PAPER

Copper-based catalysts for the efficient conversion of carbohydrate biomass into γ-valerolactone in the absence of externally added hydrogen†

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The direct production of γ-valerolactone (GVL), an essential component for next-generation biorefineries, by a straightforward conversion of bio-derived levulinic acid (LA)/formic acid (FA) streams without the externally added fossil-fuel H_2 has rarely been achieved. We describe here a sustainable, cost-effective and highly efficient protocol for directly converting a 1 : 1 aqueous mixture of LA and FA into GVL in high yields. The process is catalyzed by an earth-abundant and robust copper-based metal oxide catalyst, in which the high performance of the copper catalyst for the *in situ* generation of hydrogen gas in the systems by the highly selective decomposition of FA in an aqueous medium is essential. This catalytic system is also effective with raw cellulosic biomass, such as giant reed, as the starting material, thus paving a new way toward a renewable chemical industry.

Broader context

Selective hydrogenation of levulinic acid (LA) to produce γ-valerolactone (GVL), a versatile renewable compound for the production of both energy and carbon-based consumer products, is an important transformation for biorefinery concepts based on platform chemicals. Although a plethora of methods based on Group VIII catalytic metals are known to be effective for this key transformation using hydrogen gas, it has still remained a great challenge to directly produce GVL by a convenient and straightforward conversion of bio-derived formic acid (FA)/LA streams without external hydrogen supply. Herein, we report an efficient and cost-effective protocol for the high yield production of GVL only from bio-derived FA/LA streams. In contrast to previously known procedures, our process relies solely on the use of bio-derived FA as the hydrogen source for a noble-metal-free GVL production. The process is catalyzed by an earth-abundant, inexpensive and robust copper-based metal oxide catalyst, in which the high catalytic performance of the copper catalyst for the *in situ* H_2 generation *via* selective FA decomposition is essential. The present finding opens the possibility of the cost-competitive production of GVL from biomass and the development of a new sustainable, economically affordable process for the targeted conversion of bio-derived feedstocks with minimum utilization of external fossil fuel-based hydrogen sources.

Introduction

The utilization of biomass provides an attractive way to meet the challenges concerned with the continued depletion of fossil reserves as well as the continued increase in chemical and energy demands.[1] One special opportunity to satisfy the energy and raw material requirements of society is *via* the valorization of a lignocellulosic material, which is abundant, inexpensive, and renewable.[2] Comprising the inedible component of terrestrial biomass, lignocellulosics have the added advantage that they do not directly compete with agricultural food production.[3] In this connection, one particularly attractive and viable approach is the conversion of the lignocellulosic biomass into a set of defined platform molecules that can be used as key intermediates to produce diverse value-added chemical structures.[2] A full optimization of the relevant reaction pathway is believed to be essential to build novel sustainable supply chains for the production of biorenewable transportation fuels and industrial chemicals.[2,3] The principle challenge for the implementation of such advanced biorefinery concepts lies in the development of new, innovative and economically feasible catalytic methods which can allow the selective transformation of highly functionalized bio-derived feedstocks to a broad range of valuable chemicals and materials.

One key renewable compound identified for next-generation biorefineries is γ-valerolactone (GVL),[4] which has several desirable properties that make it an excellent sustainable feedstock for the production of both energy and carbon-based consumer products. The attractiveness of GVL as a feedstock has increased with continuing advances in its application in the synthesis of many useful chemicals,[4c,4e–g] projecting an important market volume of this molecule. GVL can be obtained in

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† Electronic supplementary information (ESI) available: Experimental details and supplemented data. See DOI: 10.1039/c3ee40857d

high yields through the reduction of levulinic acid (LA),[5] a versatile precursor easily accessible from the acid-catalyzed hydrolysis of lignocellulosics. Although a plethora of Group VIII metals,[6] notably ruthenium, have been shown to facilitate LA reduction, these procedures rely mostly on the use of expensive, petrochemically derived hydrogen gas.[4,7] H_2 derived from reforming of non-renewable natural gas or petroleum makes the process dependent on fossil resources. Thus, any new strategy that can minimize the utilization of externally added H_2 would be highly desirable. An ideal sustainable protocol for this purpose is the straightforward use of bio-derived formic acid (FA) as an expedient alternative source of hydrogen.[8] Given the fact that FA is invariably co-produced in equimolar amount along with LA during the biomass dehydration process, this procedure can inherently eliminate the need for an external H_2 supply. However, the implementation of such a truly convenient and green approach for making GVL remains challenging,[8,9] largely due to the lack of readily accessible, applicable and reusable solid catalysts that are sufficiently active and selective for H_2 production from FA under the hydrothermal processing conditions.

We have recently reported an efficient heterogeneous catalytic system for the direct conversion of bio-derived aqueous LA/FA streams into GVL catalyzed by zirconia supported small Au nanoparticles (Au/ZrO_2), in which the high catalytic performance of supported Au NPs for the *in situ* generation of H_2 gas *via* selective decomposition of FA under mild aqueous conditions is essential.[9] Nevertheless, the high cost of gold and its limited availability have necessitated the development of catalysts based on earth-abundant elements for this transformation. Simple Cu-based catalysts present a promising candidate, as they are known for their high activity toward FA decomposition in the vapour phase.[10] Moreover, it is also established that Cu catalysts are very selective for a number of hydrogenation reactions,[11] for example, the conversion of bio-derived carboxylic acids to their corresponding lactones under a H_2 atmosphere.[12] Herein, we show that bio-derived LA/FA streams can be quantitatively converted to GVL using an inexpensive nanocomposite copper/zirconia catalyst under mild aqueous conditions (160–200 °C) without the need for an external hydrogen source (Scheme 1). Prior to this work, there are no precedent examples in the literature of recyclable copper-based catalysts for the direct transformation of bio-derived aqueous LA/FA streams into GVL.
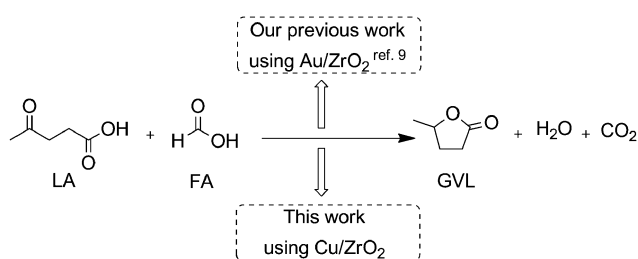
Results and discussions

At the start of our work, the selective decomposition of FA in an aqueous medium, an essential step for the desired LA transformation, was investigated over various Cu-based solid catalysts. The decomposition of FA, the simplest carboxylic acid, has long been a popular model reaction for better understanding the more complex chemistry of carboxylic acid conversion reactions. The decomposition of FA may proceed *via* decarboxylation (dehydrogenation), $HCOOH \rightarrow CO_2 + H_2$ with $\Delta G = -48.4$ kJ mol^{-1} or decarbonylation (dehydration), $HCOOH \rightarrow CO + H_2O$ with $\Delta G = -28.5$ kJ mol^{-1}.[13] As one of the main requisitions for subsequent technical applications is CO-free H_2, the key point in FA decomposition would be to avoid the formation of CO. In general, studies on the heterogeneous FA decomposition have been mostly concentrated on the gas-phase catalysis.[13,14] For the liquid-phase decomposition of FA by heterogeneous catalysts, a number of supported as well as unsupported noble metals including Pd, Pt, Au and their corresponding bimetallic alloys such as Pd–Au have been reported to be effective.[15] Nevertheless, few solid non-noble metal catalysts that can lead to the fast, selective decomposition of FA under mild aqueous conditions have been reported.

Fig. 1 shows the comparison of various Cu-based catalysts in a batch autoclave reactor for the possible direct production of H_2 and CO_2 from the decomposition of a diluted aqueous solution of FA (0.43 M) for 5 h at 160 °C. The H_2/CO_2 molar ratios obtained from most catalysts under these conditions were around 1 : 1 with very low CO contents, indicating that the selective decomposition of FA can take place under these reaction conditions. However, most catalysts were not active for the
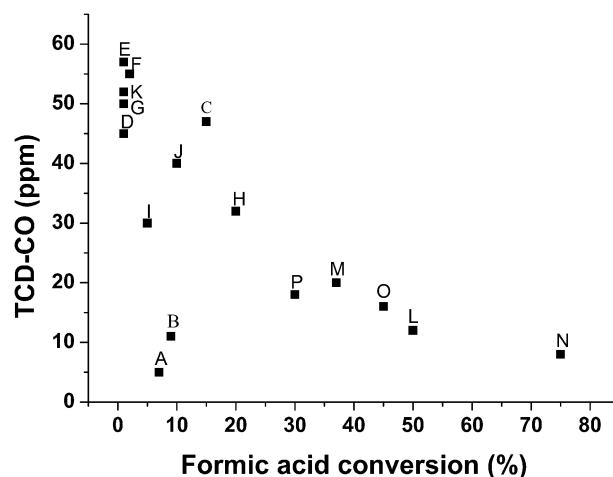
Fig. 1 FA conversion and CO content for different solid catalysts. (*Reaction conditions*: FA (18 mmol), water (40 mL), $n_{FA}/n_{metal} = 24$, $T = 160$ °C, $t = 5$ h) (A) commercial Cu/ZnO–Al$_2$O$_3$, (B) 30Cu/ZnO–Al$_2$O$_3$–CP, (C) 30Cu/ZnO–CP, (D) 30 Fe/ZrO$_2$–OG, (E) 30Co/ZrO$_2$–OG, (F) 30Ni/ZrO$_2$–OG, (G) 30Cu/SiO$_2$–Imp, (H) 30Cu/CeO$_2$–OG, (I) 30Cu/TiO$_2$–DP, (J) 30Cu/ZrO$_2$–DP, (K) 30Cu/ZrO$_2$–Imp, (L) 30Cu/ZrO$_2$–OG, (M) 10Cu/ZrO$_2$–OG, (N) 20Cu/ZrO$_2$–OG, (O) 40Cu/ZrO$_2$–OG, (P) 50Cu/ZrO$_2$–OG. Note: CP the conventional carbonate co-precipitation, DP urea deposition-precipitation (DP), OG oxalate gel-coprecipitation method, Imp incipient wetness impregnation.

Scheme 1 Transformation of LA with equimolar formic acid to GVL over heterogeneous catalysts.

direct dehydrogenation of FA (conversion level <30%) under our experimental conditions. Conventional 30Cu/ZnO(C), 30Cu/ZnO–Al$_2$O$_3$(B) and industrial Cu/ZnO–Al$_2$O$_3$ methanol synthesis catalysts (A) gave either low activity or high CO content. It is interesting to note that the Cu/ZrO$_2$-based catalysts (L) prepared from the oxalate-gel (OG) coprecipitation method can lead to good FA conversion with consistently low CO content (<20 ppm), which is of particular interest for the direct utilizing of FA as a convenient source of hydrogen. Moreover, a clear advantage of the 30Cu/ZrO$_2$–OG catalyst over other first row Group VIII metals (base metals) with the same metal loading was also noticed when FA was subjected to decomposition using identical OG-derived Fe/ZrO$_2$, Ni/ZrO$_2$ or Co/ZrO$_2$ materials under otherwise identical conditions.

As the combination of Cu with zirconia appeared to be essential for achieving high catalytic activity for selective FA decomposition, the next step was to further improve the FA conversion while keeping the CO formation at its minimum. In line with the well-established role of Cu as the main active component for methanol synthesis or related processes,[16] the dispersion of metallic copper has been documented to be especially influential for the gas-phase decomposition of FA over supported Cu catalysts.[10a,b,17] We have, therefore, further examined a series of Cu/ZrO$_2$ catalysts in which the copper loading was varied in the 10–50 wt% range. Table 1 shows the Cu dispersions and sizes of the five Cu/ZrO$_2$-based catalysts prepared from the OG method after reductive activation. As indicated in Fig. 1, the catalytic performances were strongly dependent on the copper content. Among the catalysts examined at this stage of the study, the Cu/ZrO$_2$–OG catalyst containing 20 wt% Cu exhibited, by far, the best catalytic performance. At this juncture, it is interesting to note that there is only a weak relationship between the Cu dispersion or Cu particle sizes and the performance of the Cu/ZrO$_2$-based samples, inferring that the synergistic interaction between Cu and the underlying zirconia matrix plays a key role in determining the FA decomposition activity of these samples.[15a] With the 20Cu/ZrO$_2$–OG catalyst, the FA conversion can reach an impressive value of 75% at 160 °C within 5 h. This result is remarkable, and becomes more relevant to all these experiments, with only a very low level of CO (<20 ppm) being detected in the gas phase products.

The promotion of the catalytic activity without appreciable CO formation for FA decomposition at the above mentioned conditions over 20Cu/ZrO$_2$–OG clearly reflects the fast surface kinetics due to the intimate interaction of the Cu formed after reduction with the underlying zirconia support. It is important to fully characterize the catalyst for the further development of this and the related materials for this reaction. From the X-ray diffraction (XRD) data presented in Fig. S1† (see ESI), the calcined form of the as-synthesized 20 wt% Cu/ZrO$_2$–OG catalyst showed merely tetragonal ZrO$_2$ crystallites. After pre-reduction under a 5 vol% H$_2$/Ar atmosphere at 300 °C for 2 h, a weak peak positioned at 43.3° ascribed to the (111) lattice plane of the metal Cu appeared. This, together with the fact that no bands for CO adsorbed on Cu$^+$ or Cu$^{\delta+}$ can be seen from the FTIR spectra (Fig. S2†) of the reduced form of the catalyst, indicates that CuO was completely reduced into metallic Cu in the working sample.[16d] The average size of the resultant Cu^0 particles was estimated to be ca. 12 nm based on the Scherrer equation analysis. This scenario can be further corroborated by transmission electron microscopy (TEM), temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS) analyses (see Fig. S3, S4 and S8†).

Next, the reaction parameters were optimized for the FA decomposition by the variation of the temperature and feed concentration (see Table S1 in the ESI†). First, the effect of the reaction temperature was investigated. In contrast to the significantly attenuated FA decomposition observed from the experiments performed at 140 °C, an increase in temperature from 160 to 180 °C led to a dramatic increase in the FA conversion rate from 189 to 276 mmol g$_{Cu}^{-1}$ h^{-1}. As a result, at 180 °C, complete FA conversion can be readily attained within 3 h. As the temperature was further increased to 200 °C, the time required for the completion of the reaction was greatly shortened to 1 h. Of yet further interest is that an even more effective FA decomposition can be achieved through the use of a FA solution with a higher concentration (Table S1,† entry 9). In this particular case, the H$_2$ evolution rate is measured to be 2.240 mL H$_2$ min^{-1} with 0.86 M FA at 180 °C. This value compares favorably with 5.624 mL H$_2$ min^{-1} established recently with Au/ZrO$_2$.[9]

Based on the above results, we next focused on the direct use of FA as the sole hydrogen source to facilitate the reduction of LA in aqueous medium. The results in Table 2 show that it is possible to convert LA to GVL by consuming the H$_2$ generated in situ by FA decomposition over 20Cu/ZrO$_2$–OG. It can be seen from entry 1 in Table 2 that the conversion of simulated LA/FA

Table 1 Physicochemical properties of various Cu/ZrO$_2$ catalysts

Entry	Catalysts	Cu loading (wt%)	S_{BET} (m^2 g^{-1})	S_{Cu}[a] (m^2 g$_{cat}^{-1}$)	S_{Cu}[a] (m^2 g$_{Cu}^{-1}$)	D_{Cu} (%)	d_{Cu}[b] (nm)
1	Cu/ZrO$_2$–OG	10	28	2.8	28.0	4.3	11.2
2	Cu/ZrO$_2$–OG	20	40	9.5	47.5	7.4	12.3
3	Cu/ZrO$_2$–OG	30	37	12.5	41.7	6.5	14.6
4	Cu/ZrO$_2$–OG	40	63	14.7	36.7	5.7	20.8
5	Cu/ZrO$_2$–OG	50	36	16.9	33.8	5.2	21.6
6	Cu/ZrO$_2$–DP	30	31	1.2	4.0	0.6	25.3
7	Cu/ZrO$_2$–Imp	30	20	1.0	3.3	0.5	79.0

[a] Cu metal surface area determined by N$_2$O titration. [b] Estimated from XRD data using the Scherrer equation.

3310 | Energy Environ. Sci., 2013, **6**, 3308–3313

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Table 2   Conversion of LA into GVL over the 20Cu/ZrO$_2$–OG catalyst^a

Entry	T (°C)	t (h)	Conv. (%)^b	Sel. (%)^{b,c}
1	180	5	60	100
2	180	8	65	100
3	180	10	66	100
4	180	12	67	100
5	200	5	100	100
6^d	200	2	100	100

^{a} *Reaction conditions*: LA (18 mmol), FA (18 mmol), H$_2$O (40 mL), 20 Cu/ZrO$_2$–OG (240 mg, n_{LA}/n_{Cu} = 24), N$_2$ (1 MPa). ^{b} The conversion and selectivity was determined by GC with bis(2-methoxyethyl) ether as the internal standard. ^{c} GVL selectivity based on LA conversion. ^{d} LA (18 mmol), H$_2$O (40 mL), 20 Cu/ZrO$_2$–OG (240 mg, n_{LA}/n_{Cu} = 24), H$_2$ = 4 MPa.

streams containing equimolar concentrations (0.43 M) of LA and FA proceeded smoothly at 180 °C. Nevertheless, at this temperature, the reaction can only lead to the production of GVL as the target product in moderate yields. Extending the reaction time did not appreciably improve the yields of GVL (Table 2, entries 2–4). As expected, increasing the reaction temperature to 200 °C led to a substantial increase in the yields of the target product (Table 2, entry 5). Such variation is fully consistent with the results in Table S1† as shown for FA decomposition, which is more favored at elevated temperatures. At 200 °C with the 20Cu/ZrO$_2$–OG catalyst, we were finally able to attain a quantitative GVL formation within 5 h. As far as we are aware, the direct transformation of biorelevant LA/FA streams to make GVL in excellent yield using inexpensive and earth abundant materials has not been reported before this work.

As described above, H$_2$ was produced during the above FA-mediated LA reduction reactions, whose partial pressure reached 2 MPa in the closed reactor at 200 °C in the initial period of 1 h. To explore the reaction performed with 20Cu/ZrO$_2$–OG in detail, the product evolution for the direct reduction of LA with FA at 200 °C was followed by continuous sampling using gas chromatography. As shown in Fig. S5,† the desired product, GVL, was produced as the exclusive product during the whole reaction process. Furthermore, we have confirmed by a separate experiment that under identical conditions, the LA reduction can proceed to completion within 2 h when using a stoichiometric amount of high pressure H$_2$ (4 MPa) as the sole reductant (Table 2, entry 6). A careful analysis of the kinetic data allows us to estimate that the reduction rate of LA using H$_2$ (188.9 mmol g$_{Cu}^{-1}$ h^{-1}) is around 2.5 times higher than that using FA (75.5 mmol g$_{Cu}^{-1}$ h^{-1}). In contrast to the previously reported Au/ZrO$_2$ catalytic system,[9] wherein aqueous hydrogenation of LA is the rate-determining step for the overall conversion of LA with FA, it appears that both the initial FA decomposition and the subsequent LA hydrogenation reactions are the kinetically relevant steps in the present Cu/ZrO$_2$–OG-catalyzed system.

The above results show that the Cu/ZrO$_2$-based catalysts can facilitate the high yield conversion of a 1 : 1 aqueous mixture of LA and FA into GVL without any external H$_2$ supply. The catalytic activity of the 20Cu/ZrO$_2$–OG catalyst was further compared with the previously reported Au/ZrO$_2$ catalyst in the direct reduction of LA with FA at 200 °C. The intrinsic activities in terms of the mass-specific reaction rates (mmol$_{GVL}$ g$_{metal}^{-1}$ h^{-1}) based on total metal atoms as well as the turnover frequencies (TOF) based on surface metal atoms are listed in Table S2.† It is revealed that the specific activity based on the low level LA conversion over Au/ZrO$_2$ is up to 1.23 × 10^4 mmol$_{GVL}$ g$_{metal}^{-1}$ h^{-1}, which is over 130 times more active than the present Cu/ZrO$_2$ catalytic system. Despite the significantly lower mass-specific reaction rate of Cu/ZrO$_2$ relative to that of Au/ZrO$_2$ under identical reaction conditions, the use of earth abundant copper may be justified by its cost (less than 0.008069 USD g^{-1}) and availability.[18]

One of the main issues when using supported copper catalysts in the hydro-conversion of carboxylic acids in the liquid phase is their deactivation due to copper leaching.[8a,9] To examine the likely stability of the Cu/ZrO$_2$–OG catalysts for direct GVL production, the reusability of the 20Cu/ZrO$_2$–OG sample was then studied by operating the LA conversion at a high level of 80% under the conditions described in Fig. S6.† The heterogeneous nature of the catalyst makes it easy to separate from the reaction mixture by simple filtration. For each successive use, the filtered catalyst was subjected to calcination in air at 500 °C for 4 h, and then reduced with 5% H$_2$/Ar at 300 °C for 2 h. After this treatment, the activity of the recovered catalyst was essentially the same with that observed for the first run (Fig. S6†). Moreover, catalyst leaching was not observed, as indicated by the absence of the copper ion in the product solution after each catalyst reuse (the Cu content of the catalysts and solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, Table S3†). This finding further demonstrates the high stability of the 20Cu/ZrO$_2$–OG catalyst, presumably due to a strong metal-support interaction between Cu and the ZrO$_2$ matrix.[16d] The high stability and reusability of the 20Cu/ZrO$_2$–OG material in the LA hydrogenation reaction are compatible with the XRD and XPS results. Indeed, the XRD and XPS results show no obvious changes in the mean diameters of the Cu nanoparticles and in the metallic state of Cu, respectively, after four successive runs (Fig. S7 and Fig. S8†).

Given the excellent capability of the Cu-based catalyst for FA-mediated LA conversion, we have explored the possibility of a straightforward production of GVL directly from giant reed (Arundo donax L.),[19] a strategic non-food perennial grass that can deliver a high biomass productivity (approximately 40 t ha^{-1} per year of dry matter) while keeping a low input investment. These properties make giant reed an especially suitable feedstock material for next generation biofuels.[20] However, very little is known about the potential use of this herbaceous biomass as a feedstock for the synthesis of chemicals with high added value. We have performed a "one-pot" process that combines the acid conversion of giant reed to the LA/FA stream in conjunction with the direct synthesis of GVL by adopting the 20Cu/ZrO$_2$–OG catalyst. The results presented in Scheme 2 show that it is possible to achieve a GVL yield up to 18.5 wt% (calculated from the starting weight of dry biomass) through this simple one-pot procedure.[21] A high yield of GVL
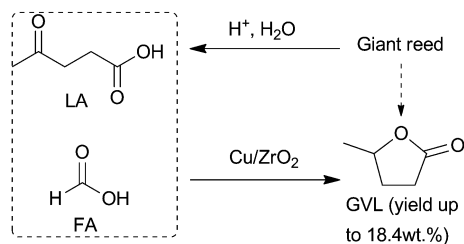
Scheme 2 "One-pot" catalytic conversion of giant reed to GVL.

(*ca.* 16.6 wt%) was reported from a LA/FA mixture that was derived from giant reed aqueous slurries with a ruthenium-based bifunctional (acid and hydrogenating) catalytic system.[19b] In addition to the lower process productivity, this noble metal-based catalyst system required external H_2 gas (5 bar) to ensure the desired reaction process was proceeded.

Conclusions

In summary, we have described a sustainable and cost-competitive catalytic process for the high yield production of GVL from biomass-derived LA/FA streams, featuring the *in situ* generation of H_2 gas in the systems using the FA produced during the acid hydrolysis of biomass. With no requirement for any external fossil-fuel hydrogen, our process relies simply on the use of bio-derived FA as an expedient source of hydrogen for GVL production. The process is catalyzed by an inexpensive, readily accessible and earth-abundant copper-based metal oxide catalyst. The observation that the copper-based metal oxide catalyst can be reused suggests that this process is compatible with high yield and continuous operation, thus paving a new way toward a renewable chemical industry. The successful utilization of renewable lignocellulosic biomass for the useful production of chemicals *via* this process would have the potential of reducing the CO_2 burden without compromising food supply.

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3312 | *Energy Environ. Sci.*, 2013, **6**, 3308–3313

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