

Letter

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Oxidation of Glycerol to Dicarboxylic Acids Using Cobalt Catalysts

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Abstract

In this paper, the performance of cobalt based catalysts was reported for oxidation of glycerol to dicarboxylic acids such as tartronic and oxalic acids. Cobalt catalysts supported on Mg₃Al(OH)_y(CO₃)_z structures prepared by a two-step modified sol-gel method showed 100% glycerol conversion with 64% and 24% selectivity towards tartronic and oxalic acids under mild conditions (55–70 °C and 0.1 MPa O₂). Surface and bulk characterization by N₂ adsorption/desorption, X-ray diffraction and temperature programmed reduction reveals that the cobalt sites interacting with surface hydroxides are catalytically more active than those incorporated in framework leading to selective glycerol oxidation to dicarboxylic acids in one pot. Based on the experiments at different cobalt contents, temperatures and concentration-time profiles, possible reaction pathways are discussed to explain the selectivity profile. Deactivation of catalyst under certain conditions has been discussed as a result of loss of surface area due to structural changes.

Key words: Oxidation, Dicarboxylic Acids, Cobalt Catalyst, Biomass, Layered Double Hydroxide, Sol-gel

Aqueous phase oxidation (APO) of bio-derived polyols and sugars is one of the most important routes to upgrade renewable biomass to value-added chemicals, particularly for synthesis of carboxylic acids.¹ Dicarboxylic acids (DCA), including glucaric acid, tartronic acid and oxalic acid, derived from biomass, provide major building blocks for everyday products, such as renewable polymers, nylon fibers and BPA-free plastics. These are considered to be among the most promising intermediates in the fledgling renewable chemicals industry, with a potential to substantially replace fossil-derived

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olefins and carboxylic acids.^{1, 2} More importantly, oxidation of biomass to carboxylic acids is feasible at mild conditions (55–70 °C and 0.1 MPa O₂) using relatively inexpensive oxygen to add value to the feedstocks with a net gain in content, showing both environmental and economic advantages over conventional hydrodeoxygenation technologies.

In this context, tartronic acid (TAR, a C₃ DCA) has been widely used as a versatile intermediate in polymer and pharmaceutical applications.²⁻⁵ While TAR production from stoichiometric oxidation of sugars and polyols (*e.g.* glucose, glycerol) by mineral acids/bases often suffers from low selectivity (~ 11%) and large amounts of toxic by-products (NO₂, NaBr),^{6, 7} catalytic oxidation using solid metal catalysts at low temperatures provides a clean atom economical route eliminating the hazards and safety issues.

During the past decade, several reports on TAR synthesis from glycerol (GLY) using supported metal catalysts have appeared in the literature, albeit with limited success. During GLY oxidation, glyceric acid (GLYA) is formed as the primary product, which undergoes further oxidation to TAR (Scheme 1), where oxalic acid (OXA, a C₂ DCA), lactic acid and glycolic acid are often generated as co-products.^{4, 8-10} GLY oxidation to GLYA is easily achievable on various noble metal catalysts. Pt, Pd and Au based catalysts supported on activated carbons, TiO₂ and graphite have been extensively studied for GLY oxidation. These noble catalysts are found to display complete conversion of GLY even under mild conditions (T: 50–70 °C, 0.1–0.7 MPa O₂). GLYA is the dominant product (S: 35–99%) with lactic, glycolic acids being major co-products (S: 19–33%). In most studies, TAR selectivity is however very low (S < 22%).¹⁰⁻¹³ Recently, optimization

of reaction conditions on Au/HY² and PdBi/C¹⁴ have shown good selectivity (Au/HY: 82%, PdBi/C: 93%) towards TAR but poor oxidation activity (Au/HY: 40 h⁻¹, PdBi/C: $0.96 h^{-1}$). Although it is observed that catalyst supports may affect selectivity during oxidation reactions due to tunable metal-support interaction, limited improvement on TAR selectivity has been achieved due to poor secondary oxidation reactions on noble metal catalysts.¹⁵⁻¹⁷ Current research efforts have been primarily focused in two directions: (1) designing well-defined bimetallic noble metal catalysts and (2) incorporating earth abundant metals to noble metal systems. In the former area, synergistic bimetallic PtPd,¹⁸ AuPd,^{5, 13, 19} AuPt^{4, 13, 16} catalysts have been proposed in recent publications (T: 60–90 °C, P_{O2}: 0.1–1 MPa). C-C cleavage reactions are however so significant that glycolic acid, formic acid and CO₂ selectivity is unfavorably enhanced (S: 13-46%).¹⁹ This is attributed to (a) the strong adsorption of aldehyde (-C=O) and carboxylic (-C=OOH) groups in products on noble metal surface that often deactivates the catalysts^{10, 13, 18, 19} and (b) strong tendency for decarbonylation or decarboxylation reactions instead of the desirable secondary oxidation to form TAR and OXA.¹⁷ On the other hand, non-noble metals are believed to be able to tune the binding strength between functional groups and noble metals.^{20, 21} Therefore, in a parallel study, research efforts have been made to incorporate trace amounts of non-noble metal promoters such as Bi, Cu, Ni to noble metal systems.²² These noble/non-noble metal combinations are found to effectively enhance Au, Pt and Pd catalyst activity as well as selectivity, by preventing C-C cleavage of GLY molecules. GLYA and lactic acid are the major products (combined S: 85–99%) while TAR selectivity on these catalysts is still poor (S ~ 32%).

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High costs of noble metal catalysts and limited availability often pose significant economic challenges in practical applications of these catalysts. Replacing expensive noble metals with cost effective non-noble metal catalysts without loss of performance will clearly make the APO of biomass economically sound and more attractive. To the best of our knowledge, there has been no known report on the selective oxidation of GLY particularly to valuable dicarboxylic acids (DCAs), using non-noble metal catalysts. Therefore, in this paper, we report the performances of Co-based catalysts for selective GLY oxidation to TAR and OXA at very mild conditions (55–70 °C, 0.1 MPa O₂ pressure).

Supported Co catalysts on MgO-Al₂O₃ oxides were prepared *via* co-precipitation and modified sol-gel methods. The effects of Co content, catalyst preparation conditions and reaction temperature on catalyst activity and selectivity were investigated systematically for GLY oxidation. Concentration-time profiles on selected Co catalysts were collected and discussed to understand possible reaction pathways for TAR formation. These results were further interpreted based on complementary surface and bulk characterization of the catalysts using N₂ adsorption/desorption measurement (BET), X-ray diffraction (XRD), temperature programmed reduction and desorption (H₂-TPR, CO₂-TPD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) techniques. It is found that the interaction between Co species and MgO-Al₂O₃ support is the key to tune catalyst activity. The information obtained from this study will provide insights into the design of active and selective non-noble metal catalysts for the oxidation of biomass to value-added carboxylic acid products.

Two methods were employed for Co catalyst preparation: (i) In co-precipitation method, a solution of Co, Mg and Al nitrates prepared with predetermined Co/Mg/Al molar ratio of x/3/1 (x = 0.15, 0.30), was precipitated by 0.25 kmol/m³ of NaOH and 0.8 kmol/m³ of Na₂CO₃ solution in a co-current fashion. (ii) In modified sol-gel method, a solution containing only Mg and Al nitrates was precipitated by the same NaOH and Na₂CO₃ solution at room temperature. After 12 h of aging, an aqueous solution of Co nitrate was added to the gel slowly and the slurry was aged for another 12 h. The catalysts obtained from the two methods were calcined and activated under H₂ atmosphere. The resultant materials are denoted as Co_x/Mg₃Al-c and Co_x/Mg₃Al-s respectively (refer supporting information for details).

Benchmark results. Two catalyst samples, $Co_{0.15}/Mg_3Al-c$ and $Co_{0.15}/Mg_3Al-s$ were chosen for characterization and oxidation tests in benchmark studies (see Figure 1). In particular, it is found that $Co_{0.15}/Mg_3Al-c$ catalyst from co-precipitation method results in relatively uniform distribution of Co, Mg and Al element in the catalyst sample [see Figure 1 (a) for bulk (TEM and ICP) and surface (SEM) element composition]. This is because Co species were incorporated into $Mg_3Al(OH)_{yt}CO_3)_z$ framework during precipitation, thus double-layered structures with uniformly incorporated -O-Co-O-groups were achieved. In contrast, for $Co_{0.15}/Mg_3Al-c$ catalyst obtained from modified sol-gel method, elemental analysis shows that Co tends to predominantly disperse on the surface of the support [see Figure 1 (b)]. It is believed that Co^{2+} species replaced the surface -OH groups of $Mg_3Al(OH)_{yt}CO_3)_z$ structure and formed surface M-O-Co-O-M (M: Mg or Al) framework during modified sol-gel process.

Oxidation of GLY (0.22 kmol/m³ in 25 mL aqueous solution) was then carried out on $Co_{0.15}/Mg_3Al$ -c and $Co_{0.15}/Mg_3Al$ -s catalysts (0.2 g) using molecular O_2 as the oxidant (refer supporting information for experimental details). The yields to major products such as GLYA, TAR and OXA (70 °C, 24 h reaction time) on the two catalysts are shown in see Figure 1 (c). It is observed that the yields of TAR and OXA on $Co_{0.15}/Mg_3Al$ -s catalyst are 63.5% and 24.0% respectively at 70 °C after 24 h reaction time, which is significantly higher than that on $Co_{0.15}/Mg_3Al$ -s catalyst [46.9% and 13.4%, see Figure 1 (c)]. The preliminary results obtained from oxidation tests and characterization (using TEM, ICP and SEM) suggest that a modified sol-gel method generates a different Co catalyst ($Co_{0.15}/Mg_3Al$ -s) which provides more accessible sites with low Co coordination numbers on catalyst surface, in comparison with co-precipitation method.

Catalyst characterization. The promising results obtained in these initial benchmark experiments motivated us to further undertake a systematic study on Co catalysts. We first compared the results of H₂-TPR and N₂ isotherms for Co_{0.15}/Mg₃Al-s and Co_{0.15}/Mg₃Al-c catalysts used in the benchmark study (Figure 2, refer Figure S1 for H₂-TPR and N₂ isotherms of other catalysts). As seen from Figure 2 (a), we observed that Co_{0.15}/Mg₃Al-s (green) displays a reduction peak at 200–310 °C while in sharp contrast, Co_{0.15}/Mg₃Al-c (red) exhibits a significant shift of the reduction peak to 290–450 °C. This characterization indicates that the latter catalyst with Co sites in framework tends to interact strongly with Mg₃Al(OH)_y(CO₃)_z structure, thus H₂ needs to overcome much higher barrier to reduce oxide species in the catalyst. Surface Co sites, however, are possibly coordinatively unsaturated and more catalytically active, which can be easily reduced. Furthermore, N₂ isotherm data show that Co_{0.15}/Mg₃Al-s catalyst [Figure 2 (b)]

from modified sol-gel method has much higher surface area (536.3 m²/g) than $Co_{0.15}/Mg_3Al$ -c [Figure 2 (c), 35.8 m²/g] obtained from the co-precipitation method. In addition, pore size and distribution analysis shows that $Co_{0.15}/Mg_3Al$ -s catalyst has relatively larger pore size compared with $Co_{0.15}/Mg_3Al$ -c. It is plausible that, in modified sol-gel method, the addition of Co species separated existing $Mg_3Al(OH)_{y}(CO_3)_z$ layers in the catalyst, replaced surface –OH groups, and peeled off the layered structures *via* electrostatic repulsion between surface Co sites on surface.^{23, 24} Larger pores were thus formed and more surface area exposed. But this is not true in co-precipitation method, where all Co, Mg and Al species formed layered structures with –OH groups on the surface, which formed compact layered structures by removal of water between layers during drying process (condensation).^{25, 26} Therefore less surface area and Co sites are exposed for catalytic reactions.

More detailed catalyst characterization such as TEM (Figure 3), XRD (Figure 4), SEM (Figure S2) and CO₂–TPD (Figure S3) were further carried out for all the catalyst samples, including Co_{0.15}/Mg₃Al-c, Co_{0.30}/Mg₃Al-c, Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s. Specifically, TEM images of Co_{0.15}/Mg₃Al-c [Figure 3 (a)] and Co_{0.30}/Mg₃Al-c [Figure 3 (b)] catalysts reveal the nature of their surface morphologies from co-precipitation method. We find that neither catalyst sample exhibits detectable Co nanoparticles, while both of them exhibit several thin layers with folded structures. EDX mapping in Figures 3 (a) and (b) clearly shows that Co, Mg and Al elements are well dispersed in the samples. This information confirms the uniform incorporation of Co species in Mg₃Al(OH)_y(CO₃)_z framework during catalyst preparation. Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s catalysts [see TEM images in Figures 3 (c) and (d)], prepared by modified sol-gel method, display

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different surface morphologies compared with Figures 3 (a) and (b). This observation implies that the addition of Co species to the Mg₃Al(OH)_{yl}CO₃)_z gel clearly influences the surface morphology of the final catalyst sample.^{25, 26} EDX analysis of Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s catalysts [Figures 3 (c) and (d)] also confirms the uniform distribution of Co element in the bulk of catalyst. SEM images for these two catalysts in Figure S2 also support this attribute. While both co-precipitation and modified sol-gel methods give Co catalysts with good element dispersion, it is found from TEM images [Figures 3 (a) to (d)] that, the observed average crystal/bulk sizes for all samples are in the range of 3–4 nm. In addition, EDX bulk analysis (from TEM) and ICP measurement further reveal that the actual Co/Mg/Al molar ratios in Co_{0.15}/Mg₃Al-c, Co_{0.30}/Mg₃Al-c and Co_{0.15}/Mg₃Al-s catalysts are approximately 1.89/30.55/9.37, 3.76/24.78/8.90 and 1.49/29.6/10.5, respectively, which are consistent with the amounts of metal precursor added during catalyst preparation.

STEM images and element mapping of used $Co_{0.15}/Mg_3Al$ -s catalyst after reaction are also shown in Figure 3 (e). A discernable morphological change is found in this sample when compared to fresh $Co_{0.15}/Mg_3Al$ -s catalyst. We find that several thin layered species, peeled off from bulky phases tend to form more folded structures. Element mapping of two selected regions [shown in Figure 3 (e)] confirms that there is still no Co agglomeration in the used catalyst sample.

To further illustrate the catalytically active species of all Co catalyst samples, XRD powder analysis was conducted (Figure 4), the results of which were also compared with the information obtained from TEM and XPS characterization. In particular, powder diffraction patterns of $Co_{0.15}/Mg_3Al$ -c (a, red), $Co_{0.30}/Mg_3Al$ -c (b, blue), $Co_{0.15}/Mg_3Al$ -s

(c, green) and $Co_{0.30}/Mg_3Al$ -s (d, orange) samples are shown in Figure 4. It is important to mention that XRD patterns in Figure 4 are very similar to the characteristic peaks for layered doubled hydroxide.²⁴⁻²⁶ But we also observe additional peaks for Co species, the intensity of which is low due to the small quantities of Co species existing in catalyst samples. It is necessary to mention that some diffraction peaks for Co and hydrotalcite peaks may overlap, therefore conclusions were made based on the observation of at least two characteristic peaks for certain crystal species. For the four solid samples, we observe characteristic peaks for Co species at 47°, 60°, 62° and 75°,²⁴ Compared to Co_{0.15}/Mg₃Al-c and Co_{0.30}/Mg₃Al-c, Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s catalysts display relatively wider and lower weak peaks at 44°, 47°, 60°, 62° and 75°, suggesting that the crystalline size of Co species is small on this sample. In particular, peaks at 47°, 60° and 62° indicate Co species might exist in the form of CoO while less intensive peaks at 44° and 75° suggest that Co is also presented but in very small quantities (The existence of CoO is also confirmed by XPS characterization shown in Figure S6). For MgO and Al_2O_3 phases, sharp peaks in all samples at 10° and 22° confirm the existence of [003] and [006] crystals of hydrotalcite (Mg₃AlO_{4.5}) structure.²⁶ We have the following findings from XRD patterns. (i) A wide peak at 16° indicates that the spinel MgAl₂O₄ structure (with [111] surface plane) exists in $Co_{0.15}/Mg_3Al$ -s [Figure 4 (c)] and $Co_{0.30}/Mg_3Al$ -s [Figure 4 (d)] catalysts, while this peak is not present in other two catalyst samples. Interestingly, we only observe low indexed [111] facet of spinel MgAl₂O₄ structure, while high index surfaces at 36° (assigned to [311] facet of spinel structure, possibly overlapped with CoO species), 44° (assigned to [400]) and 65° (assigned [440] facet) are very weak.²⁷ This observation further confirm the thin layered structures of Co_{0.15}/Mg₃Al-s and

 $Co_{0.30}/Mg_3Al$ -s catalysts, where complex high surface index structures with several layers are insignificant. (ii) Information from XRD patterns was also used to calculate the approximate crystal/bulk sizes (see detailed calculation in supporting information). The calculation is found to be well consistent with crystal sizes observed from TEM images [see discussion for Figures 3 (a) to (d)]. In particular, it is found that calculated crystal sizes for CoO and hydrotalcite structures for both $Co_{0.15}/Mg_3Al-c$ and $Co_{0.30}/Mg_3Al-c$ catalysts are 3 nm and 4.9 nm. However, for Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s catalysts, CoO particle sizes display negligible changes (~ 4 nm), while the mean particle size for hydrotalcite structure are small (~ 3 nm). The high intensity of spinel structure peaks observed on Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s catalysts suggest that thin layered structures are dominant in these two samples. (iii) In addition, the 57° peak in Co_{0.30}/Mg₃Al-s sample suggests the formation of thin layered Mg₃AlO_{4.5} [1013] structure with 8.98 Å spacing,²⁵ suggesting good stability of layered structures after calcination and activation.²⁸⁻³⁰ The following conclusions were made based on the findings discussed above. (I) It is plausible that the addition of Co species after layered double hydroxide structures form prevent condensation among hydroxide layers thus thin layered structures are retained. (II) The immobilization of Co species after the Mg₃Al(OH)_v(CO₃)_z structures were formed often results in the replacement of surface –OH groups with M– O-Co-O-M network. (III) The formation of such structures can lead to enhanced surface sites exposed for catalytic reactions.²³ (IV) CoO species should be the major active sites for oxidation reactions. The information obtained from XRD agrees very well with the observation from surface area analysis, H2-TPR and TEM images. CO2-TPD characterization was also conducted to measure the basicity on different Co catalysts, the

results of which are shown in Figure S3. In general, we find all samples exhibit strong CO_2 -TPD signals below 500 °C, indicating that basic sites with weak (~ 150 °C) or medium (~ 380 °C) strength are dominant on these catalysts. Additionally, XPS characterization data was conducted to further confirm oxidation states of Co species and nature of active sites (see Figure S6 and interpretation in supporting information). Two observations were found from XPS characterization: (i) Co species mainly exist in the form of CoO; (ii) Excitation of electrons of core holes of Co element might be the key for enhanced catalytic activity.

Oxidation reaction results. We studied the GLY oxidation on $Co_{0.15}/Mg_3Al-c$, Co_{0.30}/Mg₃Al-c, Co_{0.15}/Mg₃Al-s and Co_{0.30}/Mg₃Al-s catalysts. It is found that GLY conversion without a catalyst is only 4.3% after 6 h and 13% after 24 h (at 70 °C, 0.1 O₂, entries no. 1 and 2 in Table 1). In addition, the selectivity towards TAR is below 29% after 24 h without catalysts. At 70 °C, Co_{0.15}/Mg₃Al-c catalyst showed 16% conversion within 6 h reaction time (entry no. 3 in Table 1), the selectivity towards GLYA, TAR and OXA being 58%, 32% and 4% respectively with almost complete material balance based on liquid phase products. When more Co is present, $Co_{0.30}/Mg_3Al$ -c catalyst (entry no. 5) exhibited higher conversion (22%) and 53%, 38% and 3% selectivities towards these acids (GLYA, TAR and OXA) at the end of the 6 h run. Other carboxylic acids, including lactic, glycolic and formic acids accounted for approximately 2-5% of the products. As seen in entry no. 7, GLY conversion on $Co_{0.15}/Mg_3Al$ -s catalyst is 47%, much higher than $Co_{0.15}/Mg_3Al-c$, although selectivity to GLYA, TAR and OXA is still comparable with the previous two catalysts. Entry no. 9 shows that $Co_{0.30}/Mg_3Al$ -s display slightly higher TAR and OXA yield compared with $Co_{0.15}/Mg_3Al$ -s catalyst. Catalytic activity (TOF, see

Table S1 and S2 for detailed calculation) measured (at < 25 % conversion) on $Co_{0.15}/Mg_3Al$ -c and $Co_{0.30}/Mg_3Al$ -c catalysts are 1.06 h⁻¹ and 0.80 h⁻¹ at 70 °C, respectively. In contrast, $Co_{0.15}/Mg_3Al$ -s and $Co_{0.30}/Mg_3Al$ -s catalysts exhibit a remarkable TOF of 3.91 h⁻¹ and 3.86 h⁻¹ respectively. These results suggest that catalyst prepared by modified sol-gel method shows better oxidation performance (both activity and TAR selectivity) than the ones from co-precipitation method.

Based on the catalyst characterization as well as reaction results on catalyst from Table 1, it is clear that the crystal sizes for CoO, hydrotalcite and spinel structures are very small, suggesting uniform precipitation and deposition of Co, Mg and Al species during catalyst preparation. More importantly, by altering the sequence of Co species addition, the interaction between Co and catalyst support can be well tuned, which influences surface physical and chemical properties and catalytic performances.

When reaction time is prolonged from 6 h to 24 h, complete conversion of GLY (100%) was observed on all four catalysts. However, the selectivity towards TAR is different. Specifically, both $Co_{0.15}/Mg_3Al$ -c (entry no. 4 in Table 1) and $Co_{0.30}/Mg_3Al$ -c (entry no. 6) gave 45–47% TAR selectivity, while on $Co_{0.15}/Mg_3Al$ -s (entry no. 8) and $Co_{0.30}/Mg_3Al$ -s (entry no. 10) catalysts it is 63% and 64%. In addition, GLYA selectivity is about 29% on $Co_{0.15}/Mg_3Al$ -c and $Co_{0.3}/Mg_3Al$ -c catalysts. But this value is much lower on $Co_{0.15}/Mg_3Al$ -s catalyst (2%). For OXA, the selectivity is 16% based on $Co_{0.15}/Mg_3Al$ -c and $Co_{0.3}/Mg_3Al$ -c catalysts. Selectivities towards lactic, glycolic and formic acids are also relatively higher on $Co_{0.15}/Mg_3Al$ -s and $Co_{0.30}/Mg_3Al$ -s catalysts. Based on the

comparison of experiments in entries no. 1 and 2, with entries 3–10, it is clear that the addition of Co catalysts significantly enhance GLY oxidation to dicarboxylic acids.

We carried out further experiments on $Co_{0.15}/Mg_3Al$ -s catalyst and measured concentration-time profiles at 70 °C and 55 °C. As seen from Figure 5 (a), GLY concentration decreases from 0.22 kmol/m³ to 0.12 kmol/m³ within 6 h reaction time. The GLYA concentration increases to a maximum value of 0.058 kmol/m³ at 9 h and then decreases to almost zero during a 24 h reaction. For TAR, its concentration increases slowly at the beginning, then further increased to approximately 0.14 kmol/m³ at 24 h, suggesting that secondary oxidation (oxidation of GLYA) becomes dominant with the progress of reaction. In another parallel reaction, we find that OXA formation rate is very low when GLYA concentration is high, but its concentration is enhanced significantly after 10 h. This phenomenon indicates that C-C cleavage reaction is another major reaction when GLYA is consumed in the reaction medium.

In contrast, at 55 °C [Figure 5 (b)], GLY concentration decreases to about 0.16 kmol/m³ after 6 h reaction. The peak value of GLYA concentration is about 0.055 kmol/m³ around 18 h reaction, after which it decreases to 0.022 kmol/m³ after 36 h. TAR concentration increases gradually with reaction time, while the overall OXA concentration is as expected lower than at 70 °C.

Plausible reaction pathways. At both reaction temperatures studied, we find that the concentration of OXA (a C_2) is relatively low at the beginning but undergoes a rapid increase once GLYA (a C_3) concentration starts decreasing. This observation suggests that OXA is generated from further reaction of GLYA. Correspondingly, a C_1 species (*e.g.* formic acid) should also form at the same time. However, contradicting this

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hypothesis, the concentration of formic acid (in "Others") is always negligible throughout the reaction period. To understand this further, the conversion (X), selectivity (S) and carbon balance (C%) were plotted *vs* reaction time at 70 °C and 55 °C in Figure 6. It is observed [see Figure 6 (a)] that GLY conversion increases to 65% within 9 h reaction at 70 °C, where GLYA selectivity is almost constant. After 9 h, significant decrease in GLYA selectivity is observed while both TAR and OXA selectivities increase. The selectivity towards glycolic and formic acids ("Others") is negligible throughout the whole reaction time. The total C% decreases from 100% at the beginning to approximately 86% after 24 h. Therefore, this C deficit based on analysis of liquid phase samples might result from decarboxylation of GLYA, resulting in CO₂ generation. The CO₂ is converted into a sodium bicarbonate salt. Inorganic salts could not be quantified using HPLC analysis, thus accounting for the observed C deficit.

A similar selectivity trend with time is also observed at 55 °C [Figure 6 (b)], although the selectivity to OXA and C deficit is not as significant as at 70 °C. In both cases, the final TAR yield (complete GLY conversion) is approximately 63%, although it was obtained at different reaction times. Based on the product distribution shown in Figures 5 and 6, plausible reaction pathways for GLY oxidation to TAR is discussed here. As shown in Scheme 2, primary oxidation of GLY leads to the formation of GLYA in the presence of Co catalysts, while secondary oxidation to TAR also occurs simultaneously. As more GLYA is formed in the aqueous phase, C–C cleavage, a parallel reaction to secondary oxidation becomes significant. Therefore, OXA (C_2 species) formation is noticed. Due to decarboxylation reaction of GLYA, one C_1 is lost to carbonate. Combined selectivity towards lactic, glycolic and formic acids is almost negligible.

We also tested $Co_{0.15}/Mg_3Al$ -s catalyst for glucose oxidation at 70 °C and 0.1 MPa O₂. Complete conversion was obtained after 10 h reaction time with major products including TAR (S: 29%), GLYA (19.4%), gluconic acid (9.5%), glucaric acid (11.1%) and other monocarboxylic acids (lactic acid, glycolic acid, formic acid: 19.5%). While activity and selectivity is not as high as the recently reported bimetallic PtCu/TiO₂ catalyst,³¹ these results nevertheless show that the proposed Co catalysts containing earth-abundant metals are inexpensive alternatives for converting some cellulosic feedstocks to value-added DCAs (*e.g.* GLY to TAR). Further optimization studies aimed at enhancing selectivity to desired products are needed.

We also carried out recycle experiments to study the stability of $Co_{0.15}/Mg_3Al$ -s catalyst at 70 °C for GLY oxidation. As seen from Figure 7, the conversion of GLY decreases from 47% to 35% after 3rd recycle, suggesting gradual catalyst deactivation. However, the selectivities towards TAR and GLYA are almost unchanged. While no Co species agglomeration were observed on used $Co_{0.15}/Mg_3Al$ -s catalyst, STEM images shown in Figure 3 (e) suggest that more folded structures were formed after recycles. In addition, leaching tests on used $Co_{0.15}/Mg_3Al$ -s catalyst were also carried out. It is found that the total ratios of metal leaching for Co, Mg and Al species (based on fresh $Co_{0.15}/Mg_3Al$ -s catalyst) are 0.1%, 0.1% and 68.2%, respectively. It is clear that Co and Mg species were stable while significant amounts of Al species were leached after recycles. Therefore it is plausible that the leaching of Al species during recycles might induce loss of surface area and catalytic activity. These results suggests that layered structures are important for keeping Co catalysts active, while Al species are not stable and leached during experiments. While finding an effective way of immobilizing Co species on layered

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structures is the focus of current work, future work should be focused on redesigning stable catalyst supports.

Conclusions

The performance of non-noble metal Co-based catalysts is reported for the oxidation of glycerol at mild conditions to value added dicarboxylic acids such as tartronic acid. Co catalysts prepared by modified sol-gel method show 88% combined selectivity towards tartronic acid and oxalic acid with complete conversion of glycerol at mild reaction conditions. Concentration–time profiles reveal a possible reaction pathway involved in formation of tartronic acid and other co-products in aqueous phase. The proposed Co catalysts can eliminate the disadvantages of the conventional stoichiometric oxidation by mineral acids, as well as the need of expensive catalysts for oxidative conversion of biomass feedstocks.

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Figures, Tables and Schemes

Figure 1. Schematic description of (a) $Co_{0.15}/Mg_3Al$ -c and (b) $Co_{0.15}/Mg_3Al$ -s and (c) their catalytic performances in glycerol oxidation at 70 °C and 0.1 MPa O₂ (experimental conditions: 0.5 g glycerol, 1.5 g NaOH, 25 mL, 0.2 g solid catalysts, 24 h). Bulk and surface compositions of Co, Mg and O were analyzed by ICP/TEM-EDX and SEM-EDX respectively.





Figure 2. Characterization of $Co_{0.15}/Mg_3Al$ -c and $Co_{0.15}/Mg_3Al$ -s using (a) temperature programmed reduction by H₂ (TPR-H₂), (b, c) N₂ isotherm and pore distribution (inset).

Co_{0.15}/Mg₃Al-c

Co





(b)



(c)



(e)

Figure 3. TEM images and EDX mapping of fresh (a) $Co_{0.15}/Mg_3Al$ -c, (b) $Co_{0.30}/Mg_3Al$ -c, (c) $Co_{0.15}/Mg_3Al$ -s, (d) $Co_{0.30}/Mg_3Al$ -s and (e) STEM and element mapping used $Co_{0.15}/Mg_3Al$ -s catalysts.





Figure 4. XRD patterns of fresh (a) $Co_{0.15}/Mg_3Al$ -c, (b) $Co_{0.30}/Mg_3Al$ -c, (c) $Co_{0.15}/Mg_3Al$ -s and (d) $Co_{0.30}/Mg_3Al$ -s.



Figure 5. Concentration-time profiles of glycerol oxidation on $Co_{0.15}/Mg_3Al$ -s catalyst at (a) 70 °C and (b) 55 °C (refer to Table 1 for other experimental details).



Figure 6. Conversion/selectivity/carbon balance *vs* time profiles of glycerol oxidation on $Co_{0.15}/Mg_3Al$ -s catalyst at (a) 70 °C and (b) 55 °C (refer to Table 1 for other experimental details).





Other experimental conditions are provided in Table 1.

	Catalyst	TOF (h ⁻¹)	Time (h)	X (%)	S (%)			
no.					TAR	GLYA	OXA	"Others"
1	Blank experiments	-	6	4.3	14.6	79.1	-	3.2
2			24	13.0	28.2	54.3	4.3	9.8
3	Co _{0.15} /Mg ₃ Al-c	0.88	6	16.1	32.3	58.1	4.0	5.2
4			24	100	46.9	29.2	13.4	4.3
5	Co _{0.30} /Mg ₃ Al-c	0.64	6	21.7	38.0	52.8	3.1	2.0
6			24	100	45.4	28.8	16.2	7.6
7	Co _{0.15} /Mg ₃ Al-s	3.01	6	47.0	36.7	49.1	4.2	3.4
8			24	100	63.5	2.1	24.0	3.8
9	Co _{0.30} /Mg ₃ Al-s	2.91	6	63.2	40.1	46.1	5.9	4.4
10			24	100	64.3	2.0	24.4	2.8

Experimental conditions: 0.5 g glycerol, 1.5 g NaOH, 25 mL, 0.2 g solid catalysts. "Others": lactic, glycolic and formic acids.



Scheme 1. Glycerol conversion to mono and dicarboxylic acids



Scheme 2. Plausible reaction pathways for tartronic and oxalic acids formation from glycerol







TOC Figure