Tetrahedron 71 (2015) 9403-9407

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Bacteriogenic iron oxide as an effective catalyst for Baeyer-Villiger oxidation with molecular oxygen and benzaldehyde



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ARTICLE INFO

Article history: Received 14 September 2015 Received in revised form 16 October 2015 Accepted 20 October 2015 Available online 26 October 2015

Keywords: Iron oxide Oxidation Baeyer-Villiger oxidation Silicon Synergetic effect

1. Introduction

Iron oxides produced by aquatic iron-oxidizing bacteria are ubiquitous in nature and considered to be generated through a process in which the bacteria gain energy for their vital activity by oxidizing soluble Fe^{2+} ions into insoluble Fe^{3+} ions.¹⁻³ We refer to such iron oxides as biogenous iron oxides (BIOXs). BIOXs are found ubiquitously as ocher deposits in living and natural environments. L-BIOX is produced by Leptothrix ochracea, a species of ironoxidizing bacteria. By taking advantage of this activity, L. ochracea is used to purify drinking water at fresh water purification plants by removing iron in water.^{4,5} However, the resulting large amount of iron oxide can cause problems and needs to be disposed of as industrial waste (Fig. 1a). If the resulting waste could be used as an iron material, it should help to reduce both the cost and time, and thus promote sustainability. L-BIOX has unique features that cannot be achieved artificially; L-BIOX is an amorphous iron oxide in micro-tubular form that contains specific amounts of silicon, phosphorous (Fe:Si:P=73:22:5, except oxygen), and additional organic compounds such as polysaccharides and proteins (Fig. 1b, c). The tubules consist of mild aggregates of Fe³⁺-based amorphous iron oxide nanoparticles with a diameter of \sim 3 nm, leading to

ABSTRACT

Iron oxide produced by iron-oxidizing bacteria, *Leptothrix ochracea*, (*L*-BIOX) obtained from a freshwater purification plant, Joyo City in Kyoto, Japan catalyzed Baeyer-Villiger oxidation with molecular oxygen in the presence of benzaldehyde at 25 °C more efficiently than usual iron compounds. *L*-BIOX can promote the reactions of various substrates to give the desired products in sufficient yields and was found to be reusable. Scanning transmission electron microscopy and ⁵⁷Fe Mössbauer spectroscopy revealed that no change of the surface structure of *L*-BIOX was observed even after four times of the recycling test and the oxidation state of iron in *L*-BIOX is trivalent before and after the oxidation of cyclohexanone. An investigation with analogous amorphous iron oxides which contain silicon revealed that the catalytic activity of *L*-BIOX might stem from a synergetic effect of iron and silicon in the structure.

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a complex porous surface structure with a relatively large surface area (280 m²/g).^{4,6} Further active investigations on its structures, morphologies, and genesis have been conducted from the perspective of inorganic chemistry^{4,7} and microbiology.⁸ *L*-BIOX has been shown to be useful as an anode material for lithium-ion batteries,^{6,9} and as a precursor for pigments, magnetic nano-composites, and acidic silica.¹⁰ Especially in the field of organic chemistry, we have demonstrated that *L*-BIOX can be used as a solid support for reusable solid catalysts; i.e., immobilized enzymatic catalysts for the kinetic resolution of secondary alcohols¹¹ and immobilized palladium catalysts for solvent-free Suzuki-Miyaura



Fig. 1. (a) Photo of a brown precipitate of iron oxide produced by an iron-oxidizing bacteria, *L. ochracea*, (*L*-BIOX) at a freshwater purification plant, Joyo City, Kyoto, Japan, (b) and (c) SEM images of *L*-BIOX.



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coupling reactions.¹² Metal-porphyrin catalysts anchored on L-BIOX have also been shown to be catalytically active in the synthesis of carbonates from epoxides and carbon dioxides.¹³ L-BIOX can be exposed to diverse heating and work-up conditions. One of the derivatives of L-BIOX is magnetic iron oxide covered with silicate,^{14–16} which is used as a support for magnetically recyclable immobilized enzyme catalyst.⁵ Silica microtubules with a trace amount of an iron component can also be obtained by heat and acid treatment and reactions.^{17,18} Nevertheless, the functions of *L*-BIOX itself in organic synthesis have not yet been explored. Therefore, we investigated the catalytic ability of L-BIOX in iron oxide-catalyzed Baeyer-Villiger reactions, which were developed by Murahashi et al. in 1992 using a molecular oxygen/aldehyde system.¹⁹ Herein, we report that *L*-BIOX, which has hitherto been treated as industrial waste, is capable of promoting the Baeyer-Villiger reaction using molecular oxygen as a readily accessible oxidant and an aldehyde under ambient reaction conditions. To the best of our knowledge, this is the first example of the application of an iron oxide of bacterial origin itself as a catalyst in organic synthesis.^{20–24} Comparison of L-BIOX and typical iron compounds in the reaction and additional experiments were also performed to gain insight into the catalytic activity of *L*-BIOX.

2. Results and discussion

Initially, we set out to screen various iron compounds including L-BIOX in the Baeyer-Villiger oxidation of cyclohexanone in the presence of benzaldehyde in benzene at 25 °C under an oxygen atmosphere, referring to Murahashi's report. (Table 1).¹⁹ The iron compounds that were tested in the reaction by way of comparison were commercially available α -Fe₂O₃, γ -Fe₂O₃, Fe₃O₄, and α -Fe. The reaction of 1a with L-BIOX bearing an elemental composition of Fe:Si:P=73:22:5 gave the desired lactone **2a** in 50% yield (entry 1), while L-BIOX with Fe:Si:P=78:10:12 gave 2a in 40% yield (entry 2), suggesting that the elemental composition of L-BIOXs may influence the catalytic activity (vide infra).⁸ The reactions with Fe (III) oxides such as α -Fe₂O₃ and γ -Fe₂O₃ gave **2a** in yields of 18% and 36%, respectively (entries 3 and 4). The reactions with Fe₃O₄ and α -Fe provided the product in 44% and 36% yield, respectively (entries 5 and 6). L-BIOX with Fe:Si:P=73:22:5 definitely enhanced the reaction compared to catalyst-free conditions (entry 1 vs entry 7). L-BIOX enhanced the reaction better than the other iron compounds investigated, including two types of Fe₂O₃.²⁵

Table 1

Baeyer-Villiger oxidation of cyclohexanone with various iron compounds^a

	O iron compound (1 mol % Fe)	
	3 equiv benzaldehyde, O ₂ (1 a benzene, 25 °C, 1 h	tm) 2a
Entry	Iron compound	Yield (%) ^b
1 ^c	L-BIOX	50 (57, 56, 38)
2 ^d	L-BIOX	40 (47, 40, 34)
3	a-Fe ₂ O ₃	18 (25, 20, 10)
4	g-Fe ₂ O ₃	36 (48, 38, 24)
5	Fe ₃ O ₄	44 (55, 41, 36)
6	<i>a</i> -Fe	36 (55, 32, 22)
7	No catalyst	25 (35, 22, 18)

^a Reaction conditions: **1a** (1 mmol), iron compounds (1 mol % Fe), benzaldehyde (3 mmol) in 3 mL of benzene at 25 °C under an O_2 atmosphere (1 atm).

^b Average yields of three runs. The yield of each run is in parentheses. Determined by GC analysis using dodecane as internal standard.

^c *L*-BIOX was obtained from a freshwater purification plant in Joyo city, Kyoto, Japan. Fe:Si:P=73:22:5 (except O).

^d *L*-BIOX was obtained from a cultivation tank at Okayama University, Okayama, Japan. Fe:Si:P=78:10:12 (except O).

The effects of aldehydes and solvents in the L-BIOX-catalyzed Baeyer-Villiger oxidation of cyclohexanone are summarized in Table 2. We first carried out the reaction with various aldehydes in benzene for 1 h since the structure of the aldehyde can influence the reactivity in Baeyer-Villiger oxidation.^{26–28} While the reaction in benzene without aldehyde did not proceed (<2% yield, entry 1), the reaction with benzaldehvde gave **2a** in 48% yield (entry 2). The reaction with 3-chlorobenzaldehvde provided 2a with diminished yield (10%, entry 3) as observed in the literature for aerobic Baeyer-Villiger oxidation.^{27,29} Aliphatic aldehydes such as heptanal and isobutyraldehyde were less effective than benzaldehyde, and provided 2a in yields of 4% and 8%, respectively (entries 4 and 5); these results are consistent with previous reports.^{19,26} Further investigation of the amount of benzaldehyde revealed that the reaction with 3 equivalents of benzaldehyde proceeded efficiently (see Supplementary data, Table S1). In the reactions with other solvents, a trace amount of lactone 2a was obtained in DCM (dichloromethane) or acetonitrile (6% yield in entry 7 and 7% yield in entry 9), whereas the reaction in 1,2-DCE (1,2-dichloroethane) proceeded more efficiently to give 2a in 43% yield (entry 8). No reaction, at least within 1 h, was observed in toluene, THF (tetrahydrofuran) or DMF (N.N-dimethylformamide) (entries 6, 11, and 12). Whereas the reaction in less toxic acetonitrile performed at 50 °C for 3 h proceeded efficiently to obtain 2a in >98% yield (entry 10), benzene was a solvent of choice to facilitate the L-BIOX-catalyzed Baeyer-Villiger oxidation under milder conditions for the subsequent easy screening according to the results in entries 6–9, 11 and 12.30

Table 2

Baeyer-Villiger	oxidation	of	cyclohexanone	with	various	iron	compounds	and
aldehydes ^a								

	1a L-BIC 3 equiv a solv	DX (1 mol % Fe) hldehyde, O_2 (1 atm) yent, 25 °C, 1 h	
Entry	Solvent	Aldehyde	Yield (%) ^b
1	Benzene	None	<2
2	Benzene	Benzaldehyde	48
3	Benzene	3-chlorobenzaldehyde	10
4	Benzene	Heptanal	4
5	Benzene	Isobutyraldehyde	8
6	Toluene	Benzaldehyde	0
7	DCM	Benzaldehyde	6
8	1,2-DCE	Benzaldehyde	43
9	Acetonitrile	Benzaldehyde	7
10 ^c	Acetonitrile	Benzaldehyde	>98
11	THF	Benzaldehyde	0
12	DMF	Benzaldehyde	0

^a Same conditions as those in Table 1. *L*-BIOX with Fe:Si:P=73:22:5 was used.

^b Determined by GC analysis.

 $^{\rm c}\,$ The reaction was carried out at 50 $^{\circ}C$ for 3 h.

The range of the applicable substrates in *L*-BIOX-catalyzed Baeyer-Villiger oxidation was extended to a variety of cyclic and acyclic ketones (Table 3). Adjustment of the optimal reaction conditions for each substrate allowed Baeyer-Villiger oxidation products to form in 23–>98% yield with high regioselectivity of the oxygen insertion position at either a more substituted alkyl group or an aryl group adjacent to the carbonyl carbon. Cyclohexanone, which was used to optimize the reaction conditions, gave the lactone **2a** in >98% yield within 3 h in the oxidation with 1 mol % Fe (entry 1). Notably, the reaction with *L*-BIOX furnished the lactone **2a** effectively under milder reaction conditions in aldehyde/O₂

Table 3

Baeyer-Villiger oxidation of various ketones with L-BIOX^a



^a Same conditions as those in Table 1. *L*-BIOX with Fe:Si:P=73:22:5 was used. ^b Determined by GC analysis.

systems compared to other iron-containing heterogeneous catalysts such as iron-containing mesoporous silica^{31–34} and clay.^{35,36} The reaction with cyclopentanone **1b** proceeded with 10 mol% Fe from *L*-BIOX in 6 h to provide the lactone **2b** in 84% yield (entry 2).

The reaction with 2-methylcyclohexanone **1c** proceeded selectively to give 96% of the corresponding lactone **2c** along with 4% of **2c'** (entry 3). 4-Methylcyclohexanone **1d** provided the desired product 2d in >98% yield (entry 4) and 4-phenylcyclohexanone 1e was transformed into the product **2e** in >98% yield after 6 h (entry 5).³⁷ L-BIOX could also efficiently facilitate the reaction with adamantanone **1f** to give the product **2f** in 96% yield (entry 6). With an acvclic ketone that contains *t*-butyl and methyl groups (**1**g), only the corresponding product 2g was produced in 95% yield (entry 7). The yield of 2g was much improved in an L-BIOX-catalyzed system compared to previously reported systems with iron-containing solid catalysts.^{34,36} Acyclic acetophenone **1h** was also used in the reaction and only 23% of phenylacetate 2h was obtained (entry 8). In contrast, the process with acetophenone bearing a methoxy group at the phenyl moiety 1i gave the product 2i in 88% yield (entry 9).

We tested the recyclability of *L*-BIOX as a catalyst in Baeyer-Villiger oxidation. The test was carried out with cyclohexanone **1a** as a reaction substrate and the results are summarized in Table 4. *L*-BIOX was used five times and gave the product **2a** in high yield in each run (94 to >98% yield), revealing that *L*-BIOX is a reusable catalyst in the reaction without a significant loss of catalytic activity.



3 equiv benzaldehyde, O_2 (1 atm)1a2aRun1st2nd3rd4th50Vield (%) ² 9698>98> 20	0 L	<i>L</i> -BIOX (1 mol % Fe)					
1a 2a Run 1st 2nd 3rd 4th 5th Viald (%) ³ 96 94 98 98 98	\bigcirc	3 equi	3 equiv benzaldehyde, O ₂ (1 atm)				
Run1st2nd3rd4th5thViald $(2^{\circ})^3$ 9694989898	1a		,	,	2a		
Viald $(\%)^{a}$ 06 04 08 \sim 08	Run	1st	2nd	3rd	4th	5th	
Ticid (%) 50 54 58 >56 >56	Yield (%) ^a	96	94	98	>98	>98	

^a Determined by GC analysis.

Fig. 2 shows secondary electron images acquired by a scanning transmission electron microscope (STEM, JEOL, JEM-2100F) of L-BIOX used in the Baeyer-Villiger oxidation of cyclohexanone with 3 equivalents of benzaldehyde in benzene at 25 °C under an oxygen atmosphere after 1 h and 3 h and after the 5th run in the recycling test. By comparing the STEM images of L-BIOX to those before use in the reaction, we found no significant changes in the surface structure after the reaction and the recycling test; the characteristic surface fibrillar structure involving intricate asperities and pores was mostly maintained during the oxidation process. ⁵⁷Fe Mössbauer spectroscopy was also performed with L-BIOX before and after the Baeyer-Villiger oxidation of cyclohexanone for 3 h. The oxidation state of iron in L-BIOX is trivalent both before the reaction (isomer shift (IS)=0.385 mm/s) and after the reaction (IS=0.377 mm/s) (see Supplementary data, Fig. S1), indicating that there was no detectable change in the oxidation state of iron in L-BIOX-catalyzed Baever-Villiger oxidation in the benzaldehyde/O₂ system.

We subsequently turned our attention to the effect of the elemental composition of *L*-BIOX (Fe:Si:P) on its reactivity in Baeyer-Villiger oxidation, since *L*-BIOX with different elemental compositions showed different catalytic reactivities, as shown in Table 1 (*L*-BIOX with Fe:Si:P=73:22:5, entry 1 versus *L*-BIOX Fe:Si:P=78:10:12, entry 2). In our previous report, we stated that *L*-BIOX has an amorphous structure similar to that of 2-line ferrihydrite (2Fh).^{4,6,7,38} Thus, we prepared silicon-containing 2Fhs while varying the ratio of Fe and Si according to the report on the synthesis of silicon-containing 2Fhs,^{38,39} and decided to use these *L*-



Fig. 2. STEM images by TEM analysis of *L*-BIOX before the reaction (a) and after the Baeyer-Villiger oxidation of cyclohexanone for 1 h (b) and 3 h (c), and after the 5th run in the recycling test (d).

BIOX-analogous iron oxides in the Baeyer-Villiger reaction of cyclohexanone **1a** to examine the effect of the amount of silicon on the catalytic activity of L-BIOX (For XRD patterns of L-BIOX and silicon-containing 2Fhs, see Fig. S2 in Supplementary data). Table 5 summarizes the results obtained in the Baeyer-Villiger oxidation of cyclohexanone with silicon-containing 2Fh ($Si_x/2Fh$, x represents the molar ratio of silicon to the total amount of iron and silicon). We prepared Si_x/2Fhs with x ranging from 0 to 0.648. Aerosil[®] 300 was also examined as a pure silicon oxide. The same weights of L-BIOX, Si_x/2Fhs, and Aerosil[®] 300 were used in the reaction (1.2 mg for each 1 mmol of cyclohexanone). The yields of **2a** in Table 5 were plotted as a function of the silicon molar ratio, as shown in Fig. 3. The reactions with $Si_x/2Fhs$ with x ranging from 0 to 0.360 furnished the lactone 2a in a similar yield as L-BIOX, and the yield tended to increase as the silicon molar ratio increased (entries 1-7). Silicon molar ratios of 0.432 and 0.504 in $Si_x/2Fhs$ facilitated the reaction more efficiently, and gave the lactone 2a in 65% yield within 1 h, which reflected a higher catalytic activity than *L*-BIOX (entries 8 and 9). The use of $Si_x/2Fhs$ with x=0.576 and 0.648, however, reduced the yield of 2a to 45 and 43%, respectively (entries 10 and 11). The reaction with Aerosil[®] 300 gave the lactone **2a** in 27% yield, indicating that iron component is necessary to facilitate the reaction since the catalyst-free reaction provided the product in almost the same yield (25% yield, entry 7 in Table 1). Although there is currently no clear explanation for the relation between catalytic activity and elemental composition, the catalytic activity might arise from some cooperative effect of the iron and silicon components.⁴⁰

Table 5

Baeyer-Villiger oxidation of cyclohexanone with Si-containing 2-line ferrihydrites and $\text{Aerosil}^{\circledast}$ 300^{a}



^a Reaction conditions: **1a** (1 mmol), catalyst (1.2 mg), benzaldehyde (3 mmol) in 3 mL of benzene at 25 °C under an O_2 atmosphere (1 atm).

^b Determined by GC analysis.



Fig. 3. Plot of the yield of **2a** versus silicon content (red square: *L*-BIOX, blue circle: $Si_x/$ 2Fhs, black diamond shape: Aerosil[®] 300).

3. Conclusion

We demonstrated that *L*-BIOX could be an effective catalyst for Baeyer-Villiger oxidation using a benzaldehyde/ O_2 system. *L*-BIOX showed superior catalytic activity compared to typical commercially available iron compounds. The *L*-BIOX-catalyzed oxidation proceeded efficiently even at ambient temperature and can be applied to a variety of substrates. The catalytic activity might depend on the presence of silicon and its amount in the amorphous oxide structure. The detailed investigation on the origin of the catalytic activity of *L*-BIOX and the application of *L*-BIOX as a catalyst in other types of reactions are now underway.

4. Experimental section

4.1. General

L-BIOX was obtained as an ocher precipitate either from an experimental freshwater purifying tank in Joyo, Japan (47 wt% of Fe) or an experimental water purifying tank at Okayama, Japan (48 wt % of Fe) and purified by following the reported procedure.⁶ L-BIOX and other iron-containing materials used as catalysts were dried under reduced pressure at 100 °C for 4 h before use. α -Fe₂O₃, γ -Fe₂O₃ and Fe₃O₄ were obtained from Kanto, α -Fe was from Kojundo Chemical, and Aerosil[®] 300 was from Aerosil. Starting Materials (1a-i) were purchased from TCI, Wako, Aldrich or nacalai tesque and distilled under reduced pressure before use or used as received according to their purity checked by GC analysis. All aldehydes were distilled under reduced pressure before use. Dichloromethane, 1,2-dichloroethane, toluene, acetonitrile, dimethylformamide were distilled before use. Super dehydrated tetrahydrofuran was purchased from Wako and used as received. Benzene was purchased from Wako and used as received. Yield of

Baever-Villiger oxidation products were determined using dodecane as an internal standard by means of gas chromatography (GC) or ¹H NMR analysis. GC analysis was performed with Agilent GC-2014, capillary column, FID detector, 280 °C; injection, 280 °C, carrier gas, nitrogen; carrier gas rate, 54 mLmin⁻¹; under the following condition 5 min hold at 100 °C, then raised to 270 °C at a rate of 10 °Cmin⁻¹. Based on previous reports, Si-doped samples were prepared as follows.^{39,41} A 0.025 molL⁻¹ Fe(NO₃)₃·9H₂O (nacalai tesque, 99.0%) aqueous solution and appropriate concentrations of m-Na₂SiO₃·9H₂O (nacalai tesque) aqueous solution were prepared and then these two solutions were mixed to prepare 1L solution. Si concentrations were adjusted to x=Si/(Si+Fe)(x=0-0.90 in 0.10 increments). The solution was vigorous stirred with slowly adding NH₃ aq (nacalai tesque, 28 wt %) until pH was reached at 10.0 and then left for 15 min. The obtained precipitate was repeatedly centrifuge-washed with distilled water until the electrical conductivity of supernatant was reached to nearly 0 S/m. The precipitate was vacuum-dried and crashed to fine powder by alumina mortar.

4.2. General procedure for Baeyer-Villiger oxidation

In a two-necked 25 mL round-bottom flask was charged with L-BIOX (0.01 mmol, 1.2 mg), a ketone (1 mmol), and benzene (2 mL) before addition of benzaldehyde (3 mmol, 306 µL) and benzene (1 mL). After purging with O₂ gas, the mixture was allowed to stir at 25 °C in a water bath attached with a gas bag filled with O₂ gas (1 atm). After appropriate reaction time, to the reaction mixture was added dodecane followed by filtration through a short plug of Celite and MgSO₄ to remove a catalyst and the filtrate was analyzed by GC or ¹H NMR. Spectral properties of products (**2a**, **2b**, **2d**, **2g**, **2h**) were identical with those of commercial (TCI, nacalai tesque, Kanto) authentic sample. Spectral properties of products (2c, 2e, 2f, 2i) were identical with those of authentic sample synthesized according to the reported procedure.⁴² Spectral property of **2c**' was identical with the reported data.⁴³

4.3. Procedure for recycling test of L-BIOX

After the reaction of cyclohexanone performed according to the general procedure, L-BIOX was separated from the organic layer and washed with ethyl acetate three times and then dried under reduced pressure at 100 $^\circ\text{C}$ for 4 h. The organic layer was analyzed by GC. The dried L-BIOX was resubjected to the next reaction of cyclohexanone. This procedure was repeated until the 5th run.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.10.057.

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- 40. We also carried out the similar investigation on the effect of phosphorous using phosphorous-containing 2Fhs ($P_x/2Fh$, x = 0.1, 0.2, 0.3, 0.4, 0.5) and revealed that the catalytic activities of $P_x/2Fhs$ are lower than *L*-BIOX with Fe:Si:P = 73: 22:5 and decrease as phosphorous molar ratio increased. See Supplementary data, Table S2 and Figure S3.
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