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## ARTICLE

# Epoxidation of Cyclic Enones with Hydrogen Peroxide Catalysed by Alkylcarboxylate-Intercalated Ni-Zn Mixed Basic Salts

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The interlayer spacing of layered Ni-Zn mixed basic salts (NiZn) can be precisely controlled by the intercalation of various long alkyl chain carboxylate anions into the NiZn interlayer. The butyrate-exchanged NiZn ( $C_3H_7COO^-/NiZn$ ) catalyst effectively promotes the epoxidation of various cyclic enones with aqueous hydrogen peroxide in remarkably high yields. The  $C_3H_7COO^-/NiZn$ -catalysed epoxidation of 2-cyclohexen-1-one with an equimolar amount of  $H_2O_2$  proceeds in a highly efficient manner, with 97% efficiency of the  $H_2O_2$  utilization. This  $C_3H_7COO^-/NiZn$  catalyst can be reused without any loss of its catalytic activity and selectivity.

## Introduction

Anion-exchange within layered inorganic materials has received much attention as a means to create various types of useful inorganic-organic nanocomposites.<sup>1</sup> Layered double hydroxides (LDHs),<sup>2</sup> with the formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n}^{x-} \cdot mH_2O$ , where  $(0.51 < x < 1.00)$ , are a representative group of this class of solids. Because of their low toxicity, LDHs have been used as drug delivery matrices by intercalating active pharmaceutical ingredients into the interlayer of the inorganic materials.<sup>3</sup> In many types of LDHs, rhombohedral Mg-Al hydrotalcite ( $M^{2+}$ :  $Mg^{2+}$ ,  $M^{3+}$ :  $Al^{3+}$ , and  $A^{n-}$ :  $CO_3^{2-}$ ) has been widely applied for use as heterogeneous catalysts or catalyst supports.<sup>4</sup> Because of their great potential for use in the design of high-performance heterogeneous catalysts, various strategies for the preparation of such materials have been widely reported in recent years. The acid-base properties of hydrotalcites can be controlled by changing the identity of the metal species and/or the  $M^{2+}/M^{3+}$  ratio within the structure.<sup>5</sup> Furthermore, catalytically active species such as metal salts, organometallic complexes, or nanoparticles, can be supported on their cationic layer sheets, surfaces, or interlayer space.<sup>6</sup> Recently, it has been found that environmentally-benign organic transformation reactions can be achieved by use of the combination catalytic systems comprised of both a solid acid catalyst and solid basic hydrotalcite.<sup>7</sup>

Layered hydroxy double salts (HDSs), which consist of positively charged layers and exchangeable interlayer anions, have also received considerable interest as anion-exchangeable layered compounds.<sup>8</sup> Compounds in the HDS family follow the general formula of  $M_A^{2+}_{1-x}M_B^{2+}_{2x}A^{n-}_{2x/n}(OH)_2 \cdot mH_2O$  ( $0.15 < x < 0.25$ ), where  $M_A^{2+}$  and  $M_B^{2+}$  are divalent metal cations such as  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ , or  $Ni^{2+}$ , and  $A^{n-}$  represents various interlayer anions. The anionic guests that can be used range from simple inorganic anions ( $NO_3^-$ ,  $ClO_4^-$ ,  $Cl^-$ ,  $MnO_4^-$ ,  $SO_4^{2-}$ , etc.), and anionic metal complexes, to organic anions including drugs and dyes.<sup>9</sup> It can be considered that HDSs are also powerful candidates for advanced nano-scaled

catalysts or as catalyst supports that allow for control over the location of the catalytically active metal species.

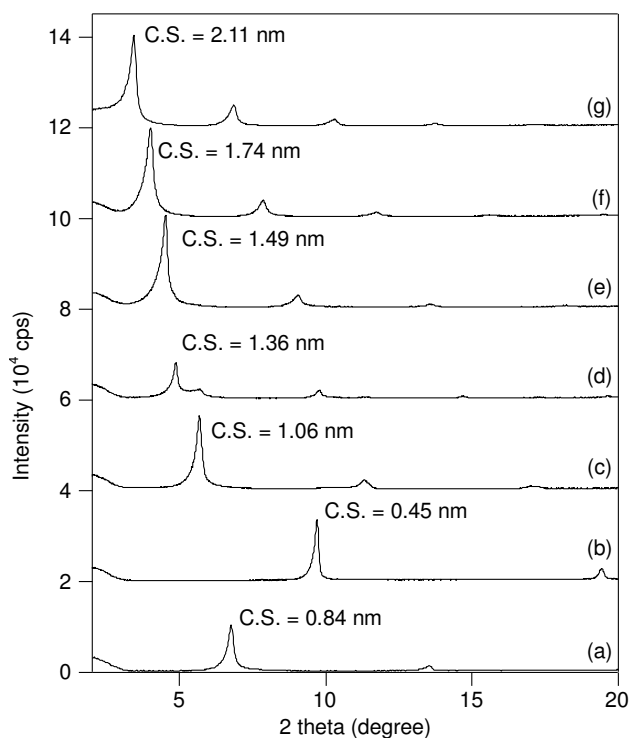
The epoxidation of C=C double bonds is one of platform synthetic processes in basic researches and industrial applications, because epoxides and their intermediates are widely employed in the synthesis of high-valued chemicals, such as cosmetics, pharmaceuticals, and polymer materials.<sup>10</sup> The epoxidation of electron deficient olefins in particular, such as  $\alpha,\beta$ -unsaturated ketones, has been an important target for the functionalisation of ketones. It is well known this type of epoxidation generally requires a nucleophilic oxidant, such as  $OOH^-$  species.<sup>11</sup> Many epoxidation procedures employ  $H_2O_2/Bu_4NF$ , TBHP/DBU, *m*CPBA/KOH, NaOCl/cinchona alkaloid,  $NaBO_3/THAHS$ , iodossyl benzene, dioxirane, or  $TBA_2S_2O_8$  as an oxidant,<sup>12</sup> however, these oxidants often yield stoichiometric amounts of their deoxygenated forms as a waste by-product. In contrast, hydrogen peroxide is an ideal oxidant because water is the only by-product. Although organometallic complexes, heteropolyacids, organic molecules, and their immobilized materials can act as an effective catalyst for the epoxidation of enones under neutral conditions,<sup>13</sup> homogeneous reaction systems with  $H_2O_2$  under alkaline conditions (NaOH, KOH, LiOH,  $Na_2CO_3$ , or  $K_2CO_3$ ) is the most common procedures. To replace these standard homogeneous systems with more practical heterogeneous alternatives, a number of solid base such as Mg-Al hydrotalcite, KF/alumina, hydroxyapatite, or sodalite catalysts have been developed.<sup>14</sup>

We have previously developed a Ni-Zn mixed basic salt (NiZn) as a solid catalyst or catalyst support based on the design idea of "Intercalation Catalysts".<sup>15</sup> The  $Ni_{1-x}Zn_x(OCOCH_3)_{2x}(OH)_2 \cdot nH_2O$  ( $0.15 < x < 0.25$ ; NiZn), classified into layered HDSs, is consisted of positively charged layers and exchangeable interlayer anions. Our selection of NiZn as a catalyst materials is motivated by its unique characteristics of (i) simple preparation, (ii) high crystallinity, (iii) strong electrostatic interactions between guest anions and  $Zn^{2+}$  cations, and (iv) high anion exchange capacity, as well as (v) the ability to fine-tune the interlayer space by modifying the size of the guest anion. Recently, interlayer space-controlled NiZn with alkyl

carboxylate anions intercalated in interlayer was found to be an effective heterogeneous Brønsted base catalyst for Knoevenagel condensation in water.<sup>15c</sup> Here, we report the successful epoxidation of cyclic enones using hydrogen peroxide in the presence of NiZn as a basic catalyst.

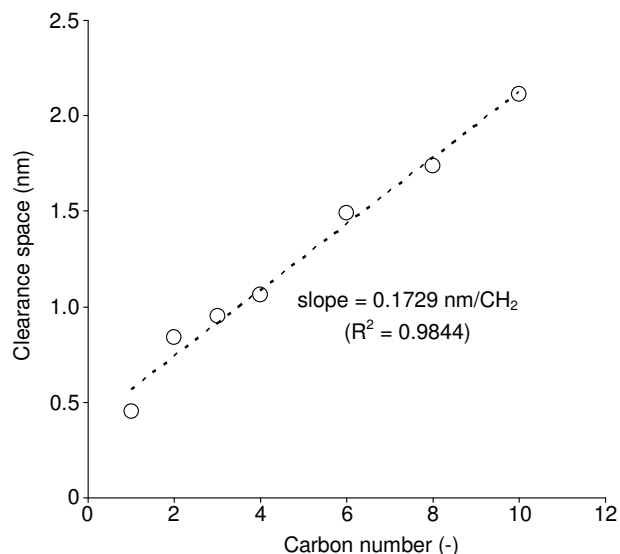
## Results and Discussion

In accordance with the previously reported literature,<sup>16</sup> the acetate-intercalated Ni-Zn mixed basic salt,  $\text{CH}_3\text{COO}^-/\text{NiZn}$ ,  $\text{Ni}_{0.63}\text{Zn}_{0.37}(\text{OAc})_{0.37}(\text{OH})_2 \cdot 1.93\text{H}_2\text{O}$  ( $\text{Ni}/\text{Zn} = 2.20$ ), was synthesized.<sup>17</sup> Anion exchange in the NiZn interlayer was performing the same procedure in water. Treatment of  $\text{CH}_3\text{COO}^-/\text{NiZn}$  with various sodium alkyl carboxylates yielded anion-exchanged NiZn catalysts ( $\text{C}_{n-1}\text{H}_{2n-1}\text{COO}^-/\text{NiZn}$ ,  $n = 1 - 10$ ) as green powders.



**Fig. 1** XRD profiles for (a)  $\text{CH}_3\text{COO}^-/\text{NiZn}$ , (b)  $\text{HCOO}^-/\text{NiZn}$ , (c)  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$ , (d) recovered  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  after epoxidation of 2-cyclohexen-1-one (**1**), (e)  $\text{C}_5\text{H}_{11}\text{COO}^-/\text{NiZn}$ , (f)  $\text{C}_7\text{H}_{15}\text{COO}^-/\text{NiZn}$ , and (g)  $\text{C}_9\text{H}_{19}\text{COO}^-/\text{NiZn}$ . The C.S. values were also given.

The powder X-ray diffraction (XRD) profiles of the synthesised NiZn catalysts are shown in Fig. 1. From the XRD results, the layered structure of NiZn was maintained in each case; however, the calculated clearance spaces of each materials (C.S. = basal spacing ( $d_{001}$ ) – thickness of layer (0.46 nm)) were changed after the intercalation procedure, also shown in Fig. 1. The C.S. of each was proportional to the length of the alkyl groups intercalated (slope: 0.17 nm/ $\text{CH}_2$ , Fig. 2). Taking the C. S. and the size of the pillared alkyl carboxylate anions into account, a suitable conformation of the  $\text{C}_{n-1}\text{H}_{2n-1}\text{COO}^-/\text{NiZn}$  can be a bilayer arrangement with a tilting angle of approximately 40 degrees.



**Fig. 2** The relation between C.S. and carbon number of alkyl groups in carboxylate anion for  $\text{C}_{n-1}\text{H}_{2n-1}\text{COO}^-/\text{NiZn}$  catalysts.

To explore the catalytic abilities of the anion-exchanged NiZn, the epoxidation of 2-cyclohexen-1-one (**1**) into 1,2-epoxycyclohexanone (**2**) was carried out in the presence of 4 equivalents of aqueous hydrogen peroxide (30 wt%) relative to the amount of **1**. The results and the C. S. values of the  $\text{C}_{n-1}\text{H}_{2n-1}\text{COO}^-/\text{NiZn}$  catalysts are shown in Table 1.

**Table 1** Epoxidation of 2-cyclohexen-1-one (**1**) with  $\text{H}_2\text{O}_2$ <sup>a</sup>

Entry	Catalyst	C.S. (nm) <sup>b</sup>	Time (h)	Conv. (%) <sup>c</sup>	Yield (%) <sup>c</sup>
1	$\text{HCOO}^-/\text{NiZn}$	0.45	1	7	6
2	$\text{CH}_3\text{COO}^-/\text{NiZn}$	0.84	1	45	45
3	$\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$	1.06	1	55	55
4	$\text{C}_5\text{H}_{11}\text{COO}^-/\text{NiZn}$	1.49	1	28	28
5	$\text{C}_7\text{H}_{15}\text{COO}^-/\text{NiZn}$	1.74	1	24	22
6	$\text{C}_9\text{H}_{19}\text{COO}^-/\text{NiZn}$	2.11	1	19	16
7 <sup>d</sup>	$\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$	-	3	trace	trace
8 <sup>e</sup>	$\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$	-	3	trace	trace
9 <sup>d</sup>	$\text{Ni}(\text{OH})_2$	-	3	trace	trace
10 <sup>e</sup>	$\text{Zn}(\text{OH})_2$	-	3	trace	trace
11 <sup>f</sup>	$\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$	0.30	3	18	18
12 <sup>g</sup>	$\text{C}_3\text{H}_7\text{COONa}$	-	3	35	35
13	Blank	-	3	-	no reaction

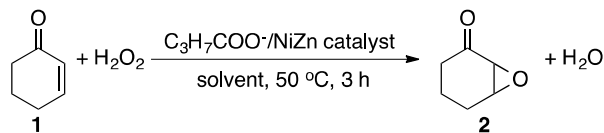
<sup>a</sup> **1** (0.5 mmol), NiZn catalyst (0.05 g), DMF (2 mL), 30 wt%  $\text{H}_2\text{O}_2$  aq. (4 eq. relative to substrate), 60 °C. <sup>b</sup> Calculated from XRD data. <sup>c</sup> Determined by GC using an internal standard technique. <sup>d</sup> Ni catalyst (Ni: 0.26 mmol). <sup>e</sup> Zn catalyst (Zn: 0.13 mmol). <sup>f</sup> Hydrotalcite (0.05 g), purchased from WAKO, was used as a catalyst. <sup>g</sup>  $\text{C}_3\text{H}_7\text{COONa}$  (1.47 mmol) was used as a catalyst.

In the case of  $\text{HCOO}^-/\text{NiZn}$ , the catalytic activity was low (Entry 1), most likely due to the mass-transfer limitation within the narrow interlayer space. The parent  $\text{CH}_3\text{COO}^-/\text{NiZn}$  catalysed this epoxidation efficiently, yielding 45% of **2** after 1 h (Entry 2). It should be noted that the  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  catalyst exhibited the highest activity, yielding only **2** in 55% yield after 1 h (Entry 3).<sup>18</sup> On the other hand, the catalysts which have more enlarged interlayer spaces such as  $\text{C}_5\text{H}_{11}\text{COO}^-/\text{NiZn}$ ,  $\text{C}_7\text{H}_{15}\text{COO}^-/\text{NiZn}$ , and  $\text{C}_9\text{H}_{19}\text{COO}^-/\text{NiZn}$  did not promote this epoxidation reaction effectively (Entries 4-6). It is likely that the substrate could not diffuse smoothly into the

interlayer space of these catalysts because these spaces are occupied by the alkyl chains of the guest anions. Ni(OCOCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Zn(OCOCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, Ni(OH)<sub>2</sub>, and Zn(OH)<sub>2</sub>, the precursors of NiZn and the partly components of the brucite-like layer of NiZn, did not show any significant catalytic activity under the test reaction conditions (entries 7-10). It is well known that Mg-Al hydrotalcite can heterogeneously catalyse the epoxidation of electron-deficient olefins with H<sub>2</sub>O<sub>2</sub>.<sup>14a-c</sup> However, the reaction rate over Mg<sub>6</sub>Al<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>16</sub>·4H<sub>2</sub>O catalyst was slow under the same reaction conditions (entry 11). By use of C<sub>3</sub>H<sub>7</sub>COONa (1.47 mmol) as a catalyst under the same reaction conditions, only 35% yield of **2** was obtained after 3 h (entry 12). The epoxidation did not proceed at all without the catalyst (entry 13).

The screening of solvents to determine their effect on the epoxidation of **1** over the C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst at 50 °C showed that *N,N*-dimethylformamide (DMF) was superior to the other solvents tested, giving only **2** as a product and at 83% yield within 3 h (Table 2, Entry 1), whereas *N,N*-dimethylacetamide (DMA), acetonitrile, methanol, *n*-hexane, 1,2-dichloroethane, toluene, and water were not effective (entries 2, 4-5, and 7-10). By use of a combined oxidant of benzonitrile, acetonitrile, or acetamide, and hydrogen peroxide in the presence of C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst, the enone epoxidation did not proceed effectively (Entries 3, 4 and 6). The fact that no formation of benzamide or acetamide in nitrile solvents is indicating that the active peroxy intermediates from nitrile or amide as oxidants were not involved in this catalytic system.<sup>19</sup>

**Table 2** Solvent effect on the epoxidation of **1** with H<sub>2</sub>O<sub>2</sub> catalysed by C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn<sup>a</sup>

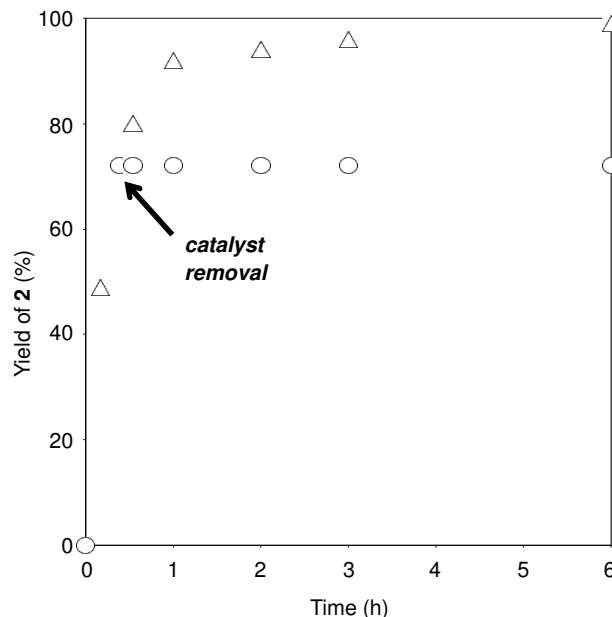


Entry	Solvent	Conv. (%) <sup>b</sup>	Yield (%) <sup>b</sup>
1	<i>N,N</i> -dimethylformamide	83	83
2	<i>N,N</i> -dimethylacetamide	39	39
3	benzonitrile	7	5
4	acetonitrile	57	57
5	methanol	38	38
6 <sup>c</sup>	methanol	42	38
7	<i>n</i> -hexane	39	34
8	1,2-dichloroethane	3	1
9	toluene	9	8
10	water	68	68

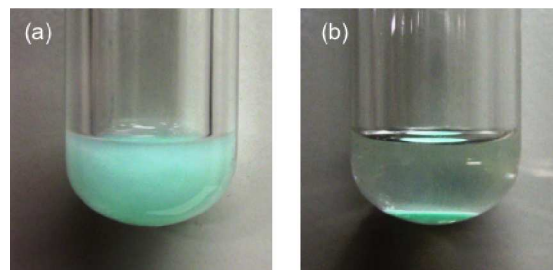
<sup>a</sup> **1** (0.5 mmol), C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst (0.05 g), solvent (4 mL), 30 wt% H<sub>2</sub>O<sub>2</sub> aq. (2 eq. relative to substrate), air, 50 °C, 3 h. <sup>b</sup> Determined by GC using an internal standard technique. <sup>c</sup> With acetamide (2 mmol).

In order to further demonstrate the requirement of the heterogeneous C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst, the catalyst was removed by filtration when an epoxidation of **1** had reached almost 70% conversion (Fig. 3). After removal of the catalyst, the reaction was monitored for an additional hour, and no additional formation of **2** was observed. These results demonstrate that oxidation proceeds in the NiZn interlayer and that any dissolved anionic species are not involved in this reaction. After the epoxidation was completed, it was possible to easily separate the C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst from the reaction mixture by a simple centrifugation (Fig. 4). From the XRD profile of the recovered C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst, it was found that the crystallinity of NiZn had decreased and that its C.S. expanded

from 1.06 nm to 1.36 nm (Fig. 1d), due to the intercalation of water molecules and/or DMF solvent during the reaction.<sup>20</sup>



**Fig. 3** Hot filtration experiment. Reaction conditions were as follows: **1** (0.5 mmol), C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst (0.1 g), DMF (2 mL), 30 wt% H<sub>2</sub>O<sub>2</sub> aq. (4 eq. relative to substrate), 60 °C.



**Fig. 4** The photograph of C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst for (a) reaction mixture during catalytic epoxidation of **1** and (b) after phase separation by centrifugation.

The epoxidation of various cyclic enones using the C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst was carried out in DMF at 60 °C (Table 3). 2-Cyclopenten-1-one and **1** were successfully oxidised into the corresponding epoxyketones within 3 and 6 h, respectively (Entries 1 and 3). The products expected from an aldol-type condensation were scarcely observed under the reaction conditions when performed over the C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst. The recovered C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst was found to be reusable without any loss of its activity and selectivity at least four times (Table 1, entry 3 and Table 3, entries 4-7). After the 4<sup>th</sup> recycling experiment (Table 3, entry 7), any nickel and zinc species and butylate anion leached into the reaction mixture were in amount small enough to be undetectable by atomic absorption spectroscopy and ion chromatography. The reactivity is affected by various factors such as an orbital energy in LUMO of substrates, contact probability, formation rate of HOO<sup>·</sup>, inhibition of side reaction, and so on. Especially, it can be explained the reactivity of enones by use of orbital energies in LUMO of substrates.<sup>21</sup>



Because the nucleophilic attack of  $\text{HOO}^-$  to substrate are known as a rate-determining step,<sup>22</sup> LUMO energies of substrates are critical to explain the difficulty of the epoxidation of enones. In the case of the epoxidation of  $\beta$ -substituted cyclic enones,<sup>23</sup> such as 3-methyl-2-cyclopenten-1-one (LUMO energy: -0.128 eV) and 3-methyl-2-cyclohexen-1-one (-0.121 eV), the reaction rates were decreased (Entries 2 and 8). The lower reactivity of those compounds compared with non-substituted ones (**1**: -0.116 eV, 2-cyclopenten-1-one: -0.126 eV) might be explained to the steric hindrance about C=C double bond of substrates. The epoxidation of  $\alpha$ -isopropenone hardly occurs (Entry 11), due to the steric hindrance of the methyl group at  $\beta$ -position and *gem*-dimethyl group.<sup>24</sup>

**Table 3** Substrate scope for  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$ -catalysed epoxidation with  $\text{H}_2\text{O}_2$ <sup>a</sup>

Entry	Substrate	Product	Time (h)	Conv. (%) <sup>b</sup>	Yield (%) <sup>b</sup>
1			3	97	97
2			12	62	62
3			6	98	98 (91) <sup>c</sup>
4 <sup>d</sup>			1	55	55
5 <sup>e</sup>			1	56	55
6 <sup>f</sup>			1	54	54
7 <sup>g</sup>			1	53	52
8			12	70	70
9 <sup>h</sup>			5	97	96
10			9	16	11
11			24	5	n.d.
12			24	13	10
13			24	20	20

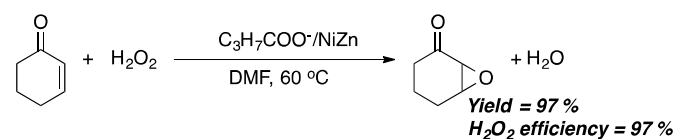
<sup>a</sup> Substrate (0.5 mmol),  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  catalyst (0.05 g), DMF (2 mL), 30 wt%  $\text{H}_2\text{O}_2$  aq. (4 eq. relative to substrate), 60 °C, air. <sup>b</sup> Determined by GC using an internal standard technique. <sup>c</sup> Value in parenthesis was isolated yield. <sup>d</sup> 1<sup>st</sup> reuse. <sup>e</sup> 2<sup>nd</sup> reuse. <sup>f</sup> 3<sup>rd</sup> reuse. <sup>g</sup> 4<sup>th</sup> reuse. <sup>h</sup> Methanol (2 mL) was used as a solvent.

The  $\beta,\beta$ -disubstituted acyclic enone, (*R*)-(+)-plegone having high LUMO energy of 0.273 eV was not transformed into an epoxyketone, even after 24 h. In contrast, the  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$ -catalysed epoxidation of 1,4-naphthoquinone, which has a low LUMO orbital energy (-1.529 eV), totally proceeded, and the corresponding product was formed almost quantitatively (Entry 9). The high reactivity of the substrates possessing low LUMO orbital energies supports the hypothesis that the catalytic epoxidation

process occurs via the nucleophilic attack of a perhydroxyl species. Conversely, 3-nonen-2-one has a high LUMO orbital energy<sup>25</sup> gave an extremely low yield of the corresponding epoxyketone (Entry 10). In addition, the epoxidation of bulky substrates such as benzalacetone and chalcone resulted in only 10% and 20% yields of 2,3-epoxy-1,3-diphenylpropanone and 2,3-epoxy-1,3-diphenylpropanone, respectively (Entries 12 and 13).

Moreover, the  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$ -catalysed epoxidation of **1** with equimolar amount of  $\text{H}_2\text{O}_2$  proceeded in a highly effective manner,<sup>26</sup> giving a 97% of **2** at 60 °C in 8 h with 97% efficiency of  $\text{H}_2\text{O}_2$  utilization, as highlighted in Scheme 1.<sup>27</sup>

**Scheme 1**  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$ -catalysed epoxidation of **1** with equimolar amount of  $\text{H}_2\text{O}_2$ : Reaction conditions: **1** (0.5 mmol),  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  catalyst (0.05 g), 30 wt%  $\text{H}_2\text{O}_2$  aq. (0.5 mmol), DMF (2 mL), 60 °C, 8 h.



Based on these results, the most plausible mechanism for  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$ -catalysed epoxidation is as follows. A perhydroxyl anion, which is formed by the reaction between base site of NiZn and  $\text{H}_2\text{O}_2$ , attacks the  $\beta$ -olefinic carbon atom of an  $\alpha,\beta$ -unsaturated ketone. Following the ring enclosure, the corresponding epoxyketone is formed and anion exchange between  $\text{OH}^-$  and  $\text{C}_3\text{H}_7\text{COO}^-$  takes place.

## Conclusions

We conclude that the  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  catalytic system presented here allows for the simple and practical epoxidation of cyclic enones, forming fine chemicals and pharmaceuticals in a manner that meets the increasing demand for environmentally friendly chemical processes.

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