



Accepted Article

Title: Utilization of Hydrogen Source from Renewable Lignocellulosic Biomass for Hydrogenation of Nitroarenes

Authors: Yang Li, Fang-Fang Tan, Kai-Li Tang, Ping Zhang, Yan-Jun Guo, and Mengnan Qu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemCatChem 10.1002/cctc.201900087

Link to VoR: http://dx.doi.org/10.1002/cctc.201900087



WILEY-VCH

www.chemcatchem.org

FULL PAPER

Utilization of Hydrogen Source from Renewable Lignocellulosic Biomass for Hydrogenation of Nitroarenes

Fang-Fang Tan,^[a] Kai-Li Tang,^[a,b] Ping Zhang,^[a,c] Yan-Jun Guo,^[a] Mengnan Qu,^[b] and Yang Li*^[a,d]

Abstract: Exploring of hydrogen source from renewable biomass, such as glucose in alkaline solution, for hydrogenation reactions had been studied since 1860s. According to proposed pathway, only small part of hydrogen source in glucose was utilized. Herein, an utilization of hydrogen source from renewable lignocellulosic biomass, one of the most abundant renewable source in nature, for a hydrogenation reaction is described. The hydrogenation is demonstrated by reduction of nitroarenes to arylamines in up to 95% yields. Mechanism studies suggest that the hydrogenation occurs via a hydrogen transformation pathway.

Introduction

An increased application of renewables is predicted in the coming decades.^[1] Hydrogenation reactions act as one of important fundamental research directions in the manufacture of bulk and fine chemicals.^[2] Hitherto hydrogen (H₂), most of which produced by reforming or pyrolysis of the non-renewable fossil resource including coal, natural gas, and oil at about 450-1315 °C, is the widely used hydrogen source for hydrogenation reactions. (Figure 1A).^[2,3] On the other hand, the combinations of protons with hydride reagents or electron donors, and other in-situ generated hydrogen sources by hydrogen transformation were also well developed (Figure 1B).^[2,4-6] Exploring of hydrogen source from renewable resource for direct hydrogenation reactions, such as glucose in alkaline solution, had been studied since 1860s (Figure 1C).^[7a] In these reactions, more than stoichiometric amounts of glucose and base were required.^[7] According to proposed pathway, only small part of hydrogen source in glucose was utilized.^[7e,7g] In addition, glucose production always relied on the hydrolysis of food-related biomass.^[8] Production of glucose from non-food biomass has been reported. But low efficiency and

[a]	FF. Tan, KL. Tang, Prof. P. Zhang, YJ. Guo and Prof. Y. Li
	Center for Organic Chemistry of Frontier Institute of Science and
	Technology and State Key Laboratory for Mechanical Behavior of
	Materials
	Xi'an Jiaotong University
	Shaanxi, 710054 (China)
	E-mail: liyang79@mail.xjtu.edu.cn
[b]	KL. Tang and Prof. M. Qu
	College of Chemistry and Chemical Engineering
	Xi'an University of Science and Technology
	Xi'an, Shaanxi, 710054, China
[c]	Prof. P. Zhang
	College of Chemistry and Chemical Engineering
	Xianyang Normal University
	Xianyang, Shaanxi, 712000, China
[d]	Prof. Y. Li
	Beijing National Laboratory for Molecular Sciences
	Beijing 100190, China
	Supporting information for this article is given via a link at the end of the document.

harsh conditions needs to be overcomed.^[9] In addition, the hydrogen source indirectly from renewable source for hydrogenation reactions, such as bioethanol and glycerol,^[10,11] were also investigated (Figure 1C). In the case of bioethanol, most of it is produced from edible biomass by fermentation, which causes a competition with food naturally. Although bioethanol was generated from non-edible biomass, its production is still in its infancy.^[12] Glycerol is generated as a by-product during the manufacture of biodiesel from renewable sources.^[13] In most cases, more than stoichiometric base were required during the hydrogenation.^[11] Thus, there is a strong incentive to develop various alternative renewable hydrogen source for hydrogenation organic reactions, such as non-food lignocellulosic biomass, one of the most abundant renewable source in nature.^[14]



Figure 1. Various [H] sources for hydrogenation reactions.

Very recently, we developed a streamlined H₂ production from biomass in up to 95% yields via a one-pot, two-step route in aqueous media.^[15] During the first step, the hydrogen source from the wheat straw was transformed into formic acid (FA) in up to quantitive yield, even in near 10-gram scale. The calculation of the yield is based on the carbon content of the cellulose and hemicellulose in the wheat straw, considering that each carbon atom can be transformed to one molecular HCO₂H. The transformation was applied air/oxygen (3-5 MPa) as oxidant with sodium metavanadate (NaVO₃, 4 mol%) as catalyst in 1v% DMSO and 0.7 wt% H₂SO₄ aqueous phase at 160 °C. On the other hand, industrial production of FA is mainly produced by the hydrolysis of methyl formate and the acidolysis of formates with sulfuric acid or phosphoric acid in this stage.^[16] These intermediates of methyl formate and formates are prepared by applying carbon monoxide and methanol or alkali hydroxide as starting materials under high carbon monoxide pressure.^[16a] The process consists of complicated multistep with consumption of a large amount of energy. More importantly, toxic carbon monoxide is normally produced in an unsustainable way from coal or natural gas by gasification at very high temperatures (>900 K).^[16a] The sustainable production of FA from biomass has also been developed by hydrolysis or hydrolysis-oxidation of biomass and biomass-derived products.^[16b] In the case of the hydrolysis, only one molecular HCO₂H can be obtained from one molecular glucose in principle based on FA and levulinic acid as the hydrolysis products.^[17] For the oxidation of primary biomass of glucose or saccharides, up to 85% yields FA or formate was obtained.^[18] However, large amount of 1-hexanol (100 g of 1hexanol/1.80 g glucose) or excessive NaOH with more than

FULL PAPER

stoichiometric H₂O₂ were required.^[18c,18d] And for the hydrolysisoxidation of complex biomass of cellulose, the FA yields always were obtained below 70%.^[18,19] Other promising catalyst systems for the extremely demanding raw biomass hydrolysis-oxidation, such as HPA-5 (H₈PV₅Mo₇O₄₀) in the presence of *p*-TSA (paratoluenesulfonic acid) and 1-hexanol, [18c, 18e, 19f] HPA-5 promoted with HCl,^[18b] and VOSO₄ in the presence of EtOH,^[19b] were investigated for the FA production.^[15]Our developed 1 v% DMSO promoted NaVO₃/H₂SO₄ hydrolysis-oxidation catalysis system displayed the best FA yield.^[15] As FA is a stable and non-toxic H₂ storage material, and conveniently releases H₂ on demand.^[20] Based on these considerations, we envisioned that the feasibility of the utilization of hydrogen source from lignocellulosic biomass for hydrogenation reactions (Figure 1D). Although cellulose material was applied in the reduction of metal ions to nanometals, the function of cellulose was proposed as electron donors.^[21] To the best of our knowledge, utilization of renewable lignocellulosic biomass as a hydrogen source for hydrogenation reactions has not been reported.

Arylamines are the key intermediates of nitrogen-containing biologically active compounds, agrochemicals, dyes, polymers, etc.^[22,23] Hydrogenation of nitroarenes is one of the most classic methods for preparation of arylamines by utilization of H₂^[23,24] and other hydrogen sources as mentioned above.^[2,4-7,10-11] Herein, we report an utilization of hydrogen source from renewable lignocellulosic biomass, one of the most abundant renewable source in nature, for a hydrogenation reaction. The hydrogenation is demonstrated by reduction of nitroarenes to corresponding arylamines (Scheme 1). Specifically, the lignocellulosic biomass hydrolysis-oxidation aqueous solution (HOAS) contained FA as a major component was employed for the hydrogenation. Thus, the complex purification procedure of FA from the HOAS mainly caused by the azeotrope of FA with water [16] would be avoided. Notably, applying FA instead of the lingocellulosic HOAS resulted in obviously decreased yield.

Scheme 1. Hydrogenation of nitroarenes by [H] source from lignocellulosic biomass

Results and Discussion

Initially, the wheat straw HOAS was applied as hydrogen source for the reduction of 4-methylnitrobenzene (1a) to 4-methylaniline (2a) at 120 °C under 10 bar argon atmosphere. Besides of the major component of FA in the wheat straw HOAS, [V] (4 mol%), DMSO (7 mol%), DMSO₂ (8 mol%), 1,4- dioxane (13 mol%), HOAc (7 mol%), MeOH (2 mol%) and Na₂SO₄ (12 mol%) were also contained.^[15] Meanwhile, some residues from degradation of lignin in wheat straw were also introduced to the reaction accompanying with the addition of the HOAS. DMF was added as an extra solvent to increase the intersolubility of the nitroarenes and FA in the wheat straw HOAS. To avoid the volatilization of FA at 120 °C, compressed argon was charged. The iridium catalyst

WILEY-VCH



Table 1. Optimization of the reaction conditions.

[a] Reaction conditions: 1a (0.5 mmol), [Ir/Ru/Pd] (2 mol%), DMF (0.5 mL), the wheat straw HOAS [contained 4.5 equiv of FA, 3.95 mL, based on the 95% yield of FA, [V] (4 mol%), DMSO (7 mol%), DMSO₂ (8 mol%), 1,4-dioxane (13 mol%), HOAc (7 mol%), MeOH (2 mol%) and Na_2SO_4 (12 mol%)] with the pH value of 2.25, $^{[15]}$ 120 °C, 24 h, Ar (10 bar). [b] Yields were determined by ^1H NMR using Cl₂CHCHCl₂ as an internal standard. [c] [IrCl(coe)₂]₂ (0.5 mol%). [d] [IrCl(coe)₂]₂ (0.1 mol%). [e] 100 °C. [f] 5 bar Ar. [g] 1 atm Ar. [h] 18 h. [i] 15 h. [j] no wheat straw HOAS.

DMF

FULL PAPER

containing the ligands of Cp* and 2,4-dihydoxypyrimidine connected with an imidazolin moiety (3a)[25] was selected as the catalyst as its excellent performance during the hydrogen production from the wheat straw HOAS^[15] (Table 1, entry 1). However, only 32% yield of 2a was obtained. Other iridium catalysts were investigated further. Iridium catalysts containing Cp* and various N,N-ligands, such as 2,4-dihydoxypyrimidine connected with a pyrazole moiety in 3b, [25] 2,2'-biimiazolin in 3c[15] and 3d^[26], 2,2',6,6'-tetrahydroxy-4,4'-bipyrimidine in 3e^[27] and 4,4'-dihydoxy-2,2'-bipyridine in 3f^[27] were investigated. Similar with the performance of catalyst 3a, no more than 33% yields of 2a were obtained (Table 1, entries 2-6). Then the iridium catalyst bearing with Cp* and C,N- ligand of 4-(1H-pyrazol-1-yl)benzoic acid in 3g^[28], the iridium catalysts bearing with the pincer ligand $\{PNP = HN[CH_2CH_2(PR_2)_2], R = i Pr\}$ in **3h**^[29] and *N*-heterocyclic carbene ligand in 3i^[30] resulted even lower yields (Table 1, entries 7-9). To our delight, commercially available [IrCl(cod)]₂ and [IrCl(coe)₂]₂ resulted in 73% and 92% vields, respectively (Table 1, entries 10-11). When the loading of [IrCl(coe)₂]₂ was decreased to 0.5 mol%, 92% yield was still remained (Table 1, entry 12). DMF obviously promoted the transformation in comparison with only 55% vield of 2a in the absence of it (Table 1, entry 14). Other water soluble solvents were investigated (Table 1, entries 15-18). 1.4-Dioxane and methanol increased the reaction efficiency to some extent (Table 1, entries 16 and 18). THF and acetonitrile obviously decreased the reaction yields (Table 1, entries 15 and 17). When the reaction was conducted at 100 °C, the reaction yield decreased to 62% (Table 1, entry 19). The argon pressure could be reduced to 5 bar and the reaction time could be shortened to 18 h without influence on the reaction efficiency (Table 1, entries 20-23). RuHCl(PPh₃)₃ was selected as an example of ruthenium catalyst to afford 2a in 27% yield (Table 1,

Table 2. Investigation of var	ous lignocellulosic biomass HOAS.
-------------------------------	-----------------------------------

la	NO ₂ lignocellulosic biomass HOAS [IrCl(coe) ₂] ₂ (0.5 mol%) DMF, 120 °C, Ar (5 bar), 24 h	NH ₂
entry	lignocellulosic biomass HOAS	yield(%) ^[b]
1	wheat straw HOAS	92
2	corn straw HOAS	77
3	rice straw HOAS	81
4	reed HOAS	76
5	bagasse HOAS	80
6	bamboo sawdust HOAS	91
7	cardboard HOAS	91
8	newspaper HOAS	90
9 ^[c]	wheat straw HOAS	92
10 ^[d]	wheat straw HOAS	68
11 ^[e]	wheat straw HOAS	85

[a] Reaction conditions: **1a** (0.5 mmol), [IrCl(coe)₂]₂ (0.5 mol%), DMF (0.50 mL), various biomass HOAS contained 4.5 equiv of FA with the pH value of 2.25, 120 °C, 24 h, Ar (5 bar). [b] ¹H NMR yield was reported using Cl₂CHCHCl₂ as an internal standard. [c] Wheat straw HOAS contained 4.0 equiv of FA. [d] Wheat straw HOAS contained 3.5 equiv of FA. [e] Wheat straw HOAS contained 4.0 equiv of FA with the pH value of 0.93, which was not treated with NaOH (10 M, 0.46 mL) to neutralize the existed catalytic H₂SO₄ in hydrolysis-oxidation step.^[15]

entry 24). The benchmark of heterogeneous catalyst Pd/C in the decomposition of FA^[31] resulted in 30% yield of **2a** (Table 1, entry 25). Without catalyst and the wheat straw HOAS, no product was detected (Table 1, entries 26 and 27).

Next, various lignocellulosic biomass HOAS were investigated (Table 2). Besides of wheat straw HOAS, the HOAS of bamboo sawdust, waste cardboard and newspaper displayed the excellent reaction efficiency (Table 2, entries 6-8, 90-91%). The HOAS of corn straw, rice straw, reed, and bagasse resulted in 76-81% yields (Table 2, entries 2-5). Furthermore, the amounts of wheat straw HOAS was investigated. It was found that wheat straw contained 4.0 equiv of FA was enough to give the excellent reaction efficiency (Table 2, entry 9). Notably, without treatment of the HOAS with NaOH for neutralization of the existed catalytic H_2SO_4 in hydrolysis-oxidation of biomass,^[15] 85% yield of **2a** was obtained (Table 2, entry 11).

Table 3. Substrate scope.^[a]



[a] Reaction conditions: **1** (0.5 mmol), [IrCl(coe)₂]₂ (0.5 mol%), DMF (0.50 mL), wheat straw HOAS contained 4.0 equiv of FA with the pH value of 2.25, 120 °C, Ar (5 bar), 24 h, isolate yields were reported; [b] 18 h; [c] 12 h. [d] (6-nitrobenzo[d][1,3]dioxol-5-yl)methanol **2A'** was obtained in 30% yield.

With the optimized reaction conditions in hand, the substrate scope was investigated (Table 3). First, the nitroarenes bearing

2a

FULL PAPER

with various electron-donating groups and electron-withdrawing groups on the para-position of the phenyl rings were studied (Table 3, 2a-k). Methyl-, methoxy-, sulphonamide-, methyl ester-, bromo-, chloro-, fluoro-substituted nitroarenes and nitrobenzene lead to excellent reaction efficiencies (2a-b, 2e-f, 2i-k, 2d, 80-95%). Free hydroxyl and cyano resulted in high yields (2c, 75%, 2g, 81%). Notably, active iodo was well tolerated (2h, 65%). Second, methoxy, methyl ester and chloro were selected as examples of electron-donating groups and electron-withdrawing groups on ortho- and meta-positions. Similar high reaction efficiencies were observed (21-p, 78-93%). The nitroarene bearing with two electron-donating groups of methyl and aminyl afforded 2q in 81% yield. Nitroarenes bearing with one electrondonating group and one electron-withdrawing group gave the corresponding arylamines in 74-91% yields (2r-u). The nitroarenes bearing with bromo and trifluoromethyloxy or trifluoromethyl afforded 2v and 2w in 86% and 80% yields, respectively. The influence of di-substituted electron-withdrawing groups was also investigated. Fluoro with chloro, chloro with bromo, and two cyanos resulted in the corresponding aryl amines 73-79% vields (2x-z). 6-Nitrobenzo[d][1.3]dioxole-5in carbaldehyde was selected as an example of tri-substituted substrate. The desired product 2A was obtained in 33% yield. The by-product (6-nitrobenzo[d][1,3]dioxol-5-yl)methanol 2A' was obtained in 30% vield, in which the aldehvde group was reduced instead of the nitro group. 9H-Fluoren-2-amine was obtained in excellent yield (2B, 93%). The nitro-substituted indole, guinolone and isoquinolines resulted in 67-82% yields (2C-E). Substituted nitropyridines with methoxyl, bromo, chloro and di-chloro resulted in high reaction efficiency (2F-I, 79-95%).

To demonstrate the potential application, gram-scale hydrogenation of **1a** by applying wheat straw HOAS produced from 1.6 g of wheat straw afforded **2a** in 82% isolated yield (Scheme 2). Notably, the catalyst loading of $[IrCl(coe)_2]_2$ could be decreased to 0.2 mol%.

wheat straw HOAS (produced by 1.6 g wheat straw) 2a [IrCl(coe)₂]₂ (0.2 mol%) 82% (74%)^[a] DMF, 120 °C, Ar (5 bar), 24 h 82% (74%)^[a]

To gain insight into the reduction of nitroarenes, a series of experiments were conducted. As the major active component for the hydrogenation in the wheat straw was considered as FA, thus FA was used instead to undergo the hydrogenation. However, the obvious decreased reaction efficiency was observed as only 65% yield in comparison with 92% yield under the optimized conditions (Table 4, entry 1). Thus, this phenomenon was detected by hydrogenation of **1a** with FA in the presence of other each component contained in wheat straw HOAS, respectively. The presence of Na₂SO₄, 1,4-dioxane, DMSO, HOAc, MeOH and DMSO₂ did not cause distinct influence on the reaction yields (Table 4, entries 2-7). The same reaction efficiency with the standard reaction was observed by the combination of FA and NaVO₃ (Table 4, entry 8). Thus, the higher reaction efficiency of the wheat straw HOAS than FA should attribute to the presence

of NaVO₃. Although the increased pH value of the reaction media with NaVO₃ was detected, the high reaction efficiency should not be caused by it as 92% and 85% yields of **2a** with pH value of 2.25 and 0.93 were obtained, respectively (Table 2, entries 9 and 11). Furthermore, it was found that V(V) was reduced to V(IV) after the hydrogenation reaction (Figure S1).

Table 4. Control experiment.

1a	+	FA	[IrCl(coe) ₂] ₂ (0.5 mol%)	
			DMF (0.5 mL), H ₂ O, additives	
			120 °C. Ar (5 bar). 24 h	

entry ^[a]	additives	pН	yield [%] ^[b]
1	-	1.86	65
2	Na ₂ SO ₄	2.00	64
3	1,4-dioxane	1.85	68
4	DMSO	1.86	64
5	HOAc	1.84	62
6	MeOH	1.85	60
7	DMSO ₂	1.84	66
8	NaVO ₃	2.16	92
9	all the above additives	2.25	92

[a] Reaction conditions: **1a** (0.5 mmol), FA (4 equiv), H₂O (3.51 mL), DMF (0.50 mL), 120 °C, Ar (5 bar), 24 h, additives: Na₂SO₄ (12 mol%, 8.5 mg), 1,4-dioxane (13 mol%, 5.5 μ L), DMSO (7 mol%, 2.5 μ L), HOAc (7 mol%, 2.0 μ L), MeOH (2 mol%, 0.4 μ L), DMSO₂ (8 mol%, 3.8 mg), NaVO₃ (4 mol%, 2.4 mg).^[15] [b] Determined by ¹H NMR using Cl₂CHCHCl₂ as an internal standard.

On the other hand, the decomposition of FA contained in the wheat straw HOAS under hydrogenation conditions was detected. In the absence of **1a**, 3.8 equiv of FA was remained in 12 h with less than 1% H₂ production. The lost FA should be caused by its volatilization at 120 °C. Meanwhile, 0.8 equiv of FA remained under the standard reaction conditions (Figure 2a). These results indicate that the hydrogenation of nitroarenes occurs via a hydrogen transformation pathway. At the same time, the transformation of **1a** to **2a** was monitored (Figure 2b). Besides the starting material **1a** and the desired product **2a**, intermediate **4a**, a condensation product of **2a** with FA, was generated. It was observed that the amount of **4a** was increased during the initial 5 h and decreased after that. This tendency should be attributed to an equilibrium among **2a**, FA and **4a**.



Figure 2. (a) The remaining FA-time profile with 1a and without of 1a. For the details, see Table S3 and S4. (b) Monitoring of the standard reaction. For the details, see Table S5.

In addition, reduction of nitrosobenzene (5d), Nphenylhydroxylamine (6d), 1,2-diphenyldiazene (7d) or 1,2diphenylhydrazine (8d) under optimized conditions afforded 2d in

ChemCatChem

FULL PAPER

moderate yields, respectively (Scheme 3, eqs. 1-4). These experiments indicate that they are possible intermediates.

Ph=NO(5d)	optimized	conditions	2d (46%)	(ea	1)
FIT NO (34)			2u (40 /0)	(09.	•/
Ph-NHOH (6d)	optimized	conditions	2d (55%)	(eq.	2)
Ph-N=N-Ph (7d)	optimized	conditions	2d (38%)	(eq.	3)
H H Ph-N-N-Ph (8d)	optimized	conditions	2d ((45%)	(eq.	4)

Scheme 3. Hydrogenation of possible intermediates.

Based on these experiments, a possible reaction pathway is proposed as shown in Figure 3. Nitroarene (1) is hydrogenated to nitrosoarene (5) by the iridium hydride complex and proton with release of one molecular water.^[6d,23] Then a sequent hydrogenation of 5 leads to hydroxylamine (6), which undergoes a followed hydrogenation with release of the second water to afford the desired arylamine (2, Path A). An equilibrium is existed between 2 and the condensation intermediate 4. The reaction pathway via the condensation of 5 and 6 could not be ruled out (Path B). The condensation product 9 undergoes three times hydrogenation to afford 2 via 7 and 8 in sequence.



Figure 3. Proposed reaction pathways.

Conclusions

In summary, we have developed an utilization of hydrogen source from renewable lignocellulosic biomass for a hydrogenation reaction, which is application to reduction of nitroarenes to arylamines. Catalyzed by commercially available iridium catalyst [IrCl(coe)₂]₂ with no more than 0.5 mol% catalyst loading, various arylamines up to 95% yields were obtained. Mechanism studies suggest that the hydrogenation occurs via a hydrogen transformation pathway. It would inspire utilization of lignocellulosic biomass as a hydrogen source to various hydrogenation reactions for the manufacture of bulk and fine chemicals.

Acknowledgements

This work was supported by the NSFC (Nos. 21472145), the Beijing National Laboratory for Molecular Sciences (BNLMS, BNLMS20160111) and the Instrument Analysis Center of the Xi'an Jiaotong University.

Keywords: renewable • hydrogen source • lignocellulosic biomass • hydrogenation • nitroarenes

- O. Ellabban, H. Abu-Rub, F. Blaabjerg, *Renew. Sust. Energy Rev.* 2014, 39, 748-764.
- [2] a) S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley-Interscience, New York, 2001; b) J. G. de Vries, C. J. Elsevier, The Handbook of Homogeneous Hydrogenation, Wiley-VCH, Weinheim, 2007.
- [3] P. Nikolaidis, A. Poullikkas, *Renew. Sust. Energy Rev.* 2017, 67, 597-611.
- [4] For selected samples of reduction by the combination of proton with hydride reagents, see: a) H. Zhao, Y. Wang, R. Wang, *Chem. Commun.* 2014, *50*, 10871-10874; b) M. Shah, Q.-X. Guo, Y. Fu, *Catal. Commun.* 2015, *65*, 85-90; c) A. Liu, C. H. H. Traulsen, J. J. L. M. Cornelissen, *ACS Catal.* 2016, *6*, 3084-3091.
- [5] For selected samples reduction by the combination of proton with electron donors, see: a) R. Ma, A.-H. Liu, C.-B. Huang, X.-D. Li, L.-N. He, *Green Chem.* 2013, *15*, 1274-1279; b) X.-J. Yang, B. Chen, L.-Q. Zheng, L.-Z. Wu, C.-H. Tung, *Green Chem.* 2014, *16*, 1082-1086; c) B. Zhou, J. Song, H. Zhou, T. Wu, B. Han, *Chem. Sci.* 2016, *7*, 463-468; for the selected review, see: d) B. Qiao, Z. Jiang, *ChemPhotoChem* 2018, *2*, 703-714.
- [6] For selected samples of reduction by hydrogen transformation, see: a) H. Imai, T. Nishiguchi, K. Fukuzumi, *Chem. Lett.* **1976**, *5*, 655-656; b) M. Coellen, C. Rüchardt, *Chem. Eur. J.* **1995**, *1*, 564-567; c) L. He, L.-C. Wang, H. Sun, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem.* **2009**, 121, 9702-9705; *Angew. Chem. Int. Ed.* **2009**, *48*, 9538-9541; d) G. Wienhofer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar, M. Beller, *J. Am. Chem. Soc.* **2011**, *133*, 12875-12879; e) D. Cantillo, M. Baghbanzadeh, C. O. Kappe, *Angew. Chem.* **2012**, *124*, 10337-10340; *Angew. Chem. Int. Ed.* **2012**, *51*, 10190-10193; f) S. Hohloch, L. Suntrup, B. Sarkar, *Organometallics* **2013**, *32*, 7376-7385; g) R. Maity, M. Meer, S. Hohloch, B. Sarkar, *Organometallics* **2015**, *34*, 3090–3096; for selected reviews, see: h) J. S. Samec, J. E. Backvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237-248; i) A. Corma, J. Navas, M. J. Sabater, *Chem. Rev.* **2018**, *118*, 1410-1459.
- [7] For selected samples, see: a) C. D. Braun, J. Prakt. Chem. 1865, 96, 411-414; b) G. Bacharach, R. Weinstein, Rec. Trav. Chim. Pays-Bas 1935, 54, 931-933; c) N. Opolonick, Ind. Eng. Chem. 1935, 27, 1045-1046; d) H. W. Galbraith, E. F. Degering, E. F. Hitch, J. Am. Chem. Soc. 1951, 73, 1323-1324; e) A. V. Ellis, M. A. Wilson, J. Org. Chem. 2002, 67, 8469-8474; f) M. Kumar, U. Sharma, S. Sharma, V. Kumar, B. Singh, N. Kumar, RSC Adv. 2013, 3, 4894-4898; g) N. Chandna, F. Kaur, S. Kumar, N. Jain, Green Chem. 2017, 19, 4268-4271.
- [8] For selected samples, see: a) L. Kunlan, X. Lixin, L. Jun, P. Jun, C. Guoying, X. Zuwei, *Carbohydr. Res.* 2001, 331, 9-12; b) M. Nagamori, T. Funazukuri, *J. Chem. Technol. Biotechnol.* 2004, 79, 229-233; for the selected review, see: c) K. Buchholz, J. Seibel, *Carbohydr. Res.* 2008, 343, 1966-1979.
- [9] For selected samples, see: a) A. Onda, T. Ochi, K. Yanagisawa, Green Chem. 2008, 10, 1033-1037; b) S. Morales-DelaRosa, J. M. Campos-Martin, J. L. G. Fierro, Catal. Today 2018, 302, 87-93; for selected reviews, see: c) Y. B. Huang, Y. Fu, Green Chem. 2013, 15, 1095-1111; d) J. Wang, J. Xi, Y. Wang, Green Chem. 2015, 17, 737-751.
- [10] For selected samples, see: a) T. Zweifel, J. V. Naubron, T. Buttner, T. Ott, H. Grutzmacher, *Angew. Chem.* 2008, *120*, 3289-3293; *Angew. Chem. Int. Ed.* 2008, *47*, 3245-3249; b) M. Pietrowski, *Green Chem.* 2011, *13*, 1633-1635; c) J. H. Park, S. M. Kim, Y. K. Chung, *Chem. Eur. J.* 2011, *17*, 10852-10856.
- [11] For selected samples, see: a) A. Azua, J. A. Mata, E. Peris, Organometallics 2011, 30, 5532-5536; b) M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. Ghumman, N. Bundaleski, O. M. Teodoro, Chem.

WILEY-VCH

FULL PAPER

Eur. J. 2012, *18*, 12628-12632; c) A. Azua, J. A. Mata, E. Peris, F. Lamaty, J. Martinez, E. Colacino, *Organometallics* 2012, *31*, 3911-3919;
d) O. Prakash, H. Joshi, K. N. Sharma, P. L. Gupta, A. K. Singh, *Organometallics* 2014, *33*, 3804-3812; e) X. Dai, X. Cui, H. Yuan, Y. Deng, F. Shi, *RSC Adv.* 2015, *5*, 7970-7975.

- [12] Y. Zhao, A. Damgaard, T. H. Christensen, Prog. Energy Combust. Sci. 2018, 67, 275-291.
- [13] M. R. Monteiro, C. L. Kugelmeier, R. S. Pinheiro, M. O. Batalha, A. da Silva César, *Renew. Sust. Energy Rev.* 2018, *88*, 109-122.
- [14] For selected reviews, see: a) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 2006, *106*, 4044-4098; b) S. N. Reddy, S. Nanda, A. K. Dalai, J. A. Kozinski, *Int. J. Hydrogen Energy* 2014, *39*, 6912-6926; c) V. S. Sikarwar, M. Zhao, P. Clough, J. Yao, X. Zhong, M. Z. Memon, N. Shah, E. J. Anthony, P. S. Fennell, *Energy Environ. Sci.* 2016, *9*, 2939-2977; d) T. Kan, V. Strezov, T. J. Evans, *Renew. Sust. Energy Rev.* 2016, *57*, 1126-1140.
- [15] P. Zhang, Y.-J. Guo, J. Chen, Y.-R. Zhao, J. Chang, H. Junge, M. Beller, Y. Li, *Nat. Catal.* **2018**, *1*, 332-338.
- [16] For selected reviews, see: a) J. Hietala, A. Vuori, P. Johnsson, I.Pollari, W. Reutemann, H.Kieczka in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, **2016**; b) D. A. Bulushev, J. R. H. Ross, *ChemSusChem* **2018**, *11*, 821-836.
- [17] For selected samples, see: a) V. E. Tarabanko, M. Y. Chernyak, S. V. Aralova, B. N. Kuznetsov, *React. Kinet. Catal. Lett.* 2002, *75*, 117-126; b) J. Ahlkvist, S. Ajaikumar, W. Larsson, J. P. Mikkola, *Appl. Catal. A* 2013, *454*, 21-29; c) S. S. Joshi, A. D. Zodge, K. V. Pandare, B. D. Kulkarni, *Ind. Eng. Chem. Res.* 2014, *53*, 18796-18805; d) J. Ahlkvist, J. Wärnå, T. Salmi, J.-P. Mikkola, *Reaction Kinetics, Mech. Catal.* 2016, *119*, 415-427; e) T. Flannelly, M. Lopes, L. Kupiainen, S. Dooley, J. J. Leahy, *RSC Adv.* 2016, *6*, 5797-5804.
- [18] For selected samples, see: a) F. Jin, J. Yun, G. Li, A. Kishita, K. Tohji, H. Enomoto, *Green Chem.* 2008, *10*, 612-615; b) J. Li, D. J. Ding, L. Deng, Q. X. Guo, Y. Fu, *ChemSusChem* 2012, *5*, 1313-1318; c) J. Reichert, B. Brunner, A. Jess, P. Wasserscheid, J. Albert, *Energy Environ. Sci.* 2015, *8*, 2985-2990; d) J. Yun, G.-D. Yao, F.-M. Jin, H. Zhong, A. Kishita, K. Tohji, H. Enomoto, L. Wang, *AIChE J.* 2016, *62*, 3657-3663; e) J. Reichert, J. Albert, *ACS Sustainable Chem. Eng.* 2017, *5*, 7383-7392.
- [19] For selected samples, see: a) J. Albert, R. Wolfel, A. Bosmann, P. Wasserscheid, *Energy Environ. Sci.* 2012, *5*, 7956-7962; b) Z.-C. Tang, W.-P. Deng, Y.-L. Wang, E.-Z. Zhu, X.-Y. Wan, Q.-H. Zhang, Y. Wang, *ChemSusChem* 2014, *7*, 1557-1567; c) W.-H. Wang, M.-G. Niu, Y.-C. Hou, W.-Z. Wu, Z.-Y. Liu, Q.-Y. Liu, S.-H. Ren, K.-N. Marsh, *Green Chem.* 2014, *16*, 2614-2618; d) J. Zhang, M. Sun, X. Liu, Y. Han, *Catal. Today* 2014, 233, 77-82; e) J. Albert, P. Wasserscheid, *Green Chem.* 2015, *17*, 5164-5171; f) J. Albert, A. Jess, C. Kern, F. Pöhlmann, K. Glowienka, P. Wasserscheid, *ACS Sustainable Chem. Eng.* 2016, *4*, 5078-5086; g) N. V. Gromov, O. P. Taran, I. V. Delidovich, A. V. Pestunov, Y. A. Rodikova, D. A. Yatsenko, E. G. Zhizhina, V. N. Parmon, *Catal. Today* 2016, *278*, 74-81; h) T. Lu, M. Niu, Y. Hou, W. Wu, S. Ren, F. Yang, *Green Chem.* 2016, *18*, 4725-4732; i) Q. Liu, D. Zhou, Z. Li, W. Luo, C. Guo, *Chin. J. Chem.* 2017, *35*, 1063-1068.
- [20] For selected reviews, see: a) M. Grasemann, G. Laurenczy, *Energy Environ. Sci.* 2012, 5, 8171-8181; b) Q.-L. Zhu, Q. Xu, *Energy Environ. Sci.* 2015, *8*, 478-512; c) D. Mellmann, P. Sponholz, H. Junge, M. Beller, *Chem. Soc. Rev.* 2016, *45*, 3954-3988; d) J. Eppinger, K. W. Huang, *ACS Energy Lett.* 2017, *2*, 188-195; e) K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* 2018, *118*, 372-433.

- [21] For selected samples, see: a) J. L. T. Hage, M. A. Reuter, R. D. Schuiling, I. S. Ramtahalsing, *Miner. Eng.* **1999**, *12*, 393-404; b) Y. Shin, I. T. Bae, B. W. Arey, G. J. Exarhos, *Mater. Lett.* **2007**, *61*, 3215-3217; c) L. Johnson, W. Thielemans, D. A. Walsh, *Green Chem.* **2011**, *13*, 1686-1693; d) X.-D. Wu, C.-H. Lu, Z.-H. Zhou, G.-P. Yuan, R. Xiong, X.-X. Zhang, *Environ. Sci.: Nano.* **2014**, *1*, 71-79; e) M. Rezayat, R. K. Blundell, J. E. Camp, D. A. Walsh, W. Thielemans, *ACS Sustainable Chem. Eng.* **2014**, *2*, 1241-1250; f) L.-H. Fu, F. Deng, M.-G. Ma, J. Yang, *RSC Adv.* **2016**, *6*, 28140-28148; for the selected review, see: g) M. Kaushik, A. Moores, *Green Chem.* **2016**, *18*, 622-637.
- [22] N. Ono, The Nitro Group in Organic Synthesis; Wiley-VCH, New York, 2001.
- [23] For selected reviews of hydrogenation of nitroarenes, see: a) H. K. Kadam, S. G. Tilve, RSC Adv. 2015, 5, 83391-83407; b) J. Song, Z.-F. Huang, L. Pan, K. Li, X. Zhang, L. Wang, J.-J. Zou, Appl. Catal. B 2018, 227, 386-408.
- For selected samples, see: a) R. V. Jagadeesh, A. E. Surkus, H. Junge, [24] M. M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schunemann, A. Bruckner, M. Beller, Science 2013, 342, 1073-1076; b) F. A. Westerhaus, R. V. Jagadeesh, G. Wienhofer, M. M. Pohl, J. Radnik, A. E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Bruckner, M. Beller, Nat. Chem. 2013, 5, 537-543; c) H. Wei, X. Liu, A. Wang, L. Zhang, B. Qiao, X. Yang, Y. Huang, S. Miao, J. Liu, T. Zhang, Nat. Commun. 2014, 5, 5634-5641; d) R. V. Jagadeesh, T. Stemmler, A. E. Surkus, H. Junge, K. Junge, M. Beller, Nat. Protoc. 2015, 10, 548-557; e) T. Schwob, R. Kempe, Angew. Chem. 2016, 128, 15400-15404; Angew. Chem. Int. Ed. 2016, 55, 15175-15179; f) P. Ji, K. Manna, Z. Lin, X. Feng, A. Urban, Y. Song, W. Lin, J. Am. Chem. Soc. 2017, 139, 7004-7011; g) Y. Tan, X.-Y. Liu, L. Zhang, A. Wang, L. Li, X. Pan, S. Miao, M. Haruta, H. Wei, H. Wang, F. Wang, X. Wang, T. Zhang, Angew. Chem. 2017, 129, 2753-2757; Angew. Chem. Int. Ed. 2017, 56, 2709-2713; h) P. Zhou, L. Jiang, F. Wang, K. Deng, K. Lv, Z. Zhang, Sci. Adv. 2017, 3, e1601945.
- [25] W.-H. Wang, M.-Z. Ertem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, ACS Catal. 2015, 5, 5496-5504.
- [26] Z. Wang, S.-M. Lu, J. Li, J. Wang, C. Li, Chem. Eur. J. 2015, 21, 12592-12595.
- [27] W.-H. Wang, S. Xu, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, *ChemSusChem* 2014, 7, 1976-1983.
- [28] Y. Maenaka, T. Suenobu, S. Fukuzumi, *Energy Environ. Sci.* 2012, 5, 7360-7367.
- [29] Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough, K. Abdur-Rashid, Organometallics 2006, 25, 4113-4117.
- [30] M. G. Manas, L. S. Sharninghausen, E. Lin, R. H. Crabtree, J. Organomet. Chem. 2015, 792, 184-189.
- [31] For the selected sample, see: a) F. Sanchez, D. Motta, A. Roldan, C. Hammond, A. Villa, N. Dimitratos, *Top Catal.* 2018, *61*, 254-266; for the selected review, see: b) H. Zhong, M. Iguchi, M. Chatterjee, Y. Himeda, Q. Xu, H. Kawanami, *Adv. Sustainable Syst.* 2018, *2*, 1700161.

WILEY-VCH

FULL PAPER

wheat straw HOAS NH₂ 102 [IrCl(coe)₂]₂ (0.2-0.5 mol%) R DMF, 120 °C, Ar (5 bar), 12-24 h 35 examples, up to 95% yields

• [H] from renewable lignocellulosic biomass • gram-scale reaction

Fang-Fang Tan, Kai-Li Tang, Ping Zhang, Yan-Jun Guo, Mengnan Qu, and Yang Li*

Page No. – Page No.

Utilization of Hydrogen Source from Renewable Lignocellulosic Biomass for Hydrogenation of Nitroarenes

Wheat straw for hydrogenation: An utilization of hydrogen source from renewable lingocellulosic biomass for a hydrogenation reaction is demonstrated. Hydrogenation of nitroarenes by wheat straw hydrolysis-oxidation aqueous solution (HOAS) afforded arylamines in up to 95% yields. Mechanism studies suggest that the hydrogenation occurs via a hydrogen transformation pathway.