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Green Chemistry

COMMUNICATION

Base free, one-pot synthesis of lactic acid from glycerol using a bifunctional Pt/Sn-MFI catalyst

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Under base free and mild reaction conditions, 80.5% selectivity of lactic acid (LA) was achieved at 89.8% conversion of glycerol using a bifunctional Pt/Sn-MFI catalyst. In the tandem reaction pathway, selective oxidation of glycerol into glyceraldehyde (GLA) and dihydroxyacetone (DHA) was cascaded with Lewis acid catalyzed isomerization of GLA/DHA into LA.

The needs to replace fossil fuels with sustainable, eco-friendly resources have driven research towards the discovery of new catalytic pathways for converting renewable and waste resources into value-added platform chemicals and fuels.[1, 2] Glycerol is an inevitable by-product from biodiesel production by the trans-esterification of vegetable oils.[3] The rapid development of oleochemistry leads to a dramatic increase in glycerol production from about 600,000 tons in 1992 to 1.1-1.5 million tons in 2010 with an average increase of 3.75% per year.[4] Glycerol can be also potentially obtained from non-edible biomass, such as microalgae, cellulose and its derivatives in the near future.[1, 5, 6] For these reasons, the conversion of glycerol to high-value chemicals has attracted much attention from both academia and industry.[3] Compared to hydrocarbons, glycerol is a highly functionalized molecule consisting of three hydroxyl groups. Selective hydrogenolysis, oxidation and dehydration of hydroxyl group of glycerol have been extensively studied to synthesize valuable chemicals or intermediates.[3, 7-10] In particular, the oxidation of glycerol can generate a series of reaction pathways capable of producing various valuable oxygenated derivatives. However, due to the complex nature of these reaction pathways, it is still a grand challenge to control the selectivity to desired products.

Lactic acid (LA) and alkyl lactates have been widely used in food, pharmaceutical and chemical industries as platform chemicals and green solvents.[11-13] In particular, LA has been used as a precursor to synthesize polylactate or polylactic acid (PLA), the second most manufactured bioplastic in the world.[14] LA can be produced from petroleum feedstocks in high yields using mineral acid catalysts. However, the use of toxic chemicals (*e.g.* hydrogen cyanide) and the high cost for product separation could lead to significant environmental issues. Therefore, currently LA is mainly manufactured by the fermentation of carbohydrates. However, the efficiency and productivity of the fermentation process are still low and need substantial improvements because of the high cost of enzyme catalysts and the need for precise control of operating conditions.[15-17] There is thus a persistent need to develop efficient thermochemical pathways for the production of LA from new starting materials.[18, 19]

Although many research efforts have been devoted to tailor the selectivity in glycerol oxidation, only a few reaction pathways can selectively convert glycerol into LA. Kishida *et al.* reported that LA can be directly produced from the hydrothermal reaction of glycerol in the presence of NaOH at 300 °C.[20] During the hydrogenolysis of glycerol in alkaline solutions at 200 °C and 4.0 MPa H_2, LA has also been detected.[21, 22] These studies highlighted the potential of the production of LA from glycerol although the efficiencies or harsh reaction conditions of the reaction pathways may present significant hurdles to their commercialization. Recently, a tandem reaction pathway has been developed to selectively transform glycerol into LA. In this route, glycerol is first selectively oxidized into dihydroxyacetone (DHA) and glyceraldehydes (GLA) on metal catalysts, and then undergoes base-catalyzed dehydration and benzilic acid rearrangement to produce LA. Shen *et al.* first reported that 85.6% of LA selectivity was achieved from this reaction pathway using Au-Pt/TiO_2 catalyst in the presence of NaOH, and confirmed that DHA and GLA were formed during the reaction as intermediates.[23] Similar performances have also been achieved on Au/CeO_2 and Au-Pt/nanocrystalline CeO_2 catalysts under basic conditions.[24, 25] The use of base in the tandem reaction pathway is crucial because hydroxide ions not only facilitate H-abstraction in the initial dehydrogenation of hydroxyl group of glycerol but also catalyze the reaction from DHA/GLA to LA.[8, 23, 26, 27] Although a high yield of LA can be achieved from this reaction pathway, the use of base catalysts causes the formation of acid salt (*i.e.* lactate). Additional reaction and separation steps are required to produce LA, which not only increase the cost of production but also produce a stoichiometric amount of salt wastes. Development of a base-free reaction pathway for the production of LA from glycerol using heterogeneous catalysts is thus highly desired. In this scenario, Xu and coworkers succeeded in attaining 66.6% of LA selectivity at 13.6% of glycerol conversion by employing Au-Pd/TiO_2 in the presence of $AlCl_3$, and proposed that the second step reaction from DHA/GLA to LA was catalyzed by $AlCl_3$.[28] Although no base catalyst was used in the reaction, separation of $AlCl_3$ catalyst and catalyst poison by chlorine were still issues for the catalytic process.

In order to overcome the challenges, herein we developed an efficient base-free reaction pathway to selectively convert glycerol into LA in aqueous phase using a bifunctional Pt/Sn-containing zeolite catalyst. In the reaction pathway, glycerol is first oxidized into DHA/GLA with O_2 on Pt nanoparticles under mild oxidation conditions. Water tolerant Lewis acid catalyst, Sn-MFI, then

catalyzes the isomerization of DHA/GLA into LA with high selectivity. Zeolites are microcrystalline materials consisting of distinct pore dimension, framework and composition. Because of remarkable hydrothermal stability and molecular sieving capability for various reactions, zeolites have been widely used as catalysts for petrochemical and biomass processing.[12, 17] In this study, Sn containing zeolites were selected due to their outstanding Lewis acidity in aqueous phase. Under optimized reaction conditions over 80% yield of LA was achieved from the bifunctional catalyst.

Bifunctional Pt/Sn-containing zeolite catalysts were prepared by the reduction of Pt precursors deposited on Sn-containing zeolites with MFI structure (Sn-MFI). Details for syntheses of the catalysts are available in Supplementary Information. Sn-MFI was chosen in this study because of its outstanding Lewis acidity for catalyzing the isomerization of sugar molecules in aqueous phase, in particular for C_3 sugar derivatives, such as DHA, GLA and pyruvaldehyde (PA). Sn-MFI was synthesized according to a method published in literature.[29] Characteristic XRD peaks corresponding to the MFI structure were observed for the Sn-MFI catalyst (Fig. S1, ESI†), revealing a highly crystalline sample with MFI structure was synthesized without any other impurity phase. Lewis acidity of Sn-MFI catalyst was confirmed by FT-IR measurement of the sample adsorbed with pyridine. As shown in Fig. 1a, Sn-MFI provided a strong absorption band at 1454 cm^{-1}, assigned to the pyridine bound with the Lewis acid Sn sites.[17, 30] A very weak absorption feature at 1547 cm^{-1} related to Brønsted acid was also observed in the spectrum,[17, 30] demonstrating that in the conversion of the triose sugars into LA Sn-MFI might be able to catalyze both dehydration and intramolecular 1,2 hydride shift after hydration of PA.[17, 31, 32]

Pt precursors ($H_2PtCl_6 \cdot 6H_2O$) were loaded on the Sn-MFI sample using an incipient wetness method, and subsequently reduced to Pt nanocrystals. The Pt/Sn-MFI sample possesses a diffraction peak at $2\theta = 39.8°$, corresponding to the (111) plane of Pt crystal with a cubic close-packed structure.[33] It is evident that the formation of crystalline Pt nanoparticles onto Sn-MFI does not influence the original crystalline structure of Sn-MFI catalyst. The TEM image confirms that the Pt nanoparticles were well dispersed on the Sn-MFI catalyst surface (Fig. 1c). Particle size distribution of Pt calculated from TEM images was shown in Fig. 1b. The size of Pt nanoparticle mainly lies between 4 and 7 nm with an average of 6.7 nm, in good agreement with the size of 7.9 nm determined by H_2 chemisorption (Table S1, ESI†). Pt on siliceous MFI (silicalite-1), Sn containing zeolite with BEA structure (Sn-BEA) and TiO_2 were also synthesized using the method applied for Pt/Sn-MFI. The particle sizes of Pt on the samples are in a range of 6.4 nm to 9.5 nm, similar to Pt/Sn-MFI sample (Table S1, ESI†). The crystalline structure of these supports is also well retained during the loading of Pt (Fig. S1, ESI†).

Table 1 shows the activities and selectivities of aerobic glycerol oxidation at 0.62 MPa of O_2 and 100 °C on the bifunctional catalysts prepared in this work. Pt/Sn-MFI catalyzed glycerol oxidation to LA with an activity of 1.95 h^{-1} and 80.5% selectivity to LA at 89.8% conversion of glycerol. To the best of our knowledge, it is the highest yield of LA achieved using heterogeneous catalysts in the absence of base. Concentration profiles of reactant and various products as well as the selectivity to LA are shown in Fig. 2a and b, respectively (Fig. S2, ESI†). At the beginning of the reaction, the main product is DHA formed by the oxidation of the secondary hydroxyl group of glycerol and the isomerization of GLA. GLA was also detected in the reaction with a low selectivity. With increasing the glycerol conversion, the DHA concentration decreased
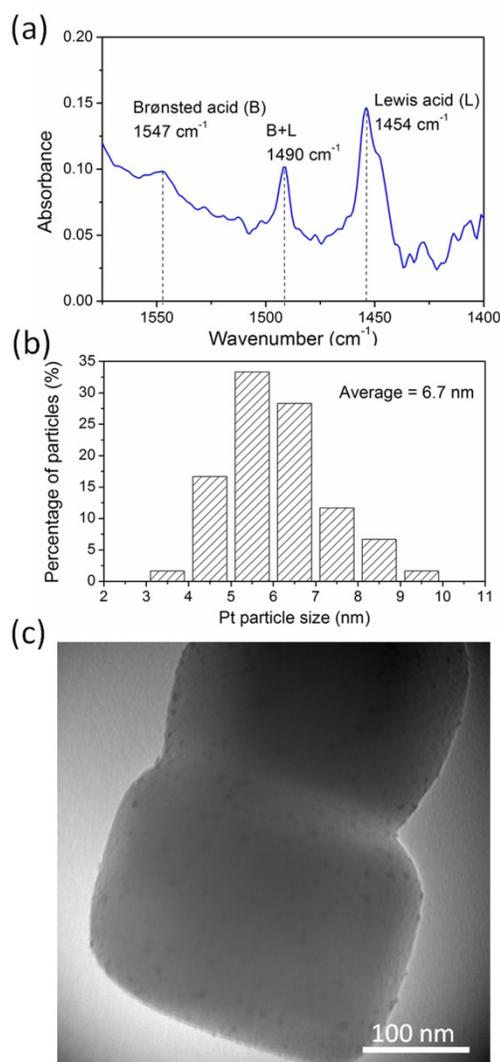
Fig. 1 (a) Pyridine FT-IR spectrum, (b) Pt particle size distribution and (c) TEM image for the Pt/Sn-MFI catalyst. The average Pt particle size was estimated using the equation $\sum d^3 / \sum d^2$ where d is a size for each Pt particle.

concurrently with an increase in the selectivity to LA, suggesting DHA is an intermediate for the formation of LA. When the glycerol conversion is higher than 90%, LA selectivity began to decrease with the formation of pyruvic acid (PyA) and acetic acid (AA) which are due to further oxidation of the produced LA.[34] The reaction pathways were studied by starting the reactions from LA and PyA on the Pt/Sn-MFI catalyst, respectively (Table 1, entries 2 and 3). It was found that PyA is selectively converted into AA. LA oxidation produced PyA and AA at a reaction rate slower than PyA oxidation under the same reaction conditions. Moreover, as shown in Table 1, TOF value for the oxidation of LA is 39 times lower than that for the oxidation of glycerol, which allows us to optimize the reaction conditions to achieve a high selectivity to LA. Other by-products formed during the course of the reaction were glyceric acid (GlyA) and tartronic acid (TarA) which are formed by the sequential oxidation of GLA.[34, 35] The overall carbon balance obtained from the analyses is above 94%.

Although previous studies have suggested that Sn-BEA is a highly active Lewis acid catalyst for the isomerization of triose sugars in aqueous phase,[12, 31, 36, 37] Pt/Sn-BEA catalyst provided

Table 1 Oxidation of glycerol and other substrates on the catalysts synthesized in the study [a]

Entry	Catalyst	Substrate	TOF [b] (s^{-1})	Conv.[c] (%)	Selectivity (%)							
					DHA	GLA	PA	LA	PyA	AA	GlyA	TarA
1	Pt/Sn-MFI	Glycerol	1.95	89.8	0.9	0.6	4.4	80.5	1.6	2.1	8.7	0.8
2 [d]	Pt/Sn-MFI	LA	0.05 [d]	4.7	-	-	-	-	40.4	46.8	-	-
3 [d]	Pt/Sn-MFI	PyA	0.23 [d]	22.5	-	-	-	-	-	94.7	-	-
4 [e]	Pt/Sn-BEA	Glycerol	2.33	93.4	6.2	4.9	29.8	28.1	1.0	3.7	18.4	3.0
5	Pt/silicalite-1	Glycerol	1.11	83.8	9.7	42.0	0.0	0.0	0.0	5.4	32.7	4.2
6	Pt/AC + Sn-MFI	Glycerol	0.07	53.6	0.0	0.0	0.0	80.8	0.0	0.9	7.8	0.9
7	Pt/TiO2	Glycerol	2.21	92.3	3.6	18.6	0.0	0.0	0.0	5.9	55.4	7.8

[a] Reaction conditions: 0.2 M substrate in H_2O, substrate/Pt (mol/mol) = 350, substrate/Sn (mol/mol) = 226, pO_2 = 0.62 MPa, 100 °C, at 24 h. [b] TOF = moles of a converted substrate divided by moles of $Pt_{surface}$ per reaction time, at 0.5 h. [c] Substrate conversion. [d] Reaction time: 4 h. [e] Substrate/Sn (mol/mol) = 211.

much lower selectivity to LA (28.1%) compared to Pt/Sn-MFI (Table 1, entry 4). 29.8% selectivity to PA was observed at 93.4% conversion of glycerol, implying that the catalytic activity of Pt/Sn-BEA catalyst is substantially lower than Pt/Sn-MFI for converting triose sugars into LA. Moreover, a large amount of GlyA was detected at the end of the reaction, indicating the sequential oxidation of GLA significantly proceeded. To further understand differences between the Pt/Sn-BEA and Pt/Sn-MFI catalysts, we studied the performance of these catalysts in the conversion of PA to LA. The reactions were first carried out over the Sn-BEA and Sn-MFI catalysts without Pt. Although BEA zeolite has larger pore sizes than MFI (Table S2, ESI†), Sn-MFI displays a 45% higher yield of LA than Sn-BEA (Fig. 3). The higher catalytic activity of Sn-MFI for PA conversion in water might be due to its relative hydrophilic surface compared to Sn-BEA catalyst. It has been known that zeolites synthesized in fluoride medium contain fewer structural defects and silanol groups than the ones made in caustic medium.[38, 39] In this study, the Sn-MFI catalyst was synthesized using a conventional approach without using fluoride ions. On the contrary, hydrofluoric acid (HF) had to be used in the synthesis of Sn-BEA

catalyst. The fewer amounts of defects and silanol groups in the Sn-BEA provide a more hydrophobic environment for the catalyst as shown in the previous literature.[39, 40] This observation is also evidenced by FT-IR measurement of the samples in the OH stretch range of 3800-3000 cm^{-1} (Fig. S3, ESI†). It is believed that different hydrophobic/hydrophilic properties of the two catalysts may affect their adsorption and catalytic performances. Higher catalytic activity of Sn-MFI in the reaction from PA to LA should be due to the synergism between the structure of Lewis acid Sn sites and adsorption property. After Pt nanoparticles were loaded, the catalytic activity of both catalysts decreased as shown in Table 2. In the case of loading Pt onto Sn-MFI, the reaction rate decreased by around 5.5%. The effect of loading Pt on the catalytic activity of Sn-BEA was more obvious, 41.5% decrease was observed. Overall, Pt/Sn-MFI provided a 2.3 times higher initial reaction rate than Pt/Sn-BEA for the conversion of PA to LA. This indicates that the loading of Pt might partially block the Lewis acid Sn sites in these two catalysts. Corma et al. reported the framework Sn in the Sn-BEA sample can stabilize the nucleation of Pt nanoparticles inside the zeolite channels and form Pt^0–Sn^{4+} sites.[41] We believe that a part of Pt
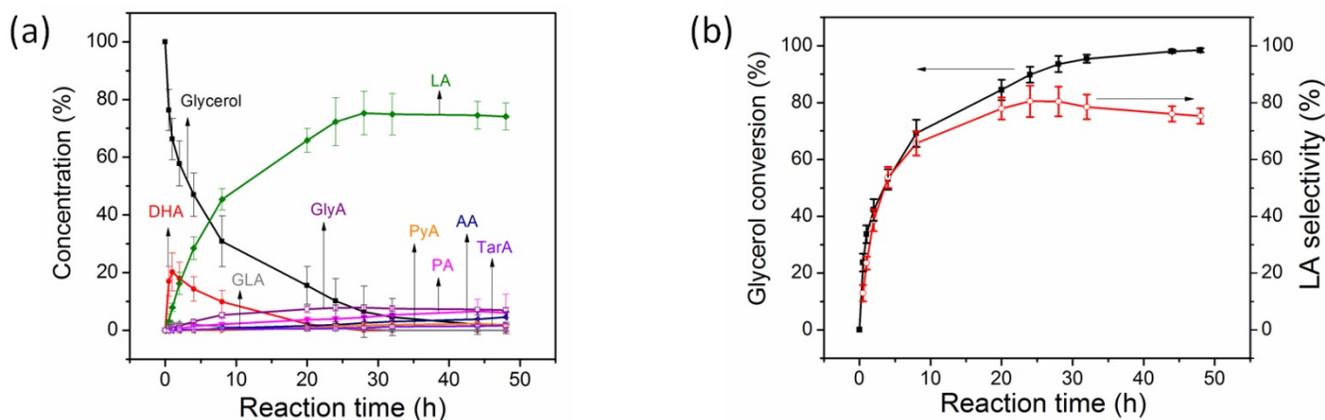
Fig. 2 (a) Concentration profile and (b) glycerol conversion and LA selectivity over Pt/Sn-MFI. Reaction conditions are as follows: 0.2 M glycerol in H_2O, glycerol/Pt (mol/mol) = 350, glycerol/Sn (mol/mol) = 226, pO_2 = 0.62 MPa and 100 °C. The error bars in the figures are from three repeated reactions.
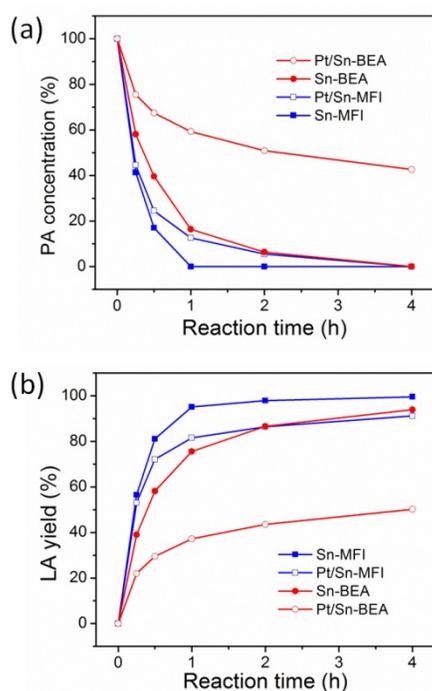
Fig. 3 Reaction profiles for the conversion of PA into LA over Pt/Sn-MFI, Sn-MFI, Pt/Sn-BEA and Sn-BEA catalysts. Reaction conditions are as follows: 0.2 M PA in H_2O, PA/Sn (mol/mol) = 226, 100 °C, batch reactor.

precursors ($H_2PtCl_6 \cdot 6H_2O$) used in our synthesis can diffuse into the zeolite BEA channels because of the large pore size of BEA structure. The Pt^0–Sn^{4+} sites might not be able to catalyze the reaction of PA to LA. In addition, the Pt nanoparticles within the zeolite channels could also block diffusion pathways of the chemicals involved in the reactions. In contrast, it is more difficult for the Pt precursors to diffuse into MFI structure due to a smaller pore size. The activity of the Sn sites in Sn-MFI was affected by the loading of Pt to a lesser extent. As a result, the remarkable catalytic performance of Pt/Sn-MFI in the studied reactions can be attributed to the accessible Sn site, open framework structure and hydrophilic surface.

To understand the reaction pathway and mechanism for the conversion of glycerol into LA over the bifunctional catalysts, additional control experiments were performed. It was found that glycerol reaction does not occur at all on Sn-MFI and Sn-BEA catalysts in the absence of Pt. On the other hand, Pt on siliceous MFI, Pt/silicalite-1, catalyzed the oxidation of glycerol predominantly to GLA (42.0%) and GlyA (32.7%, Table 1, entry 5). The fact that PA and LA were not formed in the absence of either Lewis acid or Pt suggests that the combination of selective oxidation catalyst and isomerization catalyst is indispensable for the tandem reaction pathway. Interestingly, oxidation of glycerol over Pt/silicalite-1 mainly produced GLA and GlyA, not DHA. This result clearly indicates that Pt prefers to catalyze the oxidation of the primary hydroxyl group of glycerol to produce GLA. DHA, a thermodynamically stable isomer of GLA, is formed over the Lewis

Table 2 TOF values for the conversion of PA into LA [a]

	Sn-MFI	Pt/Sn-MFI	Sn-BEA	Pt/Sn-BEA
TOF (h^{-1}) [b]	522	493	372	218

[a] Reaction conditions: 0.2 M PA in H_2O, PA/Sn (mol/mol) = 226, 100 °C, batch reactor. [b] TOF = moles of converted PA divided by moles of Sn per reaction time (h), at 15 min.
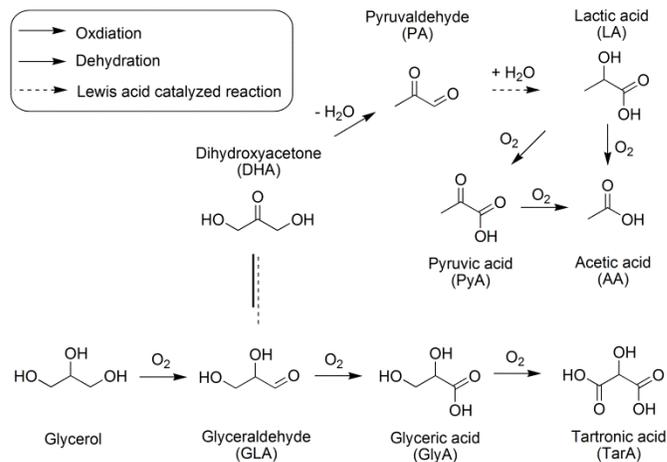
Scheme 1 Proposed tandem reaction pathways for the selective oxidation of glycerol to lactic acid over Pt/Sn-MFI catalyst.

acid sites of Pt/Sn-MFI catalyst. This finding is consistent with previous reports.[17, 42, 43] The subsequent reaction of DHA to LA also occurs over the Lewis acid catalyst. A physical mixture of Pt catalysts supported on activated carbon (Pt/AC, 5 wt% Pt, Sigma Aldrich) and Sn-MFI was also examined for this reaction (Fig. S4, ESI†). The catalytic activity of the mixture (TOF = 0.07 s^{-1}) is much lower than the Pt/Sn-MFI catalyst (TOF = 1.95 s^{-1}) even though the surface area of Pt on AC is much larger than that of Pt on Sn-MFI (Table S1, ESI†). After 20 h, LA selectivity from the physically mixed catalysts exceeded 80%, which is similar to that from Pt/Sn-MFI. However, the Pt/AC catalyst was deactivated obviously faster than the Pt/Sn-MFI and only able to convert 54% of glycerol over 24 h. It has been known that TiO_2 is also an active Lewis acid catalyst.[44] Au/TiO_2, Pt/TiO_2 and Au-Pt/TiO_2 have been used for glycerol oxidation in the presence of NaOH.[23] Under the reaction conditions of this study, Pt/TiO_2 catalyst could not produce any LA due to the weak Lewis acidity, and the main products were GLA, GlyA and TarA (Table 1, entry 7). The catalytic performance of Pt/TiO_2 is similar to Pt/silicalite-1, indicating the Lewis acidity of TiO_2 is not capable of activating the functional groups of the intermediates, GLA and DHA, under the reaction conditions. On the basis of the results, it can be concluded that Sn-MFI acts not only as a Lewis acid catalyst but also as a superior support for Pt catalyst as compared to the activated carbon and TiO_2.

Based on these reaction results, a tandem reaction pathway for selective oxidation of glycerol to LA is proposed in Scheme 1. In a base free environment, Pt nanoparticles predominantly activate the primary hydroxyl group over the secondary one in glycerol, leading to the formation of GLA. The formed GLA can undergo sequential oxidations to GlyA and TarA. In the presence of Lewis acid Sn-MFI catalyst, GLA is quickly converted into thermodynamically more stable isomer, DHA, via intramolecular 1,2 hydride shift reaction.[17, 42, 43] Previous studies have reported that weak Brønsted acid catalyzed dehydration of DHA produces PA.[17, 32] The formed PA undergoes another intramolecular 1,2 hydride shift after hydration of PA, to generate LA. The superior catalytic activity of Sn-MFI can facilitate the reaction from GLA to LA even if the competitive sequential oxidations of GLA can also occur. Moreover, further oxidation of LA on the catalyst is 39 times slower than oxidation of glycerol, which favors a cascade reaction stopping at LA.

The spent catalysts were regenerated by washing with deionized water, ethanol and acetone at room temperature. Unfortunately, a gradual decrease in catalyst activity was observed for the recycled

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catalysts (Fig. S5, ESI†). This trend has also been shown over Pt/TiO$_2$ catalyst for conversion of glycerol into lactate in the presence of base.[23] Further improvement on the reusability of the catalysts could be achieved by using bimetallic Au–Pt on Sn-MFI catalyst, which is an on-going project in our group.

Conclusions

We have developed a base free one-pot reaction pathway to produce LA in high yields from the oxidation of glycerol over a bifunctional Pt/Sn-MFI catalyst under mild conditions. In the cascade reaction route, the selective oxidation of glycerol into GLA proceeds on Pt catalyst. Sn-MFI exhibits outstanding Lewis acidity for converting GLA into DHA and DHA into the final product LA. The superior performance is mainly due to its microporous structure, accessible Sn site and Lewis acidity.

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Notes and references

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