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Zirconia-supported rhenium oxide as an efficient catalyst for the synthesis of biomass-based adipic acid ester†

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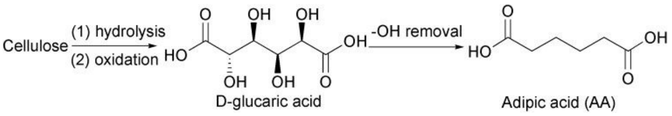
Synthesis of adipic acid, a key monomer of nylon-66 and polyurethane, from biomass is highly attractive for establishing green and sustainable chemical processes. Here, we report that zirconia-supported rhenium oxide (ReO_x/ZrO_2) efficiently catalyses the deoxydehydration of cellulose-derived D-glucaric acid, offering adipic acid ester with a yield of 82% by combining with a Pd/C catalyst in subsequent reactions.

Catalytic transformation of renewable biomass into high-value chemicals is of great importance for establishing sustainable chemical industry. Because of the high oxygen content (e.g., O/C ratio of cellulose is 0.83), lignocellulosic biomass serves as an ideal feedstock for the synthesis of oxygenated compounds such as organic acids, many of which are monomers of key polymers.[1] A variety of multi-functional catalysts have been reported for the conversion of cellulose, the most abundant component in lignocellulosic biomass, or its derivatives to hydroxyl acids such as gluconic acid and lactic acid.[1-3] However, few studies have been devoted to the transformation of cellulose into adipic acid, an important dicarboxylic acid and a monomer for the production of nylon-66 and polyurethanes.[4,5]

Currently, the production of adipic acid relies on petroleum via a route including hydrogenation of benzene to cyclohexane, selective oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone (KA oil) and subsequent oxidation of KA oil by concentrated nitric acid. However, this route suffers from high energy input, low efficiency due to the low cyclohexane conversion, use of corrosive nitric acid and emission of nitrous oxide. The catalytic transformation of biomass or its derivatives into adipic acid would provide a green and sustainable route for the synthesis of this key monomer of Nylon-66 and polyurethane. Very recently, we reported that adipic acid could be synthesized by catalytic conversion of cellulose-derived 5-hydroxymethylfurfural (HMF).[6] Another promising route for adipic acid synthesis from cellulose is via D-glucaric acid intermediate (Scheme 1). Several studies have succeeded in converting cellulose or its monomer (D-glucose) to D-glucaric acid.[7] However, the conversion of D-glucaric acid to adipic acid by removing four hydroxyl groups remains challenging. Brønsted acids and supported metal nanoparticles can catalyse the dehydration and hydrogenolysis of alcohols, but these systems are normally limited to cleaving one C–OH bond.[8] A patent disclosed that hydrogen halide (e.g., HBr or HI) facilitated the removal of OH groups in glucaric acid in an organic acid (e.g., acetic acid) solvent and an adipic acid yield of 89% was achieved by combining HBr with a Pt-Rh catalyst under H_2 at 433 K.[9] However, the use of halogen and acid solvent would cause corrosive and environmental problems, and would increase the complexity and cost in product separation. The development of environmental benign catalytic systems for removal of multiple OH groups is highly challenging but very attractive for biomass valorisation.



Scheme 1 Conversion of cellulose into adipic acid via D-glucaric acid.

Catalytic deoxydehydration (DODH) is an effective method to remove two adjacent hydroxyl groups in diols, and the product is the corresponding alkene. DODH is generally catalysed by Re-, Mo- and V-based catalysts.[10] In particular, Re-based homogeneous and heterogeneous catalysts have shown high activity in DODH of polyols, in which the vicinal OH groups are in *cis*-form.[11,12] For example, mucic acid with two pairs of *cis*-diols, which could readily coordinate to Re catalyst, underwent facile removal of four OH groups, forming muconic acid, a dicarboxylic acid with conjugate diene.[11] On the other hand, only low efficiencies were obtained for the removal of

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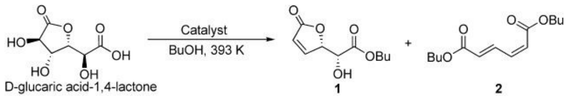
four OH groups in D-glucaric acid, which contains one pair of *cis*-diols and one pair of *trans*-diols.[11]

So far, only a homogeneous $KReO_4$ catalyst in combination with Pd/C has shown a considerable efficiency for the conversion of D-glucaric acid lactone derived from calcium glucarate in alcohol to adipate esters in the presence of various additives (H_3PO_4 and activated carbon).[13] The development of active heterogeneous catalysts for DODH of D-glucaric acid remains challenging. Here, we report an efficient heterogeneous rhenium oxide-based catalyst for DODH of D-glucaric acid in butanol solvent, forming alkenyl dicarboxylic acid ester. A high yield of adipic acid ester has been achieved by combining subsequent hydrogenation using a Pd/C catalyst.

Table 1 shows catalytic performances of V, Mo, W and Re oxides loaded on ZrO_2 as well as a homogeneous methyltrioxorhenium (CH_3ReO_3) catalyst for the conversion of D-glucaric acid-1,4-lactone, which is a structure-stable molecule of D-glucaric acid. All the supported metal oxides catalysed the DODH reaction except for the VO_x/ZrO_2, forming product **1**, a five-membered ring lactone with one OH group, and product **2**, dibutyl hexa-2,4-dienedioate, a linear ester with conjugated alkenes. As compared to MoO_x/ZrO_2 and WO_x/ZrO_2, the ReO_x/ZrO_2 catalyst showed remarkably higher activity for the removal of OH groups. The milder reaction temperature (393 K) used in this work probably caused the lower activities of VO_x-, MoO_x- and WO_x-based catalysts, which are known to catalyse DODH reactions at higher temperatures.[10b] It is of interest that the ReO_x/ZrO_2 catalyst was more efficient than the homogeneous CH_3ReO_3 catalyst. The support played a key role in determining the catalytic behaviour. The ReO_x/ZrO_2 showed the highest activity, offering product **2** with all OH groups removed with a yield of 41%. The total yield of DODH products was 93% over this catalyst. The ReO_x/TiO_2 and ReO_x/SiO_2 showed similar performances, which were lower than that of ReO_x/ZrO_2 but higher than those of ReO_x/Al_2O_3 and ReO_x/MgO.

Table 1 Catalytic performances of supported rhenium catalysts for the deoxydehydration of D-glucaric acid-1,4-lactone[a]



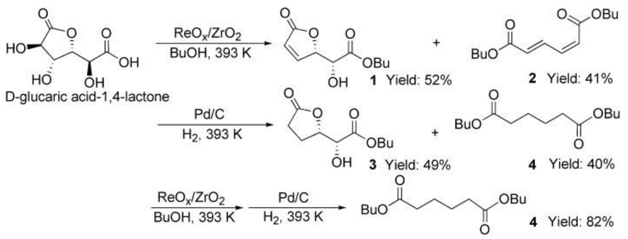
Entry	Catalyst	Yield (%)		Total yield of DODH products (%)
		1	2	
1	CH_3ReO_3	32	18	50
2	ReO_x/ZrO_2	52	41	93
3	VO_x/ZrO_2	0	0	0
4	MoO_x/ZrO_2	9.7	0	9.7
5	WO_x/ZrO_2	2.9	0	2.9
6	ReO_x/TiO_2	48	29	77
7	ReO_x/SiO_2	43	28	71
8	ReO_x/Al_2O_3	23	21	44
9	ReO_x/MgO	13	2.0	15
10[b]	ReO_x/ZrO_2	39	35	74

[a] Reaction conditions: D-glucaric acid-1,4-lactone, 0.10 mmol; catalyst, 20 mg; butanol (BuOH), 5.0 mL; N_2, 20 mL/min; reaction temperature, 393 K; reaction time, 24 h. [b] Reaction time, 48 h.

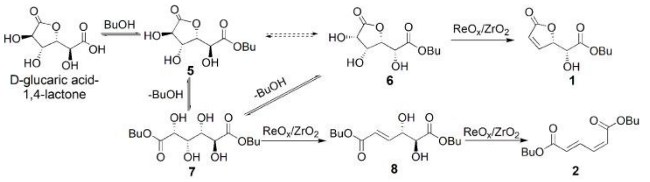
The H_2 temperature-programmed reduction (H_2-TPR) studies revealed that the reducibility of ReO_x species changed by changing the support (Fig. S1 and Table S1, ESI†). ReO_x/ZrO_2, ReO_x/TiO_2 and ReO_x/SiO_2 catalysts showed reduction peaks in a range of 610-720 K, whereas the peaks shifted to 700-900 K for ReO_x/Al_2O_3 and ReO_x/MgO catalysts. It is likely that ReO_x species strongly interact with Al_2O_3 or MgO via Re-O-Al or Re-O-Mg bonds,[14] decreasing the reducibility of ReO_x species. Combining this result with the catalytic behaviors of supported ReO_x catalysts (Table 1), we speculate that the reducibility of ReO_x species is a key parameter in determining DODH reactions, which may involve the redox of ReO_x species (e.g., Re(VI)/Re(IV)).[11,12] The redox of ReO_x species loaded on Al_2O_3 and MgO becomes not easy due to the strong interaction, thus leading to low efficiencies of these catalysts in DODH reactions.

The X-ray photoelectron spectroscopy (XPS) studies showed that Re species on ReO_x/Al_2O_3 and ReO_x/MgO surfaces existed as Re(VII), while those on ReO_x/ZrO_2, ReO_x/TiO_2 and ReO_x/SiO_2 surfaces were composed of Re(VI) and a small fraction of Re(IV) (Fig. S2, ESI†). After the catalytic reaction, almost no change in Re oxidation state was observed on the former two catalysts, whereas the fraction of Re(IV) increased significantly on the later three catalysts. This suggests that the redox between Re(VI) and Re(IV) occurs during the reaction on ReO_x/ZrO_2, ReO_x/TiO_2 and ReO_x/SiO_2 catalysts. Furthermore, the ReO_x/ZrO_2 catalyst exhibited the highest fraction of Re(IV) after the reaction, indicating that ReO_x species could facilely be reduced on ZrO_2 surfaces. The high reducibility of surface ReO_x species may contribute to the superior catalytic performance of the ReO_x/ZrO_2 catalyst.

We performed further studies for the conversion of D-glucaric acid-1,4-lactone using the most efficient ReO_x/ZrO_2 catalyst. The recycling uses of ReO_x/ZrO_2 showed no significant changes in the yield of DODH products from the second to the fifth cycles (Fig. S3, ESI†). The prolonging of reaction time from 24 to 48 h rather decreased the yield of DODH products due to the polymerization of products **1** and **2** as well as the side reactions with butanol solvent (Table 1). We designed a DODH-hydrogenation strategy to enhance the yield of products with all the OH groups removed (Scheme 2). Because the co-presence of a hydrogenation catalyst may exert a negative effect on the performance of ReO_x/ZrO_2 catalyst (Table S2, ESI†), the DODH and hydrogenation reactions were conducted separately. After the conversion of D-glucaric acid-1,4-lactone



Scheme 2 Catalytic deoxydehydration-hydrogenation strategy for the conversion of D-glucaric acid-1,4-lactone into dibutyl adipate.



Scheme 3 Proposed reaction scheme for ReO_x/ZrO_2-catalysed conversion of D-glucaric acid-1,4-lactone.

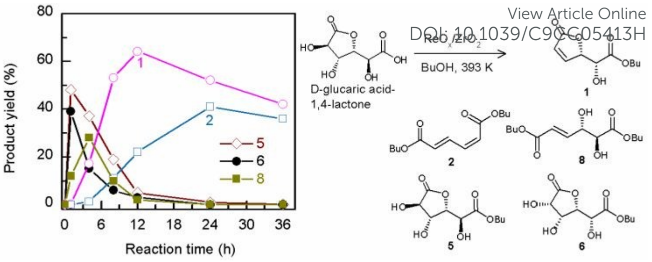


Fig. 1 Time course for ReO_x/ZrO_2-catalysed DODH reaction of D-glucaric acid-1,4-lactone.

at 393 K for 24 h, the solid ReO_x/ZrO_2 was removed from the reaction system by filtration. Then, a commercial Pd/C (Pd loading, 5 wt%) catalyst was added into the system, followed by hydrogenation under H_2 flow (flow rate, 20 mL min^{-1}) at 393 K for 4 h. Products **3** and **4**, dibutyl adipate, which is our target product, were formed. After the removal of Pd/C by filtration, the ReO_x/ZrO_2 catalyst was added back into the reaction system for further conversion of product **3** at 393 K for 24 h, followed by addition of the Pd/C catalyst for hydrogenation for 4 h under H_2 flow. We finally obtained dibutyl adipate (**4**) with a yield of 82%. To the best our knowledge, this is highest yield of adipic acid ester obtained by heterogeneous catalytic conversion of cellulose derivatives.

Our control experiments for the conversion of D-glucaric acid-1,4-lactone without a catalyst revealed that the esterification with butanol occurred at 393 K (Fig. S4, ESI†). Three major esterification products were identified by gas chromatography-mass spectrometry (GC-MS) with a silylation method. These products were butyl ester of D-glucaric acid-1,4-lactone (**5**), butyl ester of D-glucaric acid-3,6-lactone (**6**) and dibutyl ester of D-glucaric acid (**7**) with a molar ratio of 54: 32: 14 (Scheme 3 and Fig. S5, ESI†). This ratio did not change upon prolonging the reaction time, suggesting that an equilibrium was reached among the ring-lactone and chain esters (Scheme 3). The addition of ReO_x/ZrO_2 resulted in product **2**, dibutyl hexa-2,4-dienedioate, with a yield of 41% after a reaction at 393 K for 24 h. As compared to the lower fraction (14%) of linear esterification product **7** without a catalyst, the enhanced formation of linear product **2** in the presence of ReO_x/ZrO_2 indicates that the esterification equilibrium is driven to ring-open products by ReO_x catalyst.

The change in the product yield with reaction time during the conversion of D-glucaric acid-1,4-lactone with the ReO_x/ZrO_2 catalyst showed that products **5** and **6** were the major products at a short reaction time (Fig. 1). This indicates that the esterification occurs at the initial reaction stage. Upon prolonging the reaction time, the yields of **5** and **6** decreased and those of **1** and **2** increased. A linear product **8**, which should be derived from **7** through the removal of two vicinal *cis*-diols at C2 and C3 positions (Scheme 3), was also formed. The yield of **8** first increased and then decreased with reaction time, indicating that it is a reaction intermediate. Our result suggests that **6** is more reactive than **5** in the DODH reaction. This can be explained by the fact that the OH groups in a *cis*-diol can be removed more readily than those in a *tran*-diol in Re-catalysed DODH reactions.[10b,10c] Product **5** could be transformed to **6** and **7** through a ring-chain equilibrium reaction and subsequent conversions of **6** and **7** resulted in DODH products **1** and **2**. The relatively higher formation rate of **1** than that of **2** agrees well with that the removal of two OH groups in a *cis*-diol is easier. Based on these results, we propose a possible reaction scheme for the conversion of D-glucaric acid-1,4-lactone (Scheme 3). In brief, D-glucaric acid-1,4-lactone first reacts with solvent, butanol, and an equilibrium of esterification is established among ring-form (**5** and **6**) and chain-form products (**7**). Because of the *trans*-diol structure, the OH groups in **5** cannot be easily removed to form alkenyl product, but **6** and **7** can undergo DODH reactions. In the presence of ReO_x/ZrO_2 catalyst, **6** was converted to **1**, and **7** was transformed to **2** via 8. The product **8** also has a pair of OH groups in *trans*-diol structure. We speculate that the removal of the two OH groups from **8** is more feasible than that from **5**. This is because **8** is a chain molecule, in which the vicinal *trans*-diol can be transformed to *cis*-diol by rotation of the –CH(OH)COOBu group along the C4-C5 axis. The transformation of *trans*- to *cis*- form may need to overcome a certain energy barrier, leading to a lower formation rate of **2**.

How the Re species functions for DODH reactions is a fundamentally important issue. We performed *in-situ* Fourier-transform infrared (FT-IR) spectroscopy studies to gain insights into the possible interactions between the Re species and reactants. To simplify the assignment of IR bands and to gain adequate signal intensity, we chose CH_3ReO_3 as a model catalyst and dibutyl tartrate with *cis*-diol structure as a model reactant. IR spectra for interactions between CH_3ReO_3 and dibutyl tartrate in butanol were displayed in Fig. 2A. No IR band was observed in a range of 1020-920 cm^{-1} for dibutyl tartrate without CH_3ReO_3 (Fig. 2A, a). The addition of CH_3ReO_3 into dibutyl tartrate resulted in two bands at ~967 and ~948 cm^{-1} (Fig. 2A, b-f), which could be assigned to symmetric and asymmetric stretching vibrations of Re=O bond (Fig. S6, Table S3, ESI†). The increase in the concentration of CH_3ReO_3 led to increased intensities of the two bands. As compared to CH_3ReO_3 alone (Fig. 2A, g), the presence of dibutyl tartrate significantly enhanced the intensity of IR band at 967 cm^{-1}, whereas the band at 948 cm^{-1} blue-shifted slightly, indicating the change in the dipole moment of the Re catalyst. This suggests the formation of CH_3ReO_2-diolate complex,[15] which can change the catalyst symmetry, decreasing the differences in dipole moments of symmetric and asymmetric Re=O stretching vibrations. Thus, the enhancement in the intensity of symmetric Re=O stretching vibration and a slight band shift were observed.

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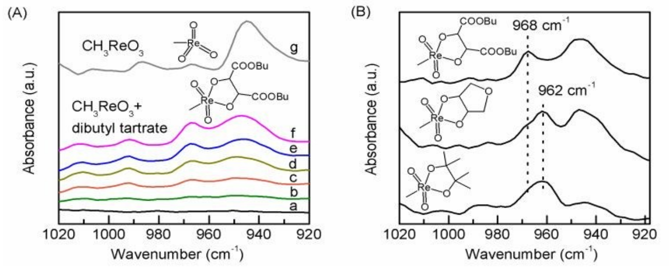
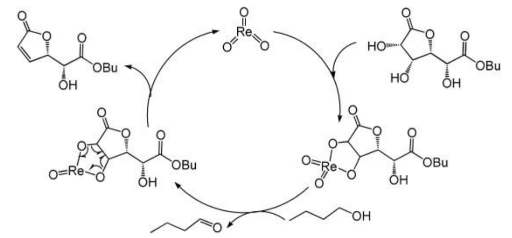


Fig. 2 FT-IR spectra at 363 K. (A) Systems composed of dibutyl tartrate and CH_3ReO_3 with different concentrations in butanol. CH_3ReO_3 concentration (mmol/L): a, 0; b, 4; c, 8; d, 16; e, 24; f and g, 32. Dibutyl tartrate concentration (mmol/L): a-f, 200; g, 0. (B) Systems composed of CH_3ReO_3 (concentration, 32 mmol/L) and different diols (concentration, 200 mmol/L) in butanol.

Further FT-IR studies for systems composed of CH_3ReO_3 and other diols demonstrated that the functional groups in the diols influenced the IR bands ascribed to the symmetric Re=O stretching vibration (Fig. 2B). As compared to the electron-withdrawing groups (e.g., –COOBu in tartrate), the electron-donating groups such as $-CH_3$ in pinacol and $-CH_2OCH_2-$ in 1,4-anhydroerythritol caused the shift of IR band to a lower wavenumber. This provides further evidence for the formation of Re-diolate complex in these systems. When the temperature rose to 393 K, these IR bands disappeared, and the corresponding alkenes were formed (Fig. S7, ESI†).

Take the DODH of D-glucaric acid-1,4-lactone to product **1** as an example, we propose a functioning mechanism of Re species in Scheme 4. As mentioned in Scheme 3, D-glucaric acid-1,4-lactone is transformed to a *cis*-diol via esterification equilibrium in butanol under reaction conditions, and then the Re species is coordinated by the two vicinal OH groups, forming a Re-diolate complex. Upon reduction by butanol, the Re-diolate complex is transformed into an alkene and the Re catalyst is recovered.

In conclusion, we have discovered that ReO_x/ZrO_2 is an efficient catalyst for the deoxydehydration of D-glucaric acid-1,4-lactone in butanol. The catalyst offers dibutyl hexa-2,4-dienedioate with a yield of 41% and the total yield of esters containing alkenyl groups was 93%. The product mixture can be further converted to butyl adipate with a yield of 82% in the subsequent hydrogenation reaction in combination with a Pd/C catalyst. The higher reducibility of ReO_x species due to weaker interactions on ZrO_2 is favourable for the removal of OH groups and the redox of ReO_x species may participate in the deoxydehydration. Re species is believed to be coordinated by the vicinal OH groups in *cis*-diol structure, forming a Re-diolate complex, a key intermediate for the formation of DODH products.



Scheme 4 A proposed reaction mechanism for Re-catalysed DODH reaction.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (*a*) S. Li, W. Deng, S. Wang, P. Wang, D. An, Y. Li, Q. Zhang and Y. Wang, *ChemSusChem*, 2018, **11**, 1995-2028; (*b*) M. Wang, J. Ma, H. Liu, N. Luo, Z. Zhao and F. Wang, *ACS Catal.*, 2018, **8**, 2129-2165.

2 (*a*) X. Tan, W. Deng, M. Liu, Q. Zhang and Y. Wang, *Chem. Commun.*, 2009, 7179-7181; (*b*) D. An, A. Ye, W. Deng, Q. Zhang and Y. Wang, *Chem. Eur. J.*, 2012, **18**, 2938-2947.

3 (*a*) M. Dusselier, P. V. Wouwe, A. Dewaele, E. Mkaterina and B. F. Sels, *Energy Environ. Sci.*, 2013, **6**, 1415-1442; (*b*) Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tan, Y. Wang, C. Zhu, G. Wang and H. Wan, *Nat. Commun.*, 2013, **4**, 2141.

4 S. Van de Vyver and Y. Román-Leshkov, *Catal. Sci. Technol.*, 2013, **3**, 1465-1479.

5 J. C. J. Bart and S. Cavallaro, *Ind. Eng. Chem. Res.*, 2015, **54**, 567-576.

6 L. Wei, J. Zhang, W. Deng, S. Xie, Q. Zhang and Y. Wang, *Chem. Commun.* 2019, **55**, 8013-8016.

7 (*a*) J. Lee, B. Saha and D. G. Vlachos, *Green Chem.*, 2016, **18**, 3815-3822; (*b*) E. Derrien, P. Marion, C. Pinel and M. Besson, *Org. Process Res. Dev.*, 2016, **20**, 1265-1275.

8 (*a*) Y. Nakagawa, M. Tamura and K. Tomishige, *J. Mater. Chem. A*, 2014, **2**, 6688-6702; (*b*) T. Wang, M. W. Nolte and B. H. Shanks, *Green Chem.*, 2014, **16**, 548-572.

9 T. R. Boussie, E. L. Dias, Z. M. Fresco, V. J. Murphy, J. Shoemaker, R. Archer and H. Jiang, *US8669397B2*, 2014.

10 (*a*) E. V. Makshina, M. Dusselier, W. Janssens, J. Degrève, P. A. Jacobes and B. F. Sels, *Chem. Soc. Rev.*, 2014, **43**, 7917-7953; (*b*) S. Raju, M. E. Moret and R. J. Klein Gebbink, *ACS Catal.*, 2015, **5**, 281-300; (*c*) J. R. Dethlefsen and P. Fristrup, *ChemSusChem*, 2015, **8**, 767-775; (*d*) A. R. Petersen and P. Fristrup, *Chem. Eur. J.*, 2017, **23**, 10235-10243; (*e*) C. Li, Q. Zhang and Y. Fu, *Acta Chim. Sinica*, 2018, **76**, 501-514.

11 (*a*) M. Shiramizu and F. D. Toste, *Angew. Chem. Int. Ed.*, 2013, **52**, 12905-12909; (*b*) X. Li, D. Wu, T. Lu, G. Yi, H. Su and Y. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 4200-4204.

12 (*a*) N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *Angew. Chem. Int. Ed.*, 2015, **54**, 1897-1900; (*b*) L. Sandbrink, E. Klindtworth, H. U. Islam, A. M. Beale and R. Palkovits, *ACS Catal.*, 2016, **6**, 677-680.

13 R. T. Larson, A. Samant, J. Chen, W. Lee, M. A. Bohn, D. M. Ohlmann, S. J. Zuend and F. D. Toste, *J. Am. Chem. Soc.*, 2017, **139**, 14001-14004.

14 M. A. Vuurman, D. J. Stufkens, A. Oskam, *J. Mol. Catal.* 1992, **76**, 263-285.

15 R. Dethlefsen and P. Fristrup, *ChemCatChem*, 2015, **7**, 1184-1196.