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Efficient hydrogenation of levulinic acid catalysed by spherical NHC-Ir assemblies with atmospheric pressure of hydrogen[†]

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A practical, efficient, and mild hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) under 1 atm H₂ was realized by singlesited 3D porous self-supported N-heterocyclic carbene iridium catalysts. Quantitative yields and selectivities were achieved at 0.02 mol% catalyst loading, and the catalyst could be reused for 9 runs without obvious loss of selectivity or activity.

Biomass constitutes a sustainable, inexpensive and readily available alternative to fossil resources.^{1–3} Theoretically, diverse high value-added chemicals can be easily accessed *via* selective transformation of the corresponding biomass platform molecules.^{4,5} Among them, levulinic acid (LA), readily available from lignocellulose,^{6,7} has received considerable attention due to its potential for valorization to a number of crucial and valuable chemicals.^{3–7} For instance, γ -valerolactone (GVL) is regarded as one of the most attractive precursors for the generation of biofuels, environmentally benign solvents, value-added fine chemicals and functional additives for foods and fuels.^{8–10} In this context, the hydrogenation of LA may constitute one of the most effective valorization approaches for accessing GVL.

Compared to the hydrogenation of LA to GVL with formic acid or other hydrogen sources, the direct hydrogenation of LA with hydrogen gas (H₂) may be more sustainable and straightforward, and is especially suitable for large-scale industrial application.¹¹ To date, a number of catalysts have been designed for this pivotal transformation, including Ir,¹² Ru,¹³ Pd¹⁴ and Fe¹⁵ complexes or nanocomposites¹⁶ in homogenous or heterogeneous catalytic systems. In comparison with homogenous species, heterogeneous catalysts offer a possibility for catalyst recovery and reuse, and thus have potential for industrial processes. However, harsh reaction conditions, especially high H₂ pressure, high temperature and high catalyst loadings are usually required and have strictly hampered further industrial application. Therefore, the design and preparation of powerful and recyclable catalysts that can enable the hydrogenation of LA under mild reaction conditions are highly desirable. During the preparation of our manuscript, Fu and Liu reported the nickel and cobalt-catalyzed hydrogenation, respectively, of LA with sensitive phosphine ligands under atmospheric H₂ pressure (Fig. 1a).^{17,18} Nevertheless, the catalysts in both homogeneous systems were non-recyclable, and high temperature or high catalyst loadings were still required to achieve satisfactory outcomes.

Recently, by using a "self-supporting" strategy,¹⁹ we successfully fabricated a series of one-dimensional (1D) coordination assemblies based on bis-N-heterocyclic-carbene-iridium (bis-NHC-Ir) complexes, which functioned as solid molecular catalysts and exhibited high catalyst activity and selectivity towards the hydrogenation of LA to GVL.^{20,21} The 1D solid catalysts



Fig. 1 Hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL).

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were readily recovered and reused for dozens of runs, although the reactions still had to be carried out under high H₂ pressure (50 bar, Fig. 1a).²⁰ To the best of our knowledge, there is no heterogeneous catalytic system for this transformation under atmospheric H₂ pressure. We conceived that porous catalysts with large specific surface areas may accelerate the adsorption of H₂ and the mass and heat transfer,²¹⁻²³ which may benefit the hydrogenation process. Herein, we fabricated a series of spherical three-dimensional (3D) porous NHC-Ir assemblies (Fig. 1b), which exhibited excellent activities and selectivity towards the hydrogenation of LA to GVL under atmospheric pressure of hydrogen. Quantitative yield and selectivity could be achieved at 0.02 mol% catalyst loading, and the solid catalyst could be readily recovered and reused for 9 runs without obvious loss of selectivity or activity. Remarkably, an excellent turnover number (TON) of 2.1×10^5 was achieved.

In order to fabricate the porous 3D NHC-Ir assemblies, tetraimidazolium salts^{23,24} with geometrically defined tetraphenylmethane cores were selected because the formed four NHC fragments were well-separated from each other and orientated for further binding to different Ir centers, so leading to the formation of an extended 3D structure via coordination assembly (Fig. 1b). Initially, tetraimidazolium iodide was synthesized by the N-phenylation of N-methylimidazole with tetra-parabromo-phenylmethane (Scheme S1[†]). After anion-exchange with triethyloxonium tetrafluoroborate, the corresponding salt containing BF₄⁻ was obtained in a quantitative yield. After deprotonation of these imidazolium salts by lithium hexamethyldisilazide (LiHMDS) in DMF, and coordination with different metal precursors [Ir(acac)(CO)₂] or [Ir(COD)Cl]₂ (acac = acetylacetonato and COD = 1,5-cyclooctadiene), the desired NHC-Ir solid coordination assemblies (3a-c) with different anions (I⁻ or BF₄⁻) and ancillary ligands (CO or COD) were finally obtained in excellent yields (80%-85%, Scheme S1[†]).

All NHC-Ir solid coordination assemblies 3a-c were relatively robust and insoluble in all tested conventional organic solvents and water. Therefore, solid-state analytical techniques were applied for characterization of their compositions. The morphologies of the freshly prepared coordination assemblies 3a-c were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Unexpectedly, spherical particles were found in the SEM and TEM images of the solid NHC-Ir assemblies 3a (Fig. 2a); the average particle size was 700-800 nm as measured by dynamic light scattering (DLS, Fig. S25[†]). It has to be pointed out that these spherical particles were amorphous, which was further confirmed by powder X-ray diffraction (PXRD, Fig. S12[†]). Energy dispersive spectroscopy (EDS, Fig. 2c) indicated that single iridium sites were uniformly dispersed in the matrix of solid 3a, which could be confirmed by the magnified high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of recovered solid 3a (Fig. 2e). With this information, we may regard these self-supported NHC-Ir assemblies as solid molecular catalysts that coordinate in the same way as their molecular analogues bis-NHC-Ir 5 with N-phenyl substituents.18,23,25



Fig. 2 (a and b) SEM images, (c) EDS elemental-mapping of iridium, and (d) TEM image of the freshly prepared solid NHC-Ir coordination assembly **3a**. (e) HAADF image of recovered solid **3a**. (f) XPS spectra of freshly prepared solid **3a** and recovered solid **3a**. (g) Partial solid-state ¹³C NMR spectra of solid **3a** and the corresponding analogue complex **5**.

Subsequently, the molecular nature of the solid 3a was investigated by solid-state ¹³C NMR spectroscopy, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectroscopy (XPS). Pleasingly, the signals in the solid-state ¹³C NMR spectrum of 3a were well-matched with the corresponding peaks of the bis-NHC-Ir complex 5, though slightly broadened (Fig. 2g), which confirmed that the solid assemblies 3a had the desired structure as we expected. The ICP-AES showed that the amount of Ir in 3a was 26.6%, which was quite consistent with the theoretical value (25.7%). This was further confirmed by the amount of Ir (25.5%) resolved from hydrogen temperature-programmed desorption (H₂-TPD, Fig. S26[†]). In addition, characteristic bonding energies of Ir(1) were observed at 62.0 (4 $f_{5/2}$) eV and 65.0 (4 $f_{7/2}$) eV in the XPS spectrum of 3a, which were also consistent with the signals of bis-NHC-Ir complex 5.

The porosities of the newly fabricated solid coordination assemblies were further characterized by N₂ and H₂ adsorption/desorption studies (Fig. S23 and S24†). N₂ adsorption tests revealed that solid **3a** (33 m² g⁻¹) had a higher Brunauer– Emmett–Teller (BET) specific surface area than the 1D analogue **4b** (8 m² g⁻¹), confirming the porous nature of solid **3a**. Similarly, the solid **3a** exhibited a significantly improved H₂ adsorption ability compared to the 1D solid **4b** (84 m² g⁻¹ vs. 3 m² g⁻¹), which might be beneficial for hydrogenation reactions involving H₂.

The catalytic activities of these characterized spherical porous NHC-Ir assemblies 3a-c were then investigated by the

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hydrogenation of LA to GVL. Initially, our previous reaction conditions for 1D solid coordination assemblies 4a-b (15 mmol scale with 1.1 equiv. KOH in *i*-PrOH at 30 bar H₂ pressure at 100 °C for 4 h)²⁰ were directly applied to evaluate the activity of the solids 3. To our delight, even in the presence of 0.01 mol% solid 3a, LA could be selectively transformed into GVL in 99% yield within 4 h, highlighting the excellent catalytic activity of **3a**. It is worth mentioning that lowering the amount of KOH significantly suppressed the yield of GVL (7-54%, entries 7-9, Table S1[†]), since one equivalent of KOH is required to firstly neutralize LA, and then a slight excess of KOH facilitates the transformation. This was confirmed by the excellent result (92%) achieved by the control experiment with 1 equiv. potassium levulinate and 0.1 equiv. KOH (entry 21, Table S1[†]). Increasing the amount of KOH above 1.1 equiv. also slightly decreased the yield of GVL (89%, entry 6, Table S1[†]), supporting the pivotal role of KOH. The strong base NaOH or other weak bases all resulted in inferior results (38-84%, entries 15-17, Table S1[†]). The catalytic activities of other solid assemblies 3b-c were also assessed. Inferior yields were observed with the other solid assemblies under otherwise identical reaction conditions (83-78% yields, Table S1,† entries 2-3), which may indicate that the anions, ancillary ligands and core structures of the assemblies had a great impact on the catalytic activity.

Because the porous structure of solid 3a has a higher H_2 adsorption capacity than 1D solid 4b, which may be beneficial for reactions involving H₂, a hydrogen balloon was attached to the reaction vessel to perform the reaction under atmospheric H₂ pressure. Up to 78% yield of GVL was achieved within 24 h in the presence of 0.01 mol% solid catalyst 3a, and no other by-product was generated. By increasing the catalyst loading of 3a to 0.02 mol%, a 99% yield of GVL was finally achieved under 1 atm H₂ pressure within 24 h. It is noteworthy that our protocol describes the first heterogeneous catalytic system for the selective hydrogenation of LA to GVL under 1 atm H₂ pressure. When 0.00125 mol% (12.5 ppm) solid 3a was utilized as the catalyst over an extended reaction time (72 h), a 60% yield of GVL and a TON of 4.8×10^4 were obtained under 1 atm H_2 pressure. Moreover, a record TOF of 3630 h⁻¹ could be achieved within 30 minutes under 1 atm H₂ pressure.^{17,18} Upon increasing the H₂ pressure to 50 bar, a much higher TON value of 2.1×10^5 was gained.

Several viable homogeneous catalysts **6–11**, which have been regarded as model catalysts in diverse hydrogenation reactions^{26,27} were investigated to compare with the solid **3a** (Fig. 3a). Pleasingly, the solid **3a** catalyst exhibited the highest catalytic activity under atmospheric H₂ pressure. Remarkably, the 1D NHC-Ir assembly **4b** still had higher activity than all the selected homogenous catalysts under atmospheric H₂ pressure, confirming the advantages of the "self-supporting" strategy due to the "isolated effect".²³ To further investigate the reason for the superior catalytic performance of the 3D solid compared to the 1D catalyst, additional control experiments and characterizations were carried out. The solid-state ¹³C NMR spectra (Fig. S21 and S22†) indicated that the 1D and



Fig. 3 (a) Catalyst screening: reactions were carried out with LA (15 mmol), catalyst (0.02 mol%), KOH (1.1 equiv.), H₂ (1 atm) in i-PrOH (5 mL) at 100 °C for 24 h. The yields were determined by ¹H NMR with mesitylene as an internal standard. Im denotes imidazole, BenIm denotes benzimidazole. (b) Recycling and reuse of the solid catalyst **3a** for the hydrogenation of LA to GVL under 1 atm H₂ for 4 h.

3D catalysts had similar expected structures. XPS (Fig. S16 and S19[†]) revealed that the coordination environment and valence state of the Ir(1) centers in the 3D catalyst 3a (62.0 eV and 65.0 eV) and 1D catalyst 4b (61.9 eV and 64.9 eV) were consistent. The aforementioned N₂ and H₂ sorption experiments indicated that solid **3a** had a higher BET specific surface area (33 m² g⁻¹ vs. 8 m² g⁻¹, Fig. S23[†]) and H₂ adsorption ability (84 m² g⁻¹ vs. 3 m² g⁻¹, Fig. S24^{\dagger}) than the solid analogue 4b. Moreover, when the 1D analogue 4c, with N-phenyl groups other than N-methyl groups, was applied as the catalyst under otherwise identical reaction conditions, a 79% yield of GVL was attained. This result was higher than that from solid 4b (71%) but lower than the outcome using solid 3a (99%), indicating that substituent effects contribute to the hydrogenation of LA to GVL. Therefore, the superior activity of the 3D catalyst compared to the 1D catalyst could be attributed to the porous structure and substitution effects.

In view of the insolubility of solid **3a** in common organic solvents and water, the solid catalyst was readily recovered by simple centrifugation and decantation after completion of the reaction. To our delight, after washing with *i*-PrOH, the recovered solid **3a** could be directly reused in a second run without additional activation. Simply using LA, base and solvent, no obvious decrease in the selectivity and yield of GVL was observed in the second run within 4 hours. The solid **3a** could be reused for 9 runs under atmospheric pressure of hydrogen at low catalyst loadings (0.06 mol%), without an obvious loss of catalytic activity or selectivity (Fig. 3b). Furthermore, under 30 bar of hydrogen, the recycle number could be increased to 15 runs, and the yield of GVL in the 15th run was still greater than 90% (Fig. S53[†]).

In order to investigate the stability of solid 3a during recycling, the filtrate after each run was analysed by ICP-AES for possible iridium leaching (Table S3†). Only trace amounts of iridium species could be detected in the filtrates, which may be the iridium precursors or the light-weight oligomers entrapped in the solid catalyst matrix during the coordination process.^{26,27} Moreover, no obvious morphology changes were found in the SEM, TEM and EDS mapping images between the newly prepared and the recovered solid catalysts (Fig. S1, S2, S5–S8†). Furthermore, similar signals were observed in the XPS, XRD and IR spectra, confirming that the solid catalyst **3a** preserved its structural features and functioned as a robust solid molecular catalyst. The slightly changed signals of solid **3a** after recycling (Fig. 2f and Fig. S12, S13, S49, S50†) were attributed to the dissociation of COD ligands after the reaction.²⁸

Considering the high catalytic efficiency and stability of solid 3a, the scope of the protocol was then investigated. As shown in Table 1, selected LA derivatives and analogues could be readily hydrogenated and transformed into the corresponding lactones in good to excellent yields (70-99%) under atmospheric H₂ pressure. It should be notified that slightly high catalyst loading (0.1 mol%) and amount of base (2 mol %) are required to achieve satisfactory outcomes. No obvious electronic and steric effects with the aromatic substrates were found. Selected halogens and electron-donating substituents all resulted in good to excellent yields (76%-94%, Table 1, 2b-g). When the bulky naphthalen-2-yl substrate was present, 81% yield was still achieved (2h). Furthermore, γ -acetyl butyric acid and ethyl levulinate both led to excellent yields (99%: 2i and 91%: 2a). In light of the important role of bioactive phthalide in the pharmaceutical industry, 2-carboxybenzaldehyde was

 Table 1
 Hydrogenation of levulinic acid analogues and derivatives^a



^{*a*} Reactions were carried out with acid (5 mmol), solid **3a** (0.1 mol%), KOH (2 equiv.), H_2 (1 atm) in *i*-PrOH (5 mL) at 100 °C for 24 h. HCl (1 mL) was added after the completion of the reaction and the mixture was stirred at r.t. for 1 h. The isolated yields are reported. ^{*b*} Using ethyl levulinate as the substrate. ^{*c*} For 36 h. ^{*d*} The yield was determined by ¹H NMR with mesitylene as an internal standard.

also tested, which gave a good yield of phthalide (70%, 2j) under 1 atm H_2 pressure.

To investigate the reaction mechanism, several control experiments were conducted (Fig. 4a).²⁴ The possible reaction pathways might be: (I) after dehydration of LA, α-angelica lactone could be generated, which could be further converted to GVL in the presence of a catalytic amount of solid 3a (Fig. 4a, pathway I);¹⁷ or (II) after hydrogenation of LA in the presence of solid 3a, a subsequent intramolecular cyclic esterification process could take place after further addition of HCl, leading to formation of the desired GVL (Fig. 4a, pathway II).¹⁷ When the α -angelica lactone was used as a substrate under otherwise identical reaction conditions, almost no GVL was generated (Fig. 4b, entry i). This outcome implies that pathway II via hydrogenation and esterification was involved in our newly developed heterogeneous catalytic system. A model reaction without the H₂ balloon was also carried out, and only trace GVL was produced (Fig. 4b, entry ii), which clearly indicates that a hydrogenation mechanism other than hydrogentransfer was involved.

Furthermore, to understand the influence of the solvent, reactions without solvent, and with t-BuOH, MeOH, H₂O or



Fig. 4 (a) Possible reaction pathways for the hydrogenation of LA to GVL by solid **3a**. (b) Control experiments.

i-PrOH were performed under otherwise identical reaction conditions. GVL was obtained in yields of 32%, 8%, 17%, 40%, and >99%, respectively (Fig. 4b, entries iii-vi, and Fig. 3a). These results indicate that the presence of the hydrogen transfer reagent *i*-PrOH could significantly promote the hydrogenation of LA to GVL.²¹ However, the yield of GVL in pure water could be further increased to 80% (Fig. 4b, entry vii) upon increasing the catalyst loading to 0.12 mol% and extending the reaction time (48 h), suggesting that the porous coordination assemblies **3a** could readily catalyse the hydrogen transfer" solvent. Therefore, we envisage that the synergistic effect between *i*-PrOH and the single-site 3D porous catalyst is responsible for the excellent catalytic performance of the protocol.

Conclusions

In summary, a series of spherical self-supported N-heterocyclic carbene-iridium assemblies were prepared which exhibited excellent activities and selectivities towards the hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) under the atmospheric pressure of hydrogen. Quantitative yields and selectivities could be achieved by these single-site solid molecular catalysts at catalyst loadings as low as 0.02 mol%. A catalyst could be readily recovered and reused for 9 runs without obvious loss of selectivity and activity. Remarkably, a TON of up to 2.1 \times 10⁵ was achieved. The porosity of the catalysts is believed to facilitate this crucial transformation under atmospheric pressure of hydrogen. Our protocol may facilitate future industrial biomass valorization under mild reaction conditions.

Conflicts of interest

The authors declare no competing interests.

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