Novel heterogeneous zinc triflate catalysts for the rearrangement of α-pinene oxide

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New solid acid catalysts based on silica-supported zinc triflate have been prepared for use in the rearrangement of α-pinene oxide to campholenic aldehyde. These catalysts exhibit considerable activity and can be recycled without loss of selectivity towards the aldehyde. The selectivity towards the aldehyde can be increased to 80% (at 50% conversion) when the reaction is performed at 25 °C using hexagonal mesoporous silica (HMS_{24}) as the catalyst support.

Keywords: green chemistry, clean technology, heterogeneous catalysis, α-pinene oxide, campholenic aldehyde, metal triflates

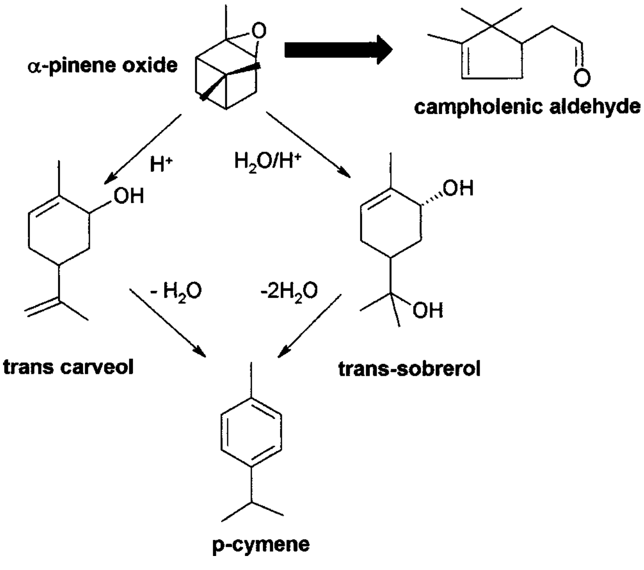
1. Introduction

Conventional homogeneously catalysed processes utilised by the fine and speciality chemicals industries produce vast amounts of waste on removal of the catalyst from the reaction. Tightening environmental legislation has led to a drive to develop new heterogeneous systems that offer ease of catalyst separation combined with high activities and selectivity, thus reducing the production of waste [1–3].

Campholenic aldehyde is an important intermediate used by the fragrance industry in the synthesis of santalol, and is currently prepared by Lewis-acid-catalysed rearrangement of α-pinene oxide [4]. The rearrangement of α-pinene oxide is facile and over 100 products have been reported under different reaction conditions. The major products formed during acid-catalysed rearrangement are summarised in scheme 1; however, a more detailed overview is available elsewhere [5,7]. The use of mild Lewis acids favours the production of campholenic aldehyde, while Brønsted acid sites will result in the formation of *trans*-carveol, *trans*-sobrerol and p-cymene. The most active and selective homogeneous systems used in this reaction are $ZnCl_2$ and $ZnBr_2$; however, rapid irreversible catalyst deactivation is observed with turnover numbers as low as 20 being reported [5]. Aqueous extraction of these catalysts from the reaction results in the formation of vast quantities of zinc-contaminated water which is environmentally unacceptable, hence alternative heterogeneous catalysts must be sought.

Previous attempts to develop heterogeneous catalysts for this reaction have involved the use of mixed oxide solid acids [6] and US-Y zeolites [7,8], for which selectivities towards campholenic aldehyde of 55–80% have been reported depending on reaction conditions. The most impressive recent reports have used Ti-Beta to rearrange α-pinene oxide in both the liquid and vapour phase, with the latter conditions forming campholenic aldehyde with an initial selectivity of ~94%, dropping to 80% after 6 h [9].

Metal trifluoromethanesulfonates (triflates ($M(SO_2CF_3)_n$)) are an interesting type of Lewis acid, which have been reported in recent years [10]. These possess stronger Lewis acidity and higher water tolerances that their halide counterparts, which readily form the hydroxide or oxide [11]. In view of their high stability towards water, which is formed as a by-product during rearrangement to p-cymene (see scheme 1), we have examined the use of unsupported and silica-supported zinc triflate ($Zn(OTf)_2$) in the isomerisation of α-pinene oxide.



Scheme 1. Major products formed in the acid-catalysed rearrangement of α-pinene oxide.

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2. Experimental

Silica-supported $Zn(OTf)_2$ catalysts with loadings of 2 $mmol\,g^{-1}$ (7.5 wt% Zn) and 0.01 $mmol\,g^{-1}$ (0.06 wt% Zn) were prepared by wet impregnation of amorphous SiO_2 (K100 (Merck), SA = 300 $m^2\,g^{-1}$), or hexagonal mesoporous silica (HMS, SA = 1100 $m^2\,g^{-1}$) with a solution of $Zn(OTf)_2$ (Aldrich, 98%) in 100 ml methanol. The slurry was stirred for 2 h at 25 °C, prior to removal of the excess methanol at 50 °C on a rotary evaporator. HMS_{24} was prepared according to the sol–gel route of Pinnavaia et al. [12] by condensing 62.5 g of tetraorthoethoxysilicate in a mixture of 123 g ethanol and 160 g H_2O with 15.3 g n-dodecylamine as the surfactant template. The resulting gel was stirred for 24 h, filtered, dried and then calcined at 600 °C for 6 h to remove the template.

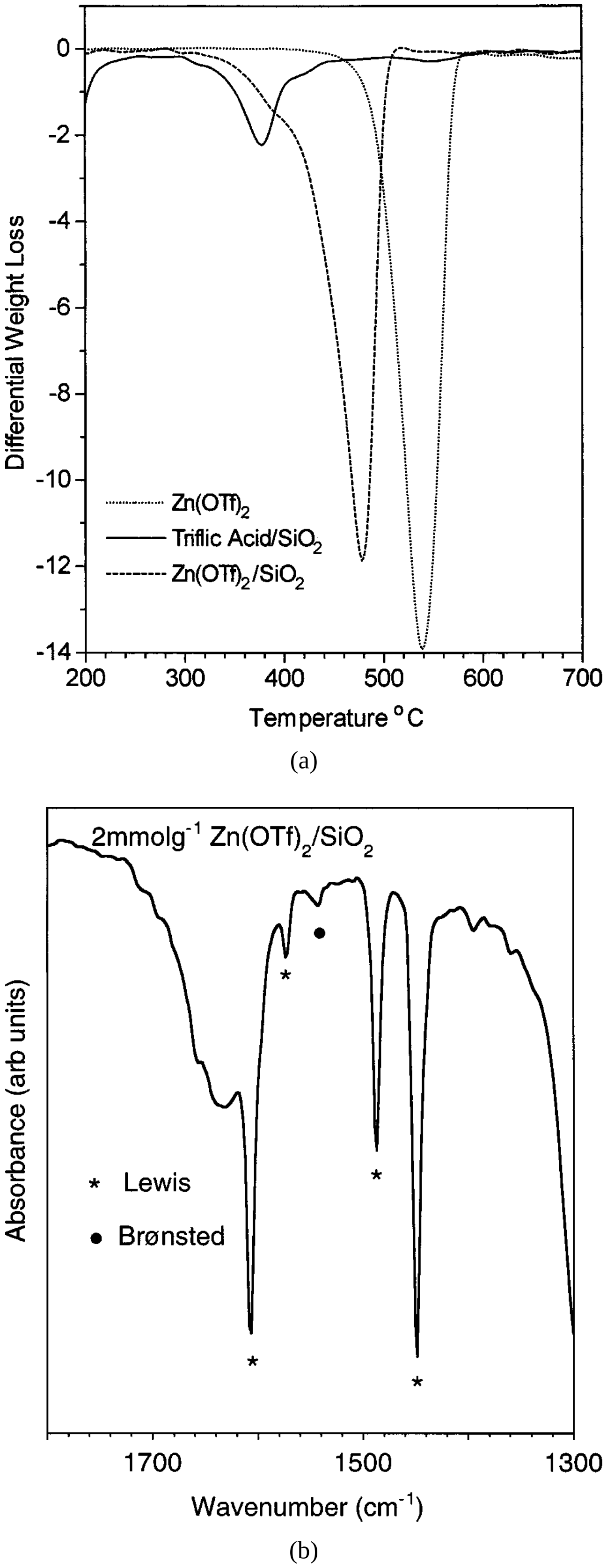
Silica-supported triflic acid samples were also prepared to compare their catalytic properties with $Zn(OTf)_2/SiO_2$. The maximum yield of triflic acid that could be obtained from the $Zn(OTf)_2/SiO_2$ samples used in these experiments is 4 and 0.02 $mmol\,g^{-1}$. Samples were therefore prepared with these loadings by stirring 5 g SiO_2 (K100) with the required amount of triflic acid (Aldrich, 99%) in 50 ml methanol for 2 h prior to removal of the excess solvent on a rotary evaporator at 50 °C.

Catalyst characterisation was performed using thermal analysis and DRIFTS. Thermal analysis was performed using a NETZSCH 409 STA with a temperature ramp of 10 °C/min. Acid site determination was performed using pyridine titration in conjunction with DRIFTS (Bruker Equinox 55 FTIR). Pyridine vapour was adsorbed over a period of 24 h prior to recording the DRIFTS spectrum.

The rearrangement of α-pinene oxide was performed in a glass batch reactor at both 25 and 85 °C, using 100 ml of 1,2-dichloroethane (Aldrich, 98%) as a solvent and 1 g α-pinene oxide (Aldrich, 99%) with 0.5 g decane (Aldrich, 99%) as an internal standard. The reaction products were analysed using a HP5890 gas chromatograph fitted with a 25 m HP1 capilliary column. Identification of major reaction products was performed using authentic samples, and a VG Autospec mass spectrometer. After filtration of catalysts, the zinc and triflic acid content of the organic media was measured by ICP (Perkin–Elmer Plasma 40 emission ICP instrument) and ^{19}F NMR (Jeol EX-270 NMR spectrometer), respectively. For ICP, zinc was extracted using 25 ml of 2% nitric acid solution.

3. Results and discussion

Following catalyst preparation, the physical properties of the $Zn(OTf)_2$ samples were examined using thermal analysis and acid site characterisation by pyridine titration [13]. Differential thermal analysis was used to determine the thermal stability of the $Zn(OTf)_2$, $Zn(OTf)_2/SiO_2$ and triflic-acid-treated SiO_2 samples. A comparison of these spectra is shown in figure 1(a), which indicates that, while $Zn(OTf)_2$



(a)

(b)

Figure 1. (a) Differential thermal analysis of 2 $mmol\,g^{-1}$ $Zn(OTf)_2/SiO_2$, $Zn(OTf)_2$ and triflic-acid-treated SiO_2. (b) DRIFTS spectrum of 2 $mmol\,g^{-1}$ $Zn(OTf)_2/SiO_2$ following adsorption of pyridine vapour at 25 °C.

Table 1
Activity of a range of $Zn(OTf)_2$-based catalysts in the rearrangement of α-pinene oxide.[a]

Catalyst	Reaction temp. (°C)	$Zn(OTf)_2$ (mmol)	100% conversion	Selectivity to campholenic aldehyde (%)	
				50% conv.	100% conv.
$Zn(OTf)_2$ homogeneous	85	0.05	30 min	59	59
2 mmol g^{-1} $Zn(OTf)_2/SiO_2$	85	0.05	<30 s	–	55
Reuse of above	85		<30 s	–	62
0.01 mmol g^{-1} $Zn(OTf)_2/SiO_2$	85	0.002	20 min	66	60
Reuse of above	85		180 min	65	61
0.01 mmol g^{-1} $Zn(OTf)_2/SiO_2$ calcined 200 °C	85	0.002	30 min	76	65
0.01 mmol g^{-1} $Zn(OTf)_2/SiO_2$ solvent-free reaction	85	0.002	30 min	60	50
2 mmol $g^{-1}$$Zn(OTf)_2/SiO_2$	25	0.05	<30 s	–	55
0.01 mmol g^{-1} $Zn(OTf)_2/HMS_{24}$	85	0.002	10 min	70	64
0.01 mmol g^{-1} $Zn(OTf)_2/HMS_{24}$	25	0.002	60 min	80	69

[a] Note that reducing the amount of DCE to 25 ml does not alter the selectivity or conversion values.

does not decompose until 540 °C, $Zn(OTf)_2/SiO_2$ decomposes at a lower temperature, with a major weight loss at 475 °C and a shoulder at 390 °C. The spectrum obtained from physisorbed triflic acid on SiO_2 shows that triflic acid desorbs at 370 °C, indicating that the weight loss observed at 475 °C from $Zn(OTf)_2/SiO_2$ cannot be assigned to physisorbed triflic acid formed during catalyst preparation. Therefore, the weight loss observed from both supported and unsupported $Zn(OTf)_2$ can be assigned to thermal decomposition of triflate groups. The reduction in thermal stability of the silica-supported material may be ascribed to the reaction of highly dispersed $Zn(OTf)_2$ with surface hydroxyl groups on silica, which will hydrolyse the Zn–(OTf) bond to form ZnO and triflic acid. Similar effects have been observed with other supported acid catalysts, where the –OH groups on silica can promote decomposition of the acid site [14].

Figure 1(b) shows the DRIFT spectra recorded following adsorption of pyridine on a 2 mmol g^{-1} loading $Zn(OTf)_2/SiO_2$ sample. The four intense peaks observed at 1450, 1490, 1580 and 1605 cm^{-1} are assigned to the presence of Lewis acid sites, indicating that zinc triflate maintains its Lewis acidity following adsorption on SiO_2. The weaker band at 1540 cm^{-1} also indicates the presence of a low level of Brønsted acidity, which most likely results from the interaction of the triflate groups with the hydroxyl groups on SiO_2. The nature of these acid sites is unchanged for lower loading samples.

The catalytic activity of these $Zn(OTf)_2$ catalysts in the rearrangement of α-pinene oxide was investigated under a range of conditions the results of which are summarised in table 1. Using 58 mg of 2 mmol g^{-1} $Zn(OTf)_2/SiO_2$ results in rapid conversion of α-pinene oxide at both 85 and 25 °C, with 100% conversion being observed in less than 30 s, even on catalyst reuse. $Zn(OTf)_2/SiO_2$ is obviously a highly active catalyst for the rearrangement of α-pinene oxide and is considerably more active than unsupported $Zn(OTf)_2$, which only reaches 100% conversion after 30 min. This observation is accounted for by the poor solubility of $Zn(OTf)_2$ in 1,2-dichloroethane, and that by supporting $Zn(OTf)_2$ on SiO_2 the dispersion of the active sites increases.

One of the problems of having such an active catalyst for α-pinene oxide rearrangement is that the products formed are themselves highly reactive, and consecutive reactions will decrease the observed selectivity towards campholenic aldehyde. Catalysts with lower loadings were therefore studied. By using 200 mg of 0.01 mmol g^{-1} $Zn(OTf)_2/SiO_2$ the reaction rate was slowed so that 100% conversion was reached after 20 min, and a selectivity to campholenic aldehyde of 60% was obtained. On reuse of the catalyst, a decrease in activity was observed with 100% conversion being achieved after 3 h. This decrease in activity is attributed active site deactivation by the deposition of heavy organic residue on the catalyst surface. The presence of such material has been observed in DRIFT spectra and by thermal analysis, even after prolonged washing of the catalyst.

The selectivity towards campholenic aldehyde can be boosted further to 65% if the 0.01 mmol g^{-1} $Zn(OTf)_2/SiO_2$ catalyst is calcined under N_2 at 200 °C prior to use. This increase in selectivity is attributed to loss of Brønsted acid sites by dehydration of the catalyst surface, which, in turn, reduces the amount of side reactions. Calcination at 400 °C decreases the activity of the catalyst due to decomposition of $Zn(OTf)_2$, as indicated by thermal analysis (figure 1(a)).

During the reaction, the selectivity to the other main products formed, p-cymene, *trans*-sobrerol, *trans*-carveol does not change. It should be noted that the formation of *trans*-sobrerol is not observed in $ZnCl_2$-catalysed rearrangement of α-pinene oxide and is formed as a consequence of the Brønsted acidity of $Zn(OTf)_2/SiO_2$. The selectivity towards campholenic aldehyde appears to be essentially dictated by subsequent reactions of campholenic aldehyde. Indeed, a control reaction using pure campholenic aldehyde with 0.01 mmol g^{-1} $Zn(OTf)_2/SiO_2$ at 85 °C shows that complete conversion of the aldehyde to a range of other products is achieved over 24 h.

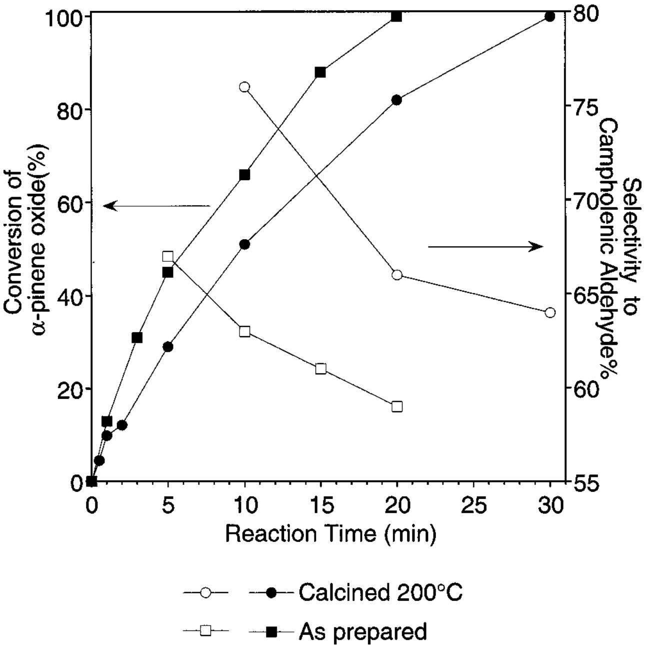


Figure 2. Plot showing the % conversion of α-pinene oxide and % selectivity to campholenic aldehyde with time, obtained using 200 mg of 0.01 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/SiO_2$ catalyst used as prepared (squares) and calcined at 200 °C (circles).

However, it should also be noted that, while a 65% selectivity to campholenic aldehyde is lower than the reported 80% obtained using homogeneous $ZnCl_2$, the superior turnover numbers of >3000 obtained with $Zn(OTf)_2$ gives this catalyst a greater production of campholenic aldehyde per active site. With careful planning of reaction conditions it should be possible to boost this selectivity further. Figure 2 shows the trends in conversion and selectivity obtained using the as-prepared and calcined 0.01 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/SiO_2$ samples. It can be seen that at 50% conversion the selectivity to campholenic aldehyde is as high as 67 and 76%, respectively, dropping to 60 and 65% on completion of the reaction. This decrease in selectivity is attributed to consecutive reactions of campholenic aldehyde as discussed above.

A further improvement in the selectivity to campholenic aldehyde can be achieved if HMS_{24} is used as a support. It was anticipated that the smaller, more regular pore structure of the HMS_{24} material (∼40 Å compared to 100 Å) and different surface polarity would alter the diffusion rates of the reactants and products through the support. An improvement in both conversion rate and selectivity was indeed observed when using 200 mg of 0.01 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/HMS_{24}$ material, with the selectivity to the aldehyde increasing to 64%. Further improvements in selectivity to 69% can be achieved if the reaction is performed at 25 °C, but under these conditions the reaction rate is slower with 100% conversion being reached after 1 h. Again, these selectivities are quoted for 100% conversion of α-pinene oxide; if the values are recorded at 50% conversion more impressive selectivities of 70 and 80% are observed, respectively. It should be noted that no improvement in selectivity was observed if $Zn(OTf)_2/SiO_2$ is used at 25 °C. These observations can be explained by the surface polarity of HMS_{24} and K100-SiO_2 being altered by the different thermal pretreatments used during catalyst preparation. The preparation of HMS_{24} involves a high-temperature (600 °C) calcination step to remove the template, after which infrared analysis indicates that the surface hydroxyl group density is reduced compared to conventional silica. This will lower the surface polarity [15], weaken the interaction of polar molecules with the catalyst surface and, in turn, increase the selectivity towards campholenic aldehyde by reducing the number of consecutive reactions.

Control experiments reveal that triflic-acid-treated SiO_2 is also highly active towards α-pinene oxide rearrangement, although the selectivity towards the aldehyde is poor (40%). Therefore, it was necessary to determine whether supported $Zn(OTf)_2$ forms triflic acid during the reaction, as this could seriously alter the trends in observed catalytic activity reported above. Likewise, it was also important to determine whether the catalyst is truly heterogeneous and, if not, what percentage of zinc is lost during the reaction.

The stability of these catalysts towards leaching and hydrolysis to form triflic acid during reaction was investigated using combined ICP and ^{19}F NMR analysis to determine the levels of Zn and triflate/triflic acid groups in the organic media after filtration of the catalyst. These revealed that following reaction with 2 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/SiO_2$ any triflic acid or triflate groups in the organic phase were below the detection limit of ^{19}F NMR. However, following reaction with triflic-acid-treated SiO_2, ^{19}F NMR reveals the presence of triflic acid in the filtrate at $\delta = -78.5$ ppm. Therefore, as triflic acid physisorbed on SiO_2 goes into solution, and no ^{19}F NMR signal is observed following reaction with $Zn(OTf)_2/SiO_2$, this confirms that under the conditions used in these experiments, $Zn(OTf)_2$ does not form triflic acid. Likewise, the absence of any $Zn(OTf)_2$ in solution (expected at $\delta = -(78.5\text{–}80)$ ppm) suggests that the loss of $Zn(OTf)_2$ is also negligible.

In agreement with these observations, ICP measurements indicate that Zn lost from 2 and 0.01 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/SiO_2$ samples was <0.5% or within the background level (0.1 ppm), respectively. Analysis even on a solvent-free reaction, where the effects of leaching should be most severe, reveals that only 7% Zn is lost from the 0.01 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/SiO_2$ catalyst. These results confirm that the use of non-polar solvents such as 1,2-dichloroethane does significantly reduce metal leaching, and that the catalysts are stable under the conditions used in these experiments. These combined analytical observations are also consistent with hot filtration leaching tests [16] using the 0.01 $\text{mmol}\,\text{g}^{-1}$ $Zn(OTf)_2/SiO_2$ catalyst, which reveal no further reaction occurs if the catalyst is filtered off midway through a reaction, which also confirms a negligible level of triflic acid formation.

To summarise, we have demonstrated that supported $Zn(OTf)_2$ catalysts are highly active for α-pinene oxide rearrangement, are stable and re-useable, and, when working at low conversions, offer selectivities towards campholenic aldehyde $>80\%$. However, while the high turnover numbers obtained with this catalyst have environmental benefits from working with small amounts of catalysts, there may be economic disadvantages with the requirement to work at low conversion. To minimise waste, the successful industrial application of this catalyst would require the use of additional distillation units to facilitate recycling of unreacted α-pinene oxide.

4. Conclusions

(1) Silica-supported zinc triflate ($Zn(OTf)_2/SiO_2$) catalysts have been prepared which are solid acids possessing mainly Lewis acid sites and a small degree of Brønsted acidity. Thermal analysis reveals that the decomposition temperature of $Zn(OTf)_2$ is lowered when it is supported on SiO_2, but this reduced temperature does not correspond to physisorbed triflic acid.

(2) These $Zn(OTf)_2/SiO_2$ catalysts are highly active in the rearrangement of α-pinene oxide exhibiting TON $>$ 3000. They are re-useable without any decrease in selectivity towards campholenic aldehyde.

(3) An optimum selectivity towards campholenic aldehyde of 80% was achieved by working at 50% conversion using $Zn(OTf)_2/HMS_{24}$ at 25 °C.

(4) Leaching studies reveal that, under the conditions used in these experiments, the loss of zinc is $<0.5\%$ or within the background level confirming that the use of non-polar solvents does reduce leaching of the active phase.

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