Hydrogen Sources in Catalytic Transfer Hydrogenation

Subjects: Chemistry, Organic

Contributor: Batoul Taleb , Rabih Jahjah , David Cornu , Mikhael Bechelany , Mohamad Al Ajami , Ghenwa Kataya , Akram Hijazi , Mohammad H. El-Dakdouki

Catalytic transfer hydrogenation has emerged as a pivotal chemical process with transformative potential in various industries. Unlike conventional direct hydrogenation, catalytic transfer hydrogenation offers numerous advantages, such as enhanced safety, cost-effective hydrogen donors, byproduct recyclability, catalyst accessibility, and the potential for catalytic asymmetric transfer hydrogenation, particularly with chiral ligands. Alcohols such as methanol and isopropanol are prominent hydrogen donors, demonstrating remarkable efficacy in various reductions. Formic acid offers irreversible hydrogenation, preventing the occurrence of reverse reactions, and is extensively utilized in chiral compound synthesis. Unconventional donors such as 1,4-cyclohexadiene and glycerol have shown a good efficiency in reducing unsaturated compounds, with glycerol additionally serving as a green solvent in some transformations.

hydrogen transfer hydrogen donor molecules alcohol formic acid amine glycerol

1. Introduction

Hydrogenation is a chemical reaction between an unsaturated molecule and a hydrogen molecule, usually in the presence of a catalyst. This reaction is crucial, especially in industry, because it is used to reduce or saturate organic compounds. It has many important uses, such as converting vegetable oils into solid fats, as well as in pharmaceuticals synthesis, plastic manufacturing, and producing chemicals from petroleum [1].

While direct hydrogenation has been the conventional method used across various sectors, transfer hydrogenation has emerged as an attractive alternative to this approach, and it has recently become the center of research in hydrogenation science. The significance of transfer hydrogenation can be attributed into several key points: (i) Enhanced safety measures, as this method eliminates the need for potentially hazardous pressurized H_2 gas; (ii) Availability of cost-effective and easily manageable hydrogen donors; (iii) The ability to recycle the primary byproduct; (iv) Accessibility and stability of the catalysts used; (v) The potential for catalytic asymmetric transfer hydrogenation in the presence of chiral ligands [2].

Transfer hydrogenation was first observed in 1925 by Meerwein–Ponndorf–Verley (MPV). They utilized alcohols as the source of hydrogen (H-source) and aluminum alkoxide as a homogeneously acting catalyst to facilitate the reduction of carbonyl compounds [3][4]. Researchers have extended the MPV reduction to carbonyl compounds using metals such as aluminum, zirconium, lanthanum, cerium, samarium, and ytterbium [5].

2. Hydrogen Donors

As mentioned above, a hydrogen source other than molecular hydrogen is needed in hydrogen transfer reactions. For the hydrogen to transfer from the donor molecule to the unsaturated compound, the hydrogen donor must satisfy two main conditions: (1) it should have a low oxidation potential, allowing hydrogen abstraction to occur in the presence of a catalyst under mild conditions; (2) it should have the capacity to loosely bind to the catalytic center [6].

There are many compounds that can act as hydrogen donors; the choice of which to use depends on a few important parameters: (1) The type of catalyst being used, whether it is MPVO or a transition metal catalyst; (2) Whether it can work well under mild conditions; (3) The nature of the functional group to be saturated; (4) The influence of the donor molecule on the equilibrium of the reaction; (5) Whether the donor molecule helps in avoiding the formation of any undesirable byproducts [7].

2.1. Alcohol Hydrogen Donor

Alcohols are frequently employed as hydrogen donors, particularly in reduction reactions utilizing the Meerwein–Ponndorf–Verley (MPV) catalyst [5]. In this context, only alcohol molecules serve as hydrogen donors, with both primary and secondary alcohols being utilized. Jainling et al. utilized methanol as a hydrogen donor in the presence of a rhodium catalyst to carry out the hydrogenation of benzaldehyde. This process achieved a substantial yield percentage and chemoselectivity, as illustrated in [8].

Furthermore, Magnus et al. used methanol as a hydrogen source to perform selective hydrogenation of alkynes with manganese pincer complex as a catalyst [9].

The term “pincer” refers to a ligand type that occupies adjacent binding sites in a metal complex and typically adopts a meridional arrangement. Pincer ligands gained significant attention from scientists in the 1990s and have become a subject of thorough investigation, as evidenced by the increasing number of review articles focusing on transition metal complexes with pincer ligands [10][11]. The significance of these ligands lies in their distinct combination of properties. They hold the donor groups in a predictable arrangement which allows them to control the nature of the coordination sphere. In addition, they are highly effective for catalyzing asymmetric reactions. They also exhibit remarkable thermal stability, making them suitable for homogeneous catalysis [12].

While ethanol has shown promise in certain reactions, its systematic exploration as a hydrogen source in transfer hydrogenation has been limited. This is mainly because ethanol often hinders the catalyst’s performance by forming stable and inactive carbonyl complexes [13][14]. It has been noted that secondary alcohols are more efficient due to their sigma inductive effects. Further, 2-propanol is, notably, the primary choice among various secondary alcohols for use as a hydrogen donor. This is because 2-propanol possesses several favorable properties, including widespread availability, affordability, a suitable boiling point, and solubility. Moreover, the acetone produced as a result of 2-propanol oxidation is non-toxic and can be easily separated from the reaction mixture [15].

Catalytic transfer hydrogenation of olefins was successfully accomplished using isopropanol as a hydrogen source. This process employed cobalt (II) pincer ligand complex which proved effective for hydrogenating different kinds of olefins, including aromatic, aliphatic, terminal, and internal alkenes. The yields obtained from this method ranged from good to excellent [16].

Homogeneous catalysts have traditionally been favored for their exceptional selectivity. Moreover, they display remarkable activity, particularly in asymmetric catalysis. However, these advantages are counterbalanced by their significant cost and the challenges associated with their separation and reuse. This prompted a shift in research focus towards heterogeneous catalysts, which are cost-effective and easily separable [17].

Francisco Alonso et al. conducted catalytic transfer hydrogenation experiments on various functionalized and non-functionalized olefins. They utilized nickel nanoparticles as the catalyst and 2-propanol as the source of hydrogen. This heterogeneous catalyst efficiently catalyzed the reaction, resulting in high yields and chemoselectivity for specific substrates [18]. In fact, the efficiency of the nickel catalyst has been demonstrated in various transfer hydrogenation reactions, including the α-alkylation of methyl ketones with primary alcohols [19][20] and the transfer hydrogenation of carbonyl compounds [21][22].

While the transfer hydrogenation reaction of carbonyl compounds has been extensively investigated in the past two decades [23][24][25][26][27], the corresponding reaction involving imines has received less attention, although it holds significant importance for the synthesis of pharmaceuticals and agrochemicals. Jan E. Bäckvall et al. explored the transfer hydrogenation of imines. They utilized $[RuCl_2(PPh_3)_3]$ as the catalyst, 2-propanol as the hydrogen donor, and K_2CO_3 as a base [28]. In a further investigation, their focus shifted to the asymmetric transfer hydrogenation of imines. For this purpose, they employed a dimeric rhodium catalyst and isopropanol as the source of hydrogen [29].

The catalytic transfer hydrogenation of furfural to furfuryl alcohol has attracted significant interest, mainly because furfural can be converted into a diverse array of chemicals and liquid transportation fuels [30]. Moreover, furfuryl alcohol has the potential to be a precursor for various valuable chemicals, including tetrahydrofurfuryl alcohol, and has various industrial applications [31].

The research attention has also turned to nitrogen-doped carbon-supported iron catalysts. These catalysts exhibit the ability to selectively hydrogenate compounds, such as nitroarenes, to anilines using molecular hydrogen (H_2) or alternative hydrogen donors, such as formic acid and hydrazine hydrate [32][33].

2.2. Water

Though the use of water as a hydrogen source has been relatively limited, it holds great promise due to: (1) Being safe and eco-friendly; (2) Its affordability; (3) The ease of tracking reactions through isotopic labeling with D_2O. However, there is a challenge when it comes to water-mediated reactions catalyzed by transition metals. These reactions result in the formation of an organometallic intermediate that does not readily mix with water. To address this issue, a reductant is utilized. Common metals such as lithium, sodium, and zinc can act as reducing agents for hydrogenating carbon-carbon π-systems, even in the presence of protic reagents such as amines, alcohols, acids, and water [34].

Yoshio Inoue et al. carried out a rhodium-catalyzed hydrogenation of olefins, including α,β-unsaturated ketones. They used H_2O or D_2O as the hydrogen source and zinc metal as the reducing agent. Various olefin substrates were tested. Terminal olefins (aromatic and aliphatic) produced fully saturated products in high yields. In contrast, internal olefins resulted in partially reduced products with moderate yields. Interestingly, α,β-unsaturated ketones yielded selective 1,4-reduced products, with no alcohol product observed [34].

Deuterium-labeling experiments showed that, when deuterium was used in the reduction of simple olefins such as styrene, a combination of mono-, di-, and tri-deuterated products emerged as a result of a deuterium scrambling process. This prompted the proposal of a mechanism that encompasses a trivalent mono-deuterio-rhodium intermediate participating in addition to a carbon-carbon double bond.

2.3. Formic Acid and Its Salts

Many studies have reported a chemical challenge encountered in the asymmetric transfer hydrogenation of ketones into alcohols when 2-propanol is utilized as the hydrogen source [35][36]. This challenge involves the potential deterioration of the enantiomeric purity of the chiral product. This is due to the occurrence of a reverse process caused by structural similarities between the hydrogen donor and the product, both of which are secondary alcohols [7]. However, when formic acid is employed as the hydrogen donor, it undergoes dehydrogenation to produce carbon dioxide. The irreversible nature of the reaction ensures that the process remains under kinetic control.

It has been reported that adding a weak base such as triethylamine is enough to facilitate hydrogen transfer, enabling the transfer hydrogenation reaction to be conducted under aqueous conditions [37]. Consequently, the combination of formic acid and an amine as a hydrogen source has been shown as a good alternative.

Bolun Yang et al. examined how the ratio of formic acid to amine (F/T) influenced the speed of reduction and the selectivity of asymmetric transfer hydrogenation of ketones, using the Ru-TsDPEN catalyst [38]. When the F/T ratio is high (acidic medium), the reaction needs a long time to reach a high conversion; at (F/T = 4.6/1), the reaction had an extended induction period and reached only 39% conversion after 150 h. On the other hand, at a lower F/T ratio (basic medium), the reaction rate significantly increases; at (F/T = 0.2/1), the reduction started instantaneously and reached a 100% conversion after 5 h with high enantiomeric excess (%*ee*). However, at (F/T = 0.09/1), the reaction reached only 80% conversion due to the limited amount of hydrogen source available relative to the substrate. Based on this result, the optimal F/T molar ratio is 0.2/1.

Catalysis in F-T mixtures has shown that both the reaction rates and enantioselectivities are controlled by pH and are affected by the F/T molar ratio. Likewise, many studies have utilized the azeotropic mixture of formic acid (HCOOH) and triethylamine (NEt_3) (F-T), with a F/T molar ratio of 2.5:1 [39][40][41].

Research in modern chemistry has focused heavily on catalysis in water due to water's role as an eco-friendly solvent [42][43]. In this context, the asymmetric transfer hydrogenation (ATH) of ketones has been investigated in water with F/T being the hydrogen source [44][45]. The reaction's efficiency and enantioselectivity are affected by the F/T ratio. For metal-catalyzed ATH of imines, the F/T molar ratio is typically 5:2 when water is the solvent [46]. The addition of methanol as a cosolvent enhances the reaction by forming hydrogen bonds and disrupting the strong hydrogen bonding in pure water, making reactants/products more soluble in the reaction mixture [47][48][49].

The main drawback of using azeotropic F-T for ATH is that certain catalysts undergo fast decomposition or lose their catalytic activity [50]. Additionally, there might be a prolonged delay before the reaction starts, leading to a long reaction time needed to achieve high conversion [44].

Suzzane Chayya et al. observed that the presence of a base significantly impacts the resulting products in the catalytic transfer hydrogenation of 4-(phenylethynl) acetophenone. Under the conditions of utilizing 2% $Pd(acac)_2$ as a catalyst for 24 h at 80 °C, two different products are obtained based on variations in the (Hydrogen Donor/Base) condition.

Formic acid has been utilized as a hydrogen donor in numerous catalytic reactions, often without the need for additional base additives. Matthias Beller et al. performed different studies using $Fe(BF_4)_2 \cdot 6H_2O$ combined with tetraphosphorus as a catalyst. The catalyst demonstrated excellent efficiency in the selective transfer hydrogenation of a broad spectrum of aromatic and aliphatic compounds, including alkyne [51], and nitro compounds [52]. The catalytic transfer hydrogenation reactions were done in the absence of base additive.

Interestingly, iron catalysts have gained significant attention due to their affordability, wide availability, and low toxicity. This has driven research efforts towards substituting precious metals with iron-based alternatives [53].

The iron catalyst showed exceptional performance in both its activity and selectivity. However, a notable drawback was observed in terms of catalyst reusability. In light of this, researchers explored an alternative approach through the development of a reusable heterogeneous catalyst. Kohki Ebitani et al. conducted a study involving a supported palladium catalyst for the reduction of aromatic carbonyl compounds, utilizing formic acid as a hydrogen source under mild reaction conditions. The most efficient support materials were found to be carbon and alumina, providing optimal results for the reduction of benzaldehyde and benzonitrile, respectively [54].

The catalytic system is not efficient in reducing aliphatic and carbonyl compounds containing heteroatoms, which is attributed to the low electron density of the carbonyl carbons and the strong interaction of heteroatoms with the active Pd sites.

Furthermore, the reusability of the Pd/Al_2O_3 catalyst was assessed in the reduction of benzonitrile using formic acid. The results indicated that the recovered catalyst could be recycled up to three times without a significant decrease in product yield and selectivity.

Similarly, several catalytic transfer hydrogenation reactions have been conducted using formic acid as a hydrogen source in combination with reusable supported catalysts under base-free conditions [55][56].

Formic acid's inherent acidity poses challenges when used for carbonyl compound reduction due to the strong interactions between the hydrogen donor and the catalytic system, leading to the inhibition or even degradation of the catalytic species [36]. To overcome this, researchers have studied the utilization of formic acid salts as hydrogen donor molecules in catalytic hydrogenation reactions. Ammonium formate, an easily manageable and cost-effective hydrogen source, has been combined with a gold catalyst to perform a selective hydrogenation of ynamides, yielding Z-enamides.

2.4. 1,4-Cyclohexadiene

Although the use of 1,4-cyclohexadiene as a hydrogen donor in catalytic transfer hydrogenation is not common, its application has shown a complete conversion with a good yield.

John F. Quinn and his team achieved efficient catalytic transfer hydrogenation of heteroaromatic nitro groups [57] by using 1,4-cyclohexadiene as a hydrogen donor under microwave heating. Notably, microwave heating technology serves as a valuable alternative to high-temperature and high-pressure conditions, allowing for rapid and safe reactions [58]. This technique has been employed in various catalytic transfer hydrogenation processes [59][60].

The reduction of 4-fluoronitrobenzene led to a remarkable yield exceeding 99%, and the reaction produced only benzene as a byproduct, which can be easily separated and removed from the product mixture. The optimal conditions for this reaction involved the use of a Pd/C catalyst, six equivalents of 1,4-cyclohexadiene, microwave heating at 120 °C, and methanol as the solvent, with a reaction time of 5 min [57].

In the process of peptide synthesis, catalytic transfer hydrogenation plays a vital role by eliminating protective groups that prevent amino acid polymerization and reduce undesired side reactions [61]. Among these protective strategies, the benzyl group is commonly employed [62][63][64]. In this context, Arthur M. Felix et al. effectively eliminated the *N*-benzyloxycarbonyl protective group from L-alanine using a catalytic transfer hydrogenation technique. Their method relied on the use of a 10% Pd/C catalyst and 1,4-cyclohexadiene as the hydrogen donor [65].

2.5. Glycerol

Glycerol has gained attention as a green solvent in various organic reactions and synthetic processes [66][67]. It is considered non-hazardous and possesses unique physical and chemical properties that enable the dissolution of acids, bases, transition metal complexes, inorganic compounds, and even organic compounds that have limited solubility in water. Notably, glycerol's high boiling point allows for efficient separation of products using a simple distillation technique.

Remarkably, glycerol has proven effective as a hydrogen donor in catalytic transfer hydrogenation reactions involving various unsaturated organic compounds. Adi Wolfson et al. explored the reduction of benzaldehyde, nitrobenzene, and styrene, using different catalysts and glycerol as the hydrogen source [68].

The reduction of benzaldehyde and benzene requires the presence of a base. In contrast, the catalytic transfer hydrogenation of styrene should be conducted without adding a base, as introducing a catalyst in the presence of a base deactivates the catalyst. This is due to the higher oxidation potential of the secondary alcohol, which causes glycerol to dehydrogenate into dihydroxyacetone. Subsequently, dihydroxyacetone decomposes under the reaction conditions.

Having mentioned above the most frequently used hydrogen donor in the catalytic transfer hydrogenation, it is important to shed the light on the remarkable studies carried out by Hai-Xu Wang et al. [69]. Different from the homogeneous counterparts, they performed an electrocatalytic hydrogen reduction reaction where hydrogen gas (H_2) was used to generate reactive hydride species directly on the surface of platinum electrodes. These reactive hydrides can then be transferred to hydride acceptors molecules, enabling the hydrogenation reaction of different unsaturated compounds.

3. Conclusions

The conventional approach of direct hydrogenation using pressurized hydrogen gas has been significantly challenged by the emergence of transfer hydrogenation methods. This innovation offers a safer and more accessible alternative, utilizing various hydrogen donors to efficiently reduce unsaturated compounds.

Notably, alcohols, formic acid, 1,4-cyclohexadiene, water, and glycerol have been investigated as versatile hydrogen sources. Each donor exhibits unique properties and characteristics that influence their compatibility with different catalysts, reaction conditions, and types of unsaturated compounds.

Alcohols, such as primary and secondary alcohols, play a crucial role in the Meerwein–Ponndorf–Verley (MPV) reduction and offer valuable hydrogen transfer capabilities. Primary alcohols, such as methanol and ethanol, have demonstrated efficacy in various reductions, while secondary alcohols, especially isopropanol, have revealed compatibility with diverse substrates and stability within catalytic systems. However, challenges related to reactivity and side reactions have led to the exploration of alternative hydrogen donors.

Formic acid and its salts stand out as efficient and irreversible hydrogen donors. Their ability to prevent reverse reactions and their compatibility with various catalysts make them attractive choices in catalytic transfer hydrogenation, particularly for producing chiral compounds.

Unconventional donors such as 1,4-cyclohexadiene and glycerol have shown excellent activity in the reduction of specific unsaturated compounds, with successful results obtained under specific conditions such as microwave heating. Glycerol, known for its green properties, also serves as an intriguing green solvent in these reactions.

References

1. Whitner, T.C. Review of hydrogenation. Oil Soap 1939, 16, 39–44.
2. Baráth, E. Hydrogen Transfer Reactions of Carbonyls, Alkynes, and Alkenes with Noble Metals in the Presence of Alcohols/Ethers and Amines as Hydrogen Donors. Catalysts 2018, 8, 671.
3. Meerwein, H.; Schmidt, R. Ein neues Verfahren zur Reduktion von Aldehyden und Ketonen. Justus Liebig Ann. Der Chem. 1925, 444, 221–238.
4. Verley, A. The exchange of functional groups between two molecules. The passage of ketones to alcohols and the reverse. Bull. Soc. Chim. Fr. 1925, 37, 871–874.
5. Chuah, G.; Jaenicke, S.; Zhu, Y.; Liu, S. Meerwein-Ponndorf-Verley Reduction over Heterogeneous Catalysts. Curr. Org. Chem. 2006, 10, 1639–1654.
6. Stahl, L. The Handbook of Homogeneous Hydrogenation, 1st ed.; de Vries, J.G., Elsevier, C.J., Eds.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007; Volumes 1–3, ISBN 978-3-527-31161-3.
7. Zassinovich, G.; Mestroni, G.; Gladiali, S. Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts. Chem. Rev. 1992, 92, 1051–1069.
8. Aboo, A.H.; Bennett, E.L.; Deeprose, M.; Robertson, C.M.; Iggo, J.A.; Xiao, J. Methanol as hydrogen source: Transfer hydrogenation of aromatic aldehydes with a rhodacycle. Chem. Commun. 2018, 54, 11805–11808.
9. Sklyaruk, J.; Zubar, V.; Borghs, J.C.; Rueping, M. Methanol as the Hydrogen Source in the Selective Transfer Hydrogenation of Alkynes Enabled by a Manganese Pincer Complex. Org. Lett. 2020, 22, 6067–6071.
10. Choi, J.; MacArthur, A.H.R.; Brookhart, M.; Goldman, A.S. Dehydrogenation and Related Reactions Catalyzed by Iridium Pincer Complexes. Chem. Rev. 2011, 111, 1761–1779.
11. Gunanathan, C.; Milstein, D. Bond Activation and Catalysis by Ruthenium Pincer Complexes. Chem. Rev. 2014, 114, 12024–12087.
12. Peris, E.; Crabtree, R.H. Key factors in pincer ligand design. Chem. Soc. Rev. 2018, 47, 1959–1968.
13. Tsuji, J.; Ohno, K. Organic syntheses by means of noble metal compounds. XXXIV. Carbonylation and decarbonylation reactions catalyzed by palladium. J. Am. Chem. Soc. 1968, 90, 94–98.
14. Chatt, J.; Shaw, B.L.; Field, A.E. 656. The formation of hydrido- and carbonyl complexes of ruthenium by reaction of certain of its complexes with alcohols. J. Chem. Soc. 1964, 3466–3475.

15. Adkins, H.; Elofson, R.M.; Rossow, A.G.; Robinson, C.C. The Oxidation Potentials of Aldehydes and Ketones. J. Am. Chem. Soc. 1949, 71, 3622–3629.
16. Zhang, G.; Yin, Z.; Tan, J. Cobalt(ii)-catalysed transfer hydrogenation of olefins. RSC Adv. 2016, 6, 22419–22423.
17. Fukuzumi, S.; Hong, D. Homogeneous versus Heterogeneous Catalysts in Water Oxidation. Eur. J. Inorg. Chem. 2013, 2014, 645–659.
18. Alonso, F.; Riente, P.; Yus, M. Transfer hydrogenation of olefins catalysed by nickel nanoparticles. Tetrahedron 2009, 65, 10637–10643.
19. Alonso, F.; Yus, M.; Riente, P. The α-Alkylation of Methyl Ketones with Primary Alcohols Promoted by Nickel Nanoparticles under Mild and Ligandless Conditions. Synlett 2007, 2007, 1877–1880.
20. Alonso, F.; Riente, P.; Yus, M. Alcohols for the α-Alkylation of Methyl Ketones and Indirect Aza-Wittig Reaction Promoted by Nickel Nanoparticles. Eur. J. Org. Chem. 2008, 2008, 4908–4914.
21. Alonso, F.; Riente, P.; Yus, M. Hydrogen-transfer reduction of carbonyl compounds promoted by nickel nanoparticles. Tetrahedron 2008, 64, 1847–1852.
22. Alonso, F.; Riente, P.; Yus, M. Hydrogen-transfer reduction of carbonyl compounds catalysed by nickel nanoparticles. Tetrahedron Lett. 2008, 49, 1939–1942.
23. Wang, R.; Tang, Y.; Xu, M.; Meng, C.; Li, F. Transfer Hydrogenation of Aldehydes and Ketones with Isopropanol under Neutral Conditions Catalyzed by a Metal–Ligand Bifunctional Catalyst . J. Org. Chem. 2018, 83, 2274–2281.
24. Bruneau-Voisine, A.; Wang, D.; Dorcet, V.; Roisnel, T.; Darcel, C.; Sortais, J.-B. Transfer Hydrogenation of Carbonyl Derivatives Catalyzed by an Inexpensive Phosphine-Free Manganese Precatalyst. Org. Lett. 2017, 19, 3656–3659.
25. Lee, J.; Ryu, T.; Park, S.; Lee, P.H. Indium Tri(isopropoxide)-Catalyzed Selective Meerwein–Ponndorf–Verley Reduction of Aliphatic and Aromatic Aldehydes. J. Org. Chem. 2012, 77, 4821–4825.
26. Mojtahedi, M.M.; Akbarzadeh, E.; Sharifi, R.; Abaee, M.S. Lithium Bromide as a Flexible, Mild, and Recyclable Reagent for Solvent-Free Cannizzaro, Tishchenko, and Meerwein−Ponndorf−Verley Reactions. Org. Lett. 2007, 9, 2791–2793.
27. Battilocchio, C.; Hawkins, J.M.; Ley, S.V. A Mild and Efficient Flow Procedure for the Transfer Hydrogenation of Ketones and Aldehydes using Hydrous Zirconia. Org. Lett. 2013, 15, 2278–2281.
28. Wang, G.-Z.; Bäckvall, J.-E. Ruthenium-catalysed transfer hydrogenation of imines by propan-2-ol. J. Chem. Soc. Chem. Commun. 1992, 14, 980–982.

29. Samec, J.S.M.; Bäckvall, J.E. Ruthenium-Catalyzed Transfer Hydrogenation of Imines by Propan-2-ol in Benzene. Chem. Eur. J. 2002, 8, 2955.
30. Lange, J.; van der Heide, E.; van Buijtenen, J.; Price, R. Furfural—A Promising Platform for Lignocellulosic Biofuels. ChemSusChem 2012, 5, 150–166.
31. Nakagawa, Y.; Tamura, M.; Tomishige, K. Catalytic Reduction of Biomass-Derived Furanic Compounds with Hydrogen. ACS Catal. 2013, 3, 2655–2668.
32. Jagadeesh, R.V.; Surkus, A.-E.; Junge, H.; Pohl, M.-M.; Radnik, J.; Rabeah, J.; Huan, H.; Schünemann, V.; Brückner, A.; Beller, M. Nanoscale Fe2O3-Based Catalysts for Selective Hydrogenation of Nitroarenes to Anilines. Science 2013, 342, 1073–1076.
33. Jagadeesh, R.V.; Natte, K.; Junge, H.; Beller, M. Nitrogen-Doped Graphene-Activated Iron-Oxide-Based Nanocatalysts for Selective Transfer Hydrogenation of Nitroarenes. ACS Catal. 2015, 5, 1526–1529.
34. Sato, T.; Watanabe, S.; Kiuchi, H.; Oi, S.; Inoue, Y. Hydrogenation of olefins using water and zinc metal catalyzed by a rhodium complex. Tetrahedron Lett. 2006, 47, 7703–7705.
35. Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Ketones Using a Formic Acid−Triethylamine Mixture. J. Am. Chem. Soc. 1996, 118, 2521–2522.
36. Gamez, P.; Fache, F.; Mangeney, P.; Lamaire, M. Enantioselective catalytic reduction of ketones using C2-symmetric diamines as chiral ligands. Tetrahedron Lett. 1993, 34, 6897–6898.
37. Gladiali, S.; Taras, R. Reduction of Carbonyl Compounds by Hydrogen Transfer. In Modern Reduction Methods; Wiley Online Library: Hoboken, NJ, USA, 2008; pp. 135–157.
38. Zhou, X.; Wu, X.; Yang, B.; Xiao, J. Varying the ratio of formic acid to triethylamine impacts on asymmetric transfer hydrogenation of ketones. J. Mol. Catal. A Chem. 2012, 357, 133–140.
39. Cheng, X.; Horton, P.N.; Hursthouse, M.B.; Hii, K.K.M. Aminohydroxy phosphine oxide ligands in ruthenium-catalysed asymmetric transfer hydrogenation reactions. Tetrahedron Asymmetry 2004, 15, 2241–2246.
40. Cheung, F.K.K.; Hayes, A.M.; Hannedouche, J.; Yim, A.S.Y.; Wills, M. “Tethered” Ru(II) Catalysts for Asymmetric Transfer Hydrogenation of Ketones. J. Org. Chem. 2005, 70, 3188–3197.
41. Mao, J.; Baker, D.C. A Chiral Rhodium Complex for Rapid Asymmetric Transfer Hydrogenation of Imines with High Enantioselectivity. Org. Lett. 1999, 1, 841–843.
42. Dwars, T.; Oehme, G. Complex-Catalyzed Hydrogenation Reactions in Aqueous Media. Adv. Synth. Catal. 2002, 344, 239–260.

43. Sinou, D. Asymmetric Organometallic-Catalyzed Reactions in Aqueous Media. Adv. Synth. Catal. 2002, 344, 221–237.
44. Wu, X.; Li, X.; King, F.; Xiao, J. Insight into and Practical Application of pH-Controlled Asymmetric Transfer Hydrogenation of Aromatic Ketones in Water. Angew. Chem. Int. Ed. 2005, 44, 3407–3411.
45. Wu, X.; Li, X.; Hems, W.; King, F.; Xiao, J. Accelerated asymmetric transfer hydrogenation of aromatic ketones in water. Org. Biomol. Chem. 2004, 2, 1818–1821.
46. Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by Chiral Ruthenium(II) Complexes. J. Am. Chem. Soc. 1995, 117, 7562–7563.
47. Shende, V.S.; Deshpande, S.H.; Shingote, S.K.; Joseph, A.; Kelkar, A.A. Asymmetric Transfer Hydrogenation of Imines in Water by Varying the Ratio of Formic Acid to Triethylamine. Org. Lett. 2015, 17, 2878–2881.
48. Shende, V.S.; Shingote, S.K.; Deshpande, S.H.; Kuriakose, N.; Vanka, K.; Kelkar, A.A. Asymmetric transfer hydrogenation of imines in water/methanol co-solvent system and mechanistic investigation by DFT study. RSC Adv. 2014, 4, 46351–46356.
49. Tang, Y.; Li, X.; Lian, C.; Zhu, J.; Deng, J. Synthesis of a water-soluble cationic chiral diamine ligand bearing a diguanidinium and application in asymmetric transfer hydrogenation. Tetrahedron Asymmetry 2011, 22, 1530–1535.
50. Gladiali, S.; Alberico, E. Asymmetric transfer hydrogenation: Chiral ligands and applications. Chem. Soc. Rev. 2006, 35, 226–236.
51. Wienhöfer, G.; Westerhaus, F.A.; Jagadeesh, R.V.; Junge, K.; Junge, H.; Beller, M. Selective iron-catalyzed transfer hydrogenation of terminal alkynes. Chem. Commun. 2012, 48, 4827–4829.
52. Wienhöfer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. General and Selective Iron-Catalyzed Transfer Hydrogenation of Nitroarenes without Base. J. Am. Chem. Soc. 2011, 133, 12875–12879.
53. Renaud, J.-L. Iron Catalysis in Organic Chemistry. Edited by Bernd Plietker. ChemSusChem 2009, 2, 351.
54. Tomar, P.; Nozoe, Y.; Ozawa, N.; Nishimura, S.; Ebitani, K. Formic Acid as a Hydrogen Source for the Additive-Free Reduction of Aromatic Carbonyl and Nitrile Compounds at Reusable Supported Pd Catalysts. Catalysts 2020, 10, 875.
55. Son, P.A.; Nishimura, S.; Ebitani, K. Production of γ-valerolactone from biomass-derived compounds using formic acid as a hydrogen source over supported metal catalysts in water solvent. RSC Adv. 2014, 4, 10525–10530.

56. Choudhary, H.; Nishimura, S.; Ebitani, K. Hydrothermal Preparation of a robust boehmite-supported N,N-dimethyldodecylamine N-oxide-capped cobalt and palladium catalyst for the facile utilization of formic acid as a hy-drogen source. ChemCatChem 2015, 7, 2361–2369.
57. Quinn, J.F.; Bryant, C.E.; Golden, K.C.; Gregg, B.T. Rapid reduction of heteroaromatic nitro groups using catalytic transfer hydrogenation with microwave heating. Tetrahedron Lett. 2010, 51, 786–789.
58. Olofsson, K.; Larhed, M. Microwave-Accelerated Metal Catalysis: Organic Transformations at Warp Speed. ChemInform 2005, 36, 23–43.
59. Quai, M.; Repetto, C.; Barbaglia, W.; Cereda, E. Fast deprotection of phenoxy benzyl ethers in transfer hydrogenation assisted by microwave. Tetrahedron Lett. 2007, 48, 1241.
60. Cini, E.; Petricci, E.; Taddei, M. Pd/C Catalysis under Microwave Dielectric Heating. Catalysts 2017, 7, 89.
61. Conda-Sheridan, M.; Krishnaiah, M. Protecting Groups in Peptide Synthesis. Methods Mol. Biol. 2020, 2103, 111–128.
62. Yamamoto, Y.; Shimizu, E.; Ban, K.; Wada, Y.; Mizusaki, T.; Yoshimura, M.; Takagi, Y.; Sawama, Y.; Sajiki, H. Facile Hydrogenative Deprotection of N-Benzyl Groups Using a Mixed Catalyst of Palladium and Niobic Acid-on-Carbon. ACS Omega 2020, 5, 2699–2709.
63. Elamin, B.; Anantharamaiah, G.M.; Royer, G.P.; Means, G.E. Removal of benzyl-type protect-ing groups from peptides by catalytic transfer hydrogenation with formic acid. J. Org. Chem. 1979, 44, 3442–3444.
64. Bieg, T.; Szeja, W. Removal of O-Benzyl Protective Groups by Catalytic Transfer Hydrogenation. Synthesis 1985, 1985, 76–77.
65. Felix, A.M.; Heimer, E.P.; Lambros, T.J.; Tzougraki, C.; Meienhofer, J. Rapid removal of protecting groups from peptides by catalytic transfer hydrogenation with 1,4-cyclohexadiene. J. Org. Chem. 1978, 43, 4194–4196.
66. Tavor, D.; Sheviev, O.; Dlugy, C.; Wolfson, A. Transfer hydrogenations of benzaldehyde using glycerol as solvent and hydrogen source. Can. J. Chem. 2010, 88, 305–308.
67. Tavor, D.; Gefen, I.; Dlugy, C.; Wolfson, A. Transfer Hydrogenations of Nitrobenzene Using Glycerol as Solvent and Hydrogen Donor. Synth. Commun. 2011, 41, 3409–3416.
68. Wolfson, A.; Dlugy, C.; Shotland, Y.; Tavor, D. Glycerol as solvent and hydrogen donor in transfer hydrogenation–dehydrogenation reactions. Tetrahedron Lett. 2009, 50, 5951–5953.
69. Wang, H.-X.; Toh, W.L.; Tang, B.Y.; Surendranath, Y. Metal surfaces catalyse polarization-dependent hydride transfer from H2. Nat. Catal. 2023, 6, 351–362.

Retrieved from https://encyclopedia.pub/entry/history/show/116326