This was done in order to compare the rate of dehydrogenation of **6** with that of another piperidine with electron donating alkyl substituents without steric hindrance. The dehydrogenation of **7**, with Pd/SiO_2 or Pd/Al_2O_3 sol–gel catalysts resulted in <3% conversion after 1 h at 170 °C. This demonstrates that the steric effect of the t-Bu groups, rather than the electronic effect, is the cause of the enhanced rate.



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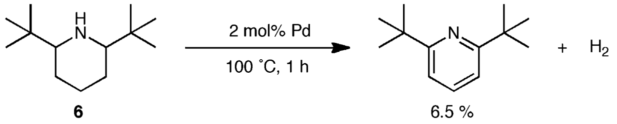
Despite the rate increase compared to piperidine itself, **6** still dehydrogenates to a lesser extent than indoline after the same amount of time. However, **6** has a higher gravimetric storage density of H_2 (3.0 wt%) than indoline (1.7%) and undergoes less degradation under the conditions employed. This gravimetric storage density is still too low to allow **6** to be a viable candidate as a hydrogen carrier on its own. However, its use in a mixed endothermic–exothermic system may be feasible.

In order to determine whether the rate-enhancing steric effect could be observed in a compound with an even better H_2 storage density, the dehydrogenation of *cis*-2,6-dimethylpiperidine, with a gravimetric H_2 density of 5.4 wt%, was investigated. In this case however, the temperature needed to be reduced to 100 °C to attempt dehydrogenation because the boiling point of *cis*-2,6-dimethylpiperidine is 127.8–128.1 °C.[19] This study revealed only trace amounts of the corresponding pyridine product after 1 h, as determined by ^1H NMR spectroscopy. Similar results were observed for piperidine itself under the same conditions.

It is known that pyridine and piperidine bind to metal surfaces quite strongly through the lone-pair of electrons on the nitrogen atom. This has been suggested as the initial binding mode of pyridine in its hydrogenation mechanism.[20] If this binding of pyridine is strongly favoured at the temperatures investigated, then pyridine binding through the nitrogen atom to the catalyst surface likely leads to poisoning or auto-inhibition. The idea of catalyst poisoning by a *N*-heterocycle (carbazole) was the topic of discussion in a recent manuscript by Sotoodeh and Smith.[21] Previously, the steric bulk around the nitrogen in 2,6-di-*tert*-butylpyridine has been shown to prevent complete adduct formation between the pyridine nitrogen and either BF_3 or a fully solvated proton.[22] 2,6-Di-*tert*-butylpiperidine should therefore only be able to bind parallel to the surface, preventing catalyst poisoning and allowing for more rapid dehydrogenation. This hypothesis was tested by reacting **6** and piperidine together in the same flask at 100 °C for 1 h with 2 mol% loading of the Pd/Al_2O_3 sol–gel catalyst discussed earlier. In the absence of piperidine, the di-substituted piperidine dehydrogenates to the extent of 6.5%, however in the presence of piperidine, only trace amounts of pyridine and 2,6-di-*tert*-butylpyridine are produced. The same effect would be expected if **6** were mixed with pyridine instead as it is a stronger base than piperidine, and would more readily bind to the catalyst surface.



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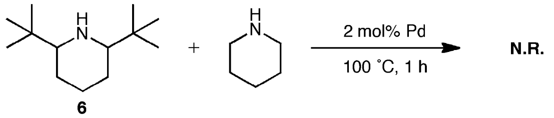

(6)

Conclusions

To eliminate the disparity in the hydrogen release rates of the endothermic and exothermic reactions of a mixed system, several strategies were analyzed. Finding ways to increase the rate of *N*-heterocycle dehydrogenations is of utmost importance as it has become apparent that the amount of Pd required to facilitate the necessary H_2 release rate from our first generation mixed system is prohibitive. Increasing the temperature, although successful in increasing the rate significantly, also decreased the selectivity for the desired indole. At 180 °C, complete indoline dehydrogenation was observed in 5 minutes, however it was accompanied by severe degradation to the hydrogenolysis and disproportionation products. Catalyst choice makes a significant difference in the dehydrogenation rate of indoline, and similar trends would be expected for other *N*-heterocycles, where Pd/SiO_2 and Pd/Al_2O_3 show enhanced activity towards the dehydrogenation.

Steric hindrance about the nitrogen atom causes a marked increase in the dehydrogenation of piperidine derivatives. The extent of dehydrogenation of 2,6-di-*tert*-butylpiperidine after 1 h at 100 °C was significantly greater than the *ortho*-unsubstituted piperidine derivatives or 2,6-dimethylpiperidine. Coupling this hindrance with an electron withdrawing and/or conjugating group, as shown by Cui *et al.*, could increase the rate further.

Despite these findings, greater rates of endothermic dehydrogenation are still required before the exothermic/endothermic mixed fuel can be practical.

Experimental

All reagents except for **6** were purchased from chemical suppliers and used as received. ^1H NMR spectra were collected at 300 K on a Bruker AV-400 spectrometer operating at 400.3 MHz and referenced to $SiMe_4$. GC/MS analyses were performed on an Agilent Technologies 6850 GC coupled with an Agilent Technologies 5975C VL MSD with a Triple-Axis Detector. MS spectra were analyzed by library comparison using NIST MS Search 2.0.

Synthesis of 2,6-di-*tert*-butylpiperidine (6)

To a 31 ml steel pressure vessel, equipped with a magnetic stir bar, 2,6-di-*tert*-butylpyridine was added with 1–2 mol% Pd/C under air. The vessel was then sealed, flushed three times with H_2, heated to 100 °C, pressurized to 80–90 bar with H_2, and stirred for 18 h. After cooling, the pressure was released from the vessel. The desired product was isolated by filtration. Purity was determined by ^1H NMR spectroscopy. In all cases, >99% hydrogenation with >99% selectivity was observed. The identity of the product was confirmed by comparing ^1H NMR spectrum to published literature data.[23]

Rate constant determination

Indoline (8.9 mmol, 1.0 ml) was injected *via* a syringe into a 10 ml round bottom flask containing 10 wt% Pd/C (1 mol% loading, 0.089 mmol, 94.6 mg) and a magnetic stir bar under air. The flask was equipped with a condenser, immersed in an oil bath pre-heated to 100 °C and stirred magnetically for 60 min with constant argon flow provided *via* a needle through a rubber septum at the top of the condenser to remove any H_2 formed *in situ*. A second needle leading to an oil-bubbler allowed gas to escape from the system. Small aliquots of the reaction mixture were obtained after 5, 10, 15, 30, 45 and 60 min, dissolved in $CDCl_3$, then filtered through Celite 545®. Yields at each time were determined by comparing relative integrations in the ^1H NMR spectra. A plot of $\ln(n/n_0)$ of the starting material (indoline) *versus* time was linear for the duration of the experiment (one half life). The slope is equal to the negative of the rate constant.

Sol–gel catalyst procedure

Tetraethoxy orthosilicate (21.5 mmol, 4.8 ml), anhydrous ethanol (2.0 ml), palladium(II) chloride (0.6 mmol, 108.0 mg) and 30% aqueous ammonium hydroxide (0.3 ml) were combined in a 15 ml round bottom flask equipped with a magnetic stir bar and a water condenser under air. The mixture was stirred magnetically and heated at 80 °C for 10 min under argon flow *via* needles at the top of the condenser. Water (2.0 ml) was then injected directly into the reaction mixture through the septum at the top of the condenser using a 30 cm needle and then stirred for an additional 4 h, during which time gel formation took place. The reaction mixture was filtered, dried under dynamic vacuum for 18 h, then further dried in an oven at 400 °C for 4 h. Other catalysts were prepared by replacing tetraethoxy orthosilicate and/or $Pd(II)Cl_2$ with similar amounts of different support precursors (aluminium triethoxide, titanium(IV) i-propoxide, zirconium(IV) ethoxide) and metal precursors (platinum(II) chloride, rhodium(III) chloride hydrate, iridium(III) chloride hydrate, ruthenium(III) chloride trihydrate, iron(III) chloride, copper(II) chloride, nickel(II) chloride, and cobalt(II) chloride hexahydrate).

Catalyst screening procedure

Indoline (3.0 mmol, 0.33 ml) was loaded into a 10 ml round bottom flask containing the catalyst to be screened (1 mol% loading, 0.03 mmol) under air. The flask, which was equipped with a magnetic stir bar and a condenser, was immersed into an oil bath pre-heated to 100 °C, under a constant argon flow and stirred magnetically. A needle leading to an oil bubbler allowed H_2 gas, generated *in situ* to escape from the system. After 60 min, the reaction was allowed to cool, and an aliquot was obtained, dissolved in $CDCl_3$, and filtered through Celite 545®. Yield was determined by ^1H NMR spectroscopy. A similar procedure was used for 2,6-di-*tert*-butylpiperidine (1.92 mmol, 378.4 mg) with Pd/SiO_2 (10 wt% Pd, 1 mol% loading).

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