Sn-based catalysts for Baeyer-Villiger oxidations by using hydrogen peroxide as oxidant

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ABSTRACT Baeyer-Villiger (BV) oxidation is one of the most important transformation reactions in synthetic organic chemistry. Catalytic versions of the BV oxidation are particularly attractive in practical applications, because the catalytic transformation substantially simplifies reaction process while minimizing reactant consumption as well as waste production. Further benefits are expected from replacing peracids, the traditionally used oxidant, by low cost and environmentally friendly hydrogen peroxide (H_2O_2). This review will first introduce very briefly the features of BV oxidation reactions, and the corresponding oxidants traditionally used. Afterwards, the emphasis will be placed on the specific Sn-based catalysts, their performance comparison for the BV oxidation reaction by using H_2O_2 as oxidant, and the catalytic mechanisms of most Sn-based catalysts reported so far, including homogeneous Sn-based catalysts (such as Sn-based fluorinated biphasic system catalysts), heterogeneous Sn-based catalysts (such as Sn-based zeolite catalysts, Sn-based mesoporous composites, Sn-incorporated clay catalysts, Sn-based metal oxide composites and polymer supported Sn catalysts). Finally, the Sn-based catalysts for BV oxidation are outlooked for their potentials and perspectives in enhancing the performance and then accelerating the practical applications of BV oxidations by using H_2O_2 . The developing direction of the Sn-based catalytic BV reaction is also illustrated.

Keywords: Baeyer-Villiger oxidation, tin based catalyst, catalysis

INTRODUCTION

The BV oxidation (also called Baeyer-Villiger rearrangement), named after Adolf Baeyer and Victor Villiger who first reported the reaction in 1899, is an organic reaction that forms an ester from a ketone as shown in Scheme 1, or a lactone from a cyclic ketone by using peroxyacids or peroxides as the oxidant [1,2]. Since valuable lactones or

esters can be obtained directly from the corresponding ketones, BV oxidation has become one of the most important transformations in organic synthesis [3–6]. Generally, percarboxylic acids (i.e., *meta*-chloroperoxybenzoic acid (*m*-CPBA), peracetic acid, etc.) are the most common and suitable oxidants used in BV oxidation, but they are becoming problematic for industrial scale use due to their generating amounts of carboxylic acid waste as side product and resulting in low ester selectivity [7–9]. Moreover, percarboxylic acids are expensive, and unstable in solution and typically require chlorinated solvents for improved performance [10]. In contrast, hydrogen peroxide (H_2O_2) is environmentally friendly and generates water as the only co-product of its reduction, which can avoid many of the problems associated with peroxy carboxylic acids as oxidants [11]. On the other hand, H_2O_2 is also commercially available, low cost, and easy to handle. In addition, H_2O_2 contains a higher concentration of active oxygen (47 wt.%) than all other oxidants except molecular oxygen, which not

Scheme 1 General BV oxidations of (a) a ketone to an ester and (b) a cyclic ketone to a lactone.

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only results in improved process economics but also leads to lower effluent outputs [12–14]. Therefore, attention is now focused on how to replace percarboxylic acids with aqueous hydrogen peroxide.

Thus, much research has focused on the development of effective catalysts for efficient BV oxidation using low cost H_2O_2 oxidants. Some successes have been achieved with homogeneous catalysts containing active centers based on Se [15], Re [16], Zr [17], W [18], Pd [19], Pt [20], Mn [21], or with solid acids [22,23]. All of these catalysts have at least one drawback, such as low activity or poor selectivity, tedious recovery and regeneration, or high costs for starting materials and/or safety precautions. Uyanik *et al.* [24,25] reported that the lipophilic $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{Ca}[\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst show highly efficient and selective catalytic activity for BV oxidation of ketones with 30 wt.% aqueous H_2O_2 to give a high yield lactones, which leads to a new development direction of BV catalysts. While the synthesis procedure of $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{Ca}[\text{B}(\text{C}_6\text{F}_5)_4]$ catalysts is complicated. ten Brink *et al.* [26] gave a comprehensive review about the new developments toward greener procedures during the BV oxidation by using H_2O_2 as green oxidants, and the development of cleaner reactions, such as nonchlorinated solvents, is still necessary, and they also pointed out that the better catalysts for the activation of hydrogen peroxide are still needed.

Tin (Sn) based catalysts, as one of the most important catalyst for the BV oxidation by using H_2O_2 as oxidant, are attracting extensive attention because of its cost-effect, special character of Lewis acid sites and the non-toxic characters, which exhibits excellent application prospect in the BV oxidation reaction. ten Brink *et al.* [26] also pointed out that the Sn-MCM-41 as solid Lewis acid catalysts are highly interesting for the large-scale BV oxidation reactions. Although several reviews on the BV reactions have been published, which covers the development of the BV oxidation, the concerned oxidants, corresponding catalysts, etc. [27,28], no review aiming at the specific Sn-based catalysts for BV oxidation by using H_2O_2 as oxidant was published.

Since the Sn-based catalysts as a kind of transitional metal based composites are extensively researched for BV oxidation, the focus of this review is on the Sn-based catalysts for the BV oxidation by using H_2O_2 as oxidant. Firstly, the progresses in the development of Sn-based catalysts were reviewed, and the catalytic activity was compared and discussed; secondly, the mechanism of Sn-based catalysts was probed to better understand the catalytic BV oxidation process, and finally, a summary and outlook were provided

to illustrate in which direction the Sn-based catalytic BV reaction is developing.

Sn-BASED CATALYSTS FOR BV OXIDATIONS BY USING H_2O_2

Sn-based catalysts, including homogeneous and heterogeneous catalysts, exhibit excellent catalytic activity for BV oxidation by using H_2O_2 because of their special Lewis acid characters, which will be reviewed and discussed in detail.

Homogeneous Sn Catalysts

One of the most important and significant progresses in the development of homogeneous Sn catalysts is the Sn-coordinated fluororous compounds used in the so-called fluororous biphasic system (FBS), which was first introduced by Horváth and Rábai in 1994 [29] and has exhibited some potential advantages over the classical homogeneous catalysts, including easy and effective separation and recycling of the catalyst [30]. The new kind of tin(IV) bis(perfluorooctanesulfonyl)amide complex ($\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$) is used as catalyst to realize the BV oxidation of several kinds of ketones in FBS, and perfluoro(methylcyclohexane) ($\text{CF}_3\text{C}_6\text{F}_{11}$) and 1,2-dichloroethane ($(\text{CH}_2\text{Cl})_2$) or 1,4-dioxane are used as solvent. The catalytic activity of Sn active center can be tuned by changing the ligand. As shown in Table 1, by using $-\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2$ as ligand, the selectivity of ester reaches 97%–99%, especially the conversion rates of BV oxidation of cyclobutanone and adamantanone can reach at 97% and 94%, respectively, which is higher than that of those using $-\text{OSO}_2\text{CF}_3$ as ligand [31,32]. Compared to other homogeneous catalysts, the catalyst completely immobilized in the fluororous phase, and therefore can be recovered and reused. On the other hand, the reaction time can be shortened by $\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$ in FBS using 35% aqueous H_2O_2 as oxidant, and moreover, the problem of oxidant H_2O_2 decomposing can be prevented. High yields and purities of lactone can also be obtained by the catalytic BV oxidation process under mild conditions.

In these respects, the fluororous Sn-based catalysts in FBS show excellent performance for BV oxidation reaction, and in the meantime, however, the toxicity of organic catalysts is in most cases unavoidable resulting in the limitation of its wide applications.

Heterogeneous Sn Catalysts

Sn-zeolite based catalysts

Zeolites also named as “molecular sieves”, as a kind of selective heterogeneous catalysts, are used widely in many important chemical processes. The microporous crystalline

Table 1 BV oxidations of ketones by using $\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$ as catalyst [31]

Entry	Substrate	Product	Conditions	Conversion (%)	Selectivity (%)
1 ^{a)}			50°C, 1 h	97	99
2 ^{a)}			50°C, 2 h	59	91
3 ^{b)}			25°C, 1 h	37	97
4 ^{c)}			25°C, 2 h	94	99
5 ^{c), d)}			50°C, 5 h	67	99
6 ^{c), d)}			70°C, 2 h	43	99

a) Substrate 2 mmol, H_2O_2 aq.(35%) 2 mmol, $\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$ 1 mol%, solvent ($\text{CF}_3\text{C}_6\text{F}_{11}$ 3 ml, 1,4-dioxane 3 mL); b) substrate 1 mmol, H_2O_2 aq.(35%) 0.8 mmol, $\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$ 1 mol%, solvent ($\text{CF}_3\text{C}_6\text{F}_{11}$ 2 ml, 1,4-dioxane 2 mL); c) substrate 2 mmol, H_2O_2 aq.(35%) 2 mmol, $\text{Sn}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$ 1 mol%, solvent ($\text{CF}_3\text{C}_6\text{F}_{11}$ 3 ml, $(\text{CH}_2)_2\text{Cl}_2$ 3 mL); d) 3 mol% of catalyst was employed with respect to the ketone; e) regioselectivity (> 99%) determined by GC and ^1H NMR.

frameworks of most aluminosilicates have high hydrothermal stability and feature attractive shape and transition-state selectivity effects [33,34]. Since zeolite material possesses microporous character, a zeolite-catalyzed reaction typically involves four steps. Firstly, reactant molecules diffuse to the active sites in the zeolite through its micropores, and are adsorbed at the active sites in the second step; thirdly, chemical reaction happens to give the product; and finally diffusion of the adsorbed product through channels in the zeolite [35]. The microporous character endows zeolite more amount of active sites existing external and/or internal pores, thus zeolite has been used widely in a variety of catalytic processes, including great numbers of oxidations and, specifically, the BV reaction for that it allows the incorporation of transition metals in framework [36–39].

Corma *et al.* [40–43] firstly reported the tin-containing beta zeolites (Sn-beta zeolite) as the efficient catalysts for

the BV reaction with 35% aqueous H_2O_2 as oxidant because of the special character of Sn species with Lewis acids, and they pointed out that the Sn-beta zeolite catalyst retained its high chemoselectivity in carrying out the BV oxidation of unsaturated ketones, such as bicyclohept-3-en-1-one, and a high conversion of >95% with 100% selectivity for lactones were obtained, which could only be reached by using enzymes as catalysts. While, using *m*-chloroperbenzoic acid (mCPBA) as an oxidant would lead to the production of lactones with a relatively low selectivity of 29% and large amount of epoxide by-products [40]. This convincingly indicates that Sn-beta zeolite can be an excellent alternative for percarboxylic acids when using H_2O_2 as oxidant. Moreover, the corresponding catalytic mechanism is given as following: the carbonyl group of ketone is activated by the Sn atoms in beta zeolite, which are Lewis acids, followed by a nucleophilic attack by H_2O_2 on the carbonyl carbon to

give an intermediate similar to the “Criegee” adduct; and then the intermediate rearranges to produce the end product, which was reviewed by Sanchidrián *et al.* [28].

However, there still exist some problems, such as much low Sn content and some amount of the Sn active sites embedded, resulting in the active activity not fully exhibited. In order to improve the Sn species amount and expose enough active sites, recently, Li *et al.* [44] reported nanosized Sn-beta zeolite (Sn-beta-PS) with Sn content of 6.2 wt.% which was synthesized by the solid-gas reaction of highly dealuminated beta zeolite with SnCl_4 vapor (as shown in Fig. 1), and this Sn-beta-PS material shows high and stable catalytic activity for the BV oxidation of 2-adamantanone with hydrogen peroxide, e.g., a high selectivity of above 99% has been obtained when using $\text{C}_6\text{H}_5\text{Cl}$ as solvent, and 80.5% conversion rate with 99% selectivity can still be obtained even after 5 cycles. The post synthesis strategy not only improves the content of isolated Sn species, but also makes the Sn active sites exposed enough, leading to the high BV reaction efficiency. By adopting similar method, Sn-beta zeolites with 3.8 wt.% SnO_2 (i.e., $\text{Si}/\text{Sn} = 83$, see the SEM images in Fig. 2) have also been synthesized, which were proved to be efficient catalysts for BV oxidation of cyclohexanone to ϵ -caprolactone with high selectivities of above 98% of the target product [45].

Besides the Sn active sites content, the structure of the zeolite also affects the activity for BV oxidation. Stannosilicate zeolites with nanosheet morphology and MFI topology (Sn-MFI-ns, as shown in Fig. 3) show much higher catalytic activity than bulk Sn-MFI in the BV oxidation of cyclic ketones using H_2O_2 [46]. Compared with bulk Sn-MFI, Sn-MFI-ns shows a significant increase in catalytic activity for the BV oxidation of cyclic ketones from the data in Table 2, e.g., the conversion rate and selectivity of target

Figure 1 Strategy for post-synthesis of Sn-beta through combination of dealumination with solid-gas reaction (atom-planting method) as a catalyst for BV oxidation of 2-admantanone. Reprinted with permission from Ref. [44], Copyright 2011, American Chemical Society.

Figure 2 Steam-assisted conversion (SAC) method for synthesis of Sn-beta zeolite as a catalyst for BV oxidation of cyclohexanone. Reprinted with permission from Ref. [45], Copyright 2013, Elsevier.

Figure 3 TEM image and schematic structure of Sn-MFI-ns. Reprinted with permission from Ref. [46], Copyright 2011, American Chemical Society.

product is 92% and >98%, respectively on Sn-MFI-ns, while the values are 13% and 95%, respectively on bulk Sn-MFI. The activities and efficiencies of Sn-MFI-ns were comparable to those of Sn-MCM-41 with Sn sites embedded in a mesoporous amorphous silica framework, indicating that the external Sn sites in Sn-MFI-ns have a performance similar to the latter, while the former show superior thermal and hydrothermal stability than Sn-MCM-41. The high catalytic activity of Sn-MFI nanosheet should be due to the surface area which makes the Sn active sites exposed enough resulting in the activity enhancement of BV oxidation reaction. On the other hand, the less diffusion limitations to the substrate with a large molecular dimension also contribute to the high catalytic activity of Sn-MFI nanosheet. Thus, the catalytic activity for BV oxidation would be enhanced for the zeolite with mesoporous structure, e.g., mesoporous Sn-beta zeolites of 20–50 nm in pore diameter (see the transmission electron microscopy (TEM) images in Fig. 4) exhibit comparable and even higher performance than the conventional Sn-beta zeolites for the BV oxidation of 2-adamantanone by H_2O_2 owing to its hierarchical micro/mesoporous structures of the former [47].

Table 2 Catalytic activities of Sn-containing catalysts for the BV oxidation of 2-adamantanone using H_2O_2 ^{a)} [46]

Catalyst	H_2O_2 ^{b)} (equiv)	Conversion ^{c)} (%)	Efficiency ^{d)} (%)	TON ^{e)}	TOF ^{f)} (h^{-1})	Selectivity ^{g)} (%)
Bulk Sn-MFI	1.5	13	13	17	5	95
Bulk Sn-beta	1.5	99	92	143	210	>98
Sn-MCM-41	1.5	99	82	137	58	>98
Sn-MFI-ns	1.5	92	8	122	38	>98
Sn-MFI-ns-e ^{h)}	1.5	87	75	120	37	>98
Bulk Sn-MFI	0.6	15	28	23	9	>98
Sn-MCM-41	0.6	62	99	99	91	>98
Sn-MFI-ns	0.6	62	99	104	86	>98
Sn-MFI-ns-sil ⁱ⁾	1.5	39	49	51	12	>98
Sn-MCM-41-sil	1.5	76	68	91	20	>98
SnO_2 -MCM-41	1.5	3	3	4	2	96

a) Reaction conditions: catalyst, 0.66 mol% of Sn with respect to the ketone; ketone, 1 mmol; 50% H_2O_2 , 1.5 or 0.6 mmol; dioxane, 3 g; 75°C, 16 h; b) H_2O_2 equivalents with respect to ketone; c) conversion = (moles of ketone converted)/(initial moles of ketone) $\times$ 100; d) oxidant efficiency = (moles of ketone converted)/(moles of H_2O_2 consumed) $\times$ 100; e) Turnover number (TON) = (moles of substrate converted)/(moles of tin centers) at 16 h; f) turnover frequency (TOF) = (moles of substrate converted)/(moles of tin centers) per hour calculated from 1 h conversions, except Sn-beta at 15 min; g) selectivity = (moles of product)/(moles of ketone reacted) $\times$ 100; h) “-e” indicates the presence of extra framework tin; i) “-sil” indicates the catalyst is silylated.

Figure 4 Strategy for synthesis of mesoporous Sn-beta and TEM (a, b) images of Meso-Sn-beta; SEM (c, d) images at different magnifications. Reprinted with permission from Ref. [47], Copyright 2014, Royal Society of Chemistry.

Delaminated zeolite with novel structure demonstrates an excellent catalytic performance for BV oxidation. Recently, Ouyang *et al.* [48] reported a heteroatom-substituted delaminated zeolites by the surfactant-free exfoliation of a MWW-type borosilicate zeolite precursor into a delaminated zeolite (shown as Fig. 5). Especially, the Sn substituted delaminated zeolites (Sn-DZ-1) exhibit much higher conversion rate than Sn-beta for the BV oxidation of 2-adamantanone according to the data in Table 3. The enhanced catalytic activity of the delaminated Sn-DZ-1 is due to the three-dimensional (3D) structure which

accelerates the species diffusion and in turn resulting in the activity enhancement. Following this, Liu *et al.* [49] synthesized a novel stannosilicate with the MWW topology, Sn-MWW, by hydrothermally synthesizing in alkali medium using boric acid as a crystallization-supporting agent, in which the Sn species were incorporated in the framework, occupying mainly the tetrahedral sites. A mild acid treatment was conducted on the Sn-MWW precursors (Sn-MWW lamellar) to induce a structural transformation to tin-containing materials structurally analogous to MCM-56 (Fig. 6). The post-synthesized Sn-MCM-56, par-

Figure 5 Schematic diagram of the surfactant-free exfoliation of a MWW-type borosilicate zeolite precursor into a delaminated zeolite consisting of high density of silanol nests and the reoccupation of the silanol nests with various heteroatoms. Reprinted with permission from Ref. [48], Copyright 2015, American Chemical Society.

Table 3 BV Oxidation of 2-adamantanone by Sn-DZ-1 and Sn-beta^{a)}[48]

Substrate	Sn-DZ-1 ^{b)}		Sn-beta ^{c)}	
	Initial rates ^{d)} [mol h ⁻¹ (mol Sn) ⁻¹]	Conversion ^{e)} (%)	Initial rates ^{d)} [mol h ⁻¹ (mol Sn) ⁻¹]	Conversion ^{e)} (%)
	866	97	1963	99
	825	95	417	66
	688	94	366	57

a) Reaction conditions: 30 wt.% H₂O₂ in H₂O, H₂O₂/ketone = 1.5:1 by mol, 1,4-dioxane as solvent, 75°C, molar ratio of Sn to ketone = 0.0066:1; b) Si/Sn = 65; c) Si/Sn = 100; d) initial rates are calculated by dividing the moles of substrates converted per hour when conversion rate of substrate is under 20% by moles of Sn sites; e) conversion = (moles of ketone converted at 24 h)/(initial moles of ketone) × 100. Selectivities for all these catalysts are nearly 100%.

tially delaminated for layered zeolitic structure, composed of partially delaminated MWW sheets and possessed larger external surface as well as more open reaction space. More importantly, the prepared Sn-MCM-56 appears to be more efficient than Sn-MWW in the BV oxidation of 2-adamantanone with H₂O₂ as oxidant, and the conversion rate of the former is 10% higher than that of the Sn-MWW at the same Sn content (Fig. 7a) or at the same reaction time (Fig. 7b). This is due to that the analogue Sn-MCM-56 can effectively alleviate the steric restriction and diffusion limitation to bulky molecules that the microporous zeolite catalysts usually encountered. Moreover, the Sn-MCM-56 turned to be more active than Sn-beta when tert-butyl hydroperoxide was employed as an oxidant, and because of that the stan-

nosilicates with large pore sizes are thus highly desirable to overcome the sluggish diffusion problems encountered in the BV oxidations. Expectedly, the active and most selective Sn-beta zeolite, as a fascinating catalyst system for heterogeneous catalysis will continuously play an important role in the catalytic applications for BV oxidations.

Different from the framework Sn-beta zeolites, Snexchanged zeolite, such as Sn(salen)-NaY with [Sn(salen)]²⁺ complex moiety *in situ* immobilized into NaY zeolite, also showed impressive catalytic performance (with high selectivity) in BV oxidation of various cyclic ketones including 2-adamantanone, cyclohexanone, cyclopentanone, 4-methylcyclohexanone, and 2-methylcyclohexanone [50]. However, tert-butyl hydroperoxide (tert-BuOOH) was

Figure 6 Schematics for the formation of Sn-MCM-56 analogues from the Sn-MWW precursors. Reprinted with permission from Ref. [49], Copyright 2013, Elsevier.

Figure 7 Dependence of ketone conversion on the Sn content (a) and the reaction time (b) in the BV oxidation of 2-adamantanone over Sn-MWW (1) and Sn-MCM-56 (2). Reprinted with permission from Ref. [49], Copyright 2013, Elsevier.

used as the oxidant during the BV oxidation by using Sn(salen)-NaY as catalyst, which is expensive and therefore undesirable in applications.

In a word, Sn-based zeolite materials are excellent catalysts for BV oxidation reaction when using H_2O_2 as oxidant. Especially, in the BV oxidations of unsaturated ketone, the chemoselectivity is especially high by using Sn-based zeolite molecular sieves as catalysts with the target product being frequently 100% ester or lactone. However, the catalytic performances for BV oxidation of bulky cycle ketones with large molecular weights need to be enhanced because

of micropore size limitation of the Sn-based zeolite molecular sieves.

Sn-containing mesoporous material catalysts

Aluminosilicate zeolites and zeolitic metallosilicate containing isolated transition metal ions have been extensively used as solid Brønsted acid catalysts in petrochemical processing and solid Lewis acid catalysts for redox reactions, thanks to their uniform, small pore size, flexible frameworks, and controlled chemistry [51–53]. However, their applications are limited to small molecules that can diffuse

through the small cavities (<1.5 nm typically) and the narrow channels (<0.8 nm) between the cavities [54]. It has been widely demonstrated that the mass transfer limitations are an important issue in industrial applications involving zeolitic materials [55–57]. To circumvent the diffusional limitations imposed by zeolitic structures, mesoporous materials with pore diameters in between 2–50 nm would be desirable. Since mesoporous material (MCM-41S) has been reported by researchers at Mobil in 1992 [58], a series mesoporous materials, such as hexagonal honeycomb MCM-41, cubic mesophase MCM-48 and layered mesophase MCM-50, have been reported sequentially.

Since Corma *et al.* [59,60] firstly reported Sn-MCM-41 as an efficient catalyst for BV oxidation, mesoporous Sn-MCM-41 opens up a new class of heterogeneous catalysts for the BV reaction with H_2O_2 . They developed, for the first time, a new class of heterogeneous catalyst Sn-MCM-4 by a direct hydrothermal synthesis method, and this catalyst exhibited high performance for BV oxidation of adamantanone with >98% conversion rate and a selectivity of >98%. Also, the Sn-MCM-4 catalyst can effectively catalyze the BV oxidations of cyclohexanone and unsaturated ketone, such as dihydrocarvone [59]. Following this, they employed a post treatment method to graft Sn species onto MCM-41, in which Sn has been incorporated in a post synthesis treatment by a grafting procedure (Sn_{graft}-MCM-41), to yield isolated, active and well-accessible metal centers, and they found that the prepared Sn_{graft}-MCM-41 showed excellent catalytic activity for BV oxidation of adamantanone with a selectivity of >99% [60]. It is satisfactory that the mesoporous molecular sieve Sn-MCM-41 can also be efficient for the BV oxidation of large molecule substrates, such as cyclocitral, safranal, myrtenal, cinnamaldehyde, *p*-methoxycinnamaldehyde and piperonal [61]. The mesoporous Sn-MCM-41 provides higher conversion rates for BV oxidation than by Sn-beta zeolite, which can be attributed to the larger pore diameter and less sterical hindrance on the diffusion by mesoporous molecular sieves [62].

In order to overcome the limitation of intraparticle diffusion of substrates at the active sites incorporated in the mesoporous framework, submicrometer-sized Sn-MCM-41 particles (Sn-MCM-41/SMPs) with short mesopore channels and stable Sn species are welcome. As expected, these Sn-MCM-41/SMPs displayed higher initial reaction rates than Sn-MCM-41 for the BV oxidation of adamantanone with H_2O_2 , for that the shorter mesoporous channels in former play an important role in accelerating the diffusion rate of reactant molecules in

the pores [63]. As another kind of hexagonal mesoporous material, Sn-SBA-15 (Fig. 8) also showed much higher catalytic activity for the BV oxidation of cyclohexanone to ϵ -caprolactone than Sn-MCM-41 from the data in Table 4, e.g., the conversion rate and selectivity can be improved from 37.3%–52.2% to 46.4%–74.4% on Sn-MCM-41, and 67.6%–82.6% to 72.5%–86.3% on Sn-SBA-15, respectively. The enhanced catalytic activity is due to the larger pore size of Sn-SBA-15 (5.5–5.6 nm) than that of Sn-MCM-41 (2.7–2.7 nm), and furthermore, this heterogeneous mesoporous Sn-SBA-15 catalyst was reusable without any appreciable loss in activity and selectivity after three cycles [64]. As mentioned above, for small molecule size substrates, Sn-beta zeolite with a regular pore size of 0.3–0.7 nm in diameter is an efficient catalyst for BV oxidation, and the sterical hindrance over substrate/product diffusion in micropore systems makes the mesoporous molecular sieve, such as Sn-MCM-41 and SBA-15, of 2-nm in channel diameter much more desirable.

Compared to hexagonal honeycomb Sn-MCM-41, cubic mesophase Sn-MCM-48 would exhibit much higher catalytic performance, as an example, Sn-MCM-48 exhibited conversion rates of 51%–100% and 53%–86% for adamantanone and norcamphor BV oxidations respectively by using H_2O_2 as oxidation agent, while Sn-MCM-41 exhibited conversion rates of 42%–90% and 32%–73%, accordingly [65]. Moreover, the selectivity to adamantanone-lactone as well as norcamphor-lactone was almost 100% for the cubic mesophase Sn-MCM-48 catalyst. This is mainly due to the faster diffusion of reactants and products in cubic pore channels than that in hexagonal pore channels. In addition, the cubic pore channels of Sn-MCM-48 make the Sn active sites exposed enough, and in contrast, partial amount of Sn was located in the pore walls of the planar hexagonal Sn-MCM-41 and inaccessible for the reactant molecules, thus, not all Sn sites will function as active Lewis acid sites and contribute to the overall catalytic activity at the same extent. This is not contradictory with the report by Corma *et al.* [66] that the catalytic active center in Sn-beta and Sn-MCM-41 zeolites for BV oxidations involves not only the framework Sn sites but also associated “basic” oxygen atoms that stabilize the reaction transition state through hydrogen bonding.

Among the reported cubic mesoporous silica materials, SBA-16 appears to be one of the best candidates as catalytic support or absorbent because of the enhanced thermal stability due to the thick wall, economical synthesis with inexpensive silica sources, and large pores [67–70]. Sn incorporated SBA-16 (Sn-SBA-16), as an ordered cubic-like

Figure 8 TEM images of Sn-MCM-41 (a, b) and Sn-SBA-15 (c, d). Reprinted with permission from Ref. [64], Copyright 2015, Springer.

Table 4 Catalytic activities of different catalyst for the BV oxidation of cyclohexanone using H_2O_2 as oxidant [64]

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)	TON
/	1.4	0	0	0
Si-MCM-41	1.6	0	0	0
Si-SBA-15	1.5	0	0	0
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	5.5	0	0	0
Sn-MCM-41(100)	37.3	73.3	27.3	70
Sn-MCM-41(50)	47.4	82.6	39.3	79
Sn-MCM-41(30)	48.4	76.2	36.9	62
Sn-MCM-41(10)	52.2	67.6	35.3	64
Sn-SBA-15(100)	46.4	72.5	33.6	87
Sn-SBA-15(50)	69.6	86.3	60.1	114
Sn-SBA-15(30)	72.5	82.6	59.9	111
Sn-SBA-15(10)	74.4	78.2	58.2	108

0.1 mol cyclohexanone; 30% H_2O_2 /cyclohexanone (mol) = 3; 30 g 1,4-dioxane; 1 g catalyst; 70°C; 6 h.

mesoporous structure, gives Lewis acid sites through the framework substitution for silica matrix. More importantly, this Sn-SBA-16 material with tetrahedral-positioned Sn species exhibited high catalytic activity for BV oxidation of adamantanone with 60% conversion rate and almost 100% selectivity of lactone at the pH value of 6 as shown

in Fig. 9a [71], which was comparable to the Sn-MCM-48 [65]. In contrast, the Zr incorporated SBA-16 (Zr-SBA-16) shows much lower conversion rate for BV oxidation of adamantanone as shown in Fig. 9b, further indicating the high catalytic activity of Sn-based SBA-16 catalyst. This is also consistent with the result reported by Nekoksová

Figure 9 (a) BV oxidation of adamantanone over Sn-SBA-16 synthesized under different pH values at 6 h of reaction. (b) BV oxidation of adamantanone over Zr-SBA-16 (with Zr/Si molar ratio in gel = 0.01) and Sn-SBA-16 (pH 6, Sn/Si molar ratio in gel = 0.01) at 90°C. Reprinted with permission from Ref. [71], Copyright 2008, Springer.

et al. [65] in which Sn-MCM-48 with a cubic mesophase of cross-linked 3D channels exhibited higher conversion rates of adamantanone and norcamphor oxidation than Sn-MCM-41 with a block of one-way hexagonal channels. The 3D channels structure facilitates the diffusion of reactants and the transport of products resulting in the enhanced BV oxidation catalytic activity.

At the same time, periodic mesoporous organosilicas (PMO) which are another kind of mesoporous materials are studied extensively, and the PMO materials show high catalytic activity in BV oxidation reaction especially combined with metalloporphyrins. Metalloporphyrins have attracted considerable interest because of their various physicochemical properties [72–75] and their capability to catalyze a variety of oxidation reactions, such as alkene epoxidation and alkane hydroxylation with molecular oxygen [76]. Jeong *et al.* [77] prepared ordered metal-tetrakis(carboxyphenyl)porphyrin (metal = Fe, Cu, Sn) bridged periodic mesoporous organosilicas (M-TCPP-PMO) with high surface areas of about 350–1087 m² g^{−1} and ordered pore channels (TEM images as shown in Fig. 10), and the M-TCPP-PMO exhibits high catalytic activity for BV oxidation of cyclohexanone. Among the high-valent M-porphyrin (M = Fe, Cu, Sn), the Fe-TCPP-PMO demonstrates the highest catalytic activity for the BV oxidation of cyclohexanone. This is due to metal species on the wall of mesoporous silica along with cyclohexanone contribute the high catalytic activity.

Besides mesoporous materials mentioned above, mesoporous silica nanospheres are becoming attractive and prospective in the fields of biology, drug delivery systems and cancer diagnosis and therapy [78–80]. Sn-containing mesoporous silica nanospheres (Sn-MSNs) with uniform crater-like mesopores (Fig. 11) and strong hydrophobicity exhibited much higher activity in the BV oxidation of

Figure 10 TEM images of samples Fe-TCPP-PMO-10% (a), Cu-TCPP-PMO-10% (b), Sn-TCPP-PMO-10% (c), Fe-TCPP-PMO-20% (d) and Cu-TCPP-PMO-20% (e), Sn-TCPP-PMO-20% (f). Reprinted with permission from Ref. [77], Copyright 2011, American Chemical Society.

bulky cyclic ketone and 2-adamantanone than mesoporous Sn-MCM-41 which possessed long one-dimensional (1D) mesopore channels [81]. As can be seen from Table 5, the yield of adamantanone-ester using Sn-MSNs as catalyst reaches 85% at a selectivity of above 94%, much higher than that of using mesoporous Sn-MCM-41 as catalyst.

On the whole, the presence of mesoporous structure in tin-containing materials will effectively offset the shortcomings of Sn-based microporous zeolite catalysts of ≤1.5 nm in its pore size, in which the diffusions of cycle ketone molecules of large molecular weights and/or bulky substituent groups will be greatly hindered. Thus, using mesostructured Sn-based zeolites as catalysts will enable the reactants to diffuse into the mesopore system of the catalysts to access most Sn active centers, thus resulting in the enhanced conversion rates.

Figure 11 TEM images of Sn-MSNs products prepared at varied calcination temperatures indicated. Reprinted with permission from Ref. [81], Copyright 2015, Elsevier.

Table 5 Catalytic activity of Sn-MSNs for the BV oxidation of 2-adamantanone using H_2O_2 as oxidant when changing the atomic ratio of Si to Sn [81]

2-adamantanone (1) 2-oxatricyclo[4.3.1.1^{4,8}]-undecan-9-one (2)

Catalyst	Si/Sn	Conversion ^{a)} (%)	Selectivity ^{b)} (%)	Yield ^{c)} (%)	TON ^{d)} (ICP) (mol/mol Sn)
Sn-MSNs (Si/Sn=43)	43	83.8	99	82.8	44
Sn-MSNs (Si/Sn=62)	62	87.2	97	84.9	65
Sn-MSNs (Si/Sn=90)	90	74.8	95	70.8	78
Sn-MSNs (Si/Sn=106)	106	58.2	94	54.5	69
Sn-MCM-41	107	49.4	91	45.1	65

a) Conversion (%) = $[n_{\text{total}}(1) - n_{\text{left}}(1)]/n_{\text{total}}(1) \times 100$; b) selectivity (%) = $n(2)/(n_{\text{total}}(1) \times \text{conversion}(\%)/100) \times 100$; c) yield (%) = $n(2)/n_{\text{total}}(1) \times 100$; d) turnover number, (moles of product)/(moles of tin centers) at 3 h.

Sn incorporated clay-based catalysts

Clay minerals are made up of layered silicates with potentials for use as catalysts because of their abundance in nature and their high surface area, sorptive and ion-exchange properties [82]. Especially, solid clay catalysts can be used as catalytically active agents, such as solid acids, as

bifunctional or “inert” support, and even as fillers to give solid catalysts with required physical properties [83]. Clays can be divided into smectite-like layered silicates (such as montmorillonite, beidellite, hectorite, and saponite) and layered double hydroxides (such as hydrotalcite, pyroaurite, takovite, and meixnerite). We mainly focus on the Sn

species incorporated clay catalysts for the BV oxidations by using H_2O_2 as oxidant.

Sn-based cationic clay catalysts

Cationic clays, such as smectites, are widely used in a variety of chemical processes, and BV oxidations have benefited from the use of these catalysts among the various oxidation reactions though they are being replaced by zeolites at an increasing rate, which provide better activity and selectivity. Especially, by incorporating a cation, such as Sn, active Sn-containing cationic clays catalysts for the BV oxidation have been formed. As a kind of cationic clay, palygorskite supported Sn(II) complexes are efficient in the BV oxidation of cyclic and acyclic ketones with H_2O_2 as oxidant [84,85]. It should be noted that the procedure for the preparation of the Sn-palygorskite is much simpler than that of Sn-beta zeolites catalysts, which is desirable in large scale application. Furthermore, palygorskite is a biocompatible and environmentally friendly natural mineral abundant in deposits all over the world. In addition, the catalyst can be prepared in large scale and can be recycled.

Except palygorskite, montmorillonite (MMT) is another kind of cationic clay material and is also featured with the characters of biocompatibility and environmentally friendliness, which is constructed of a single octahedral sheet sandwiched between two tetrahedral sheets, with the octahedral sheet sharing the apical oxygen of the tetrahedral sheets (Fig. 12). MMT possesses large specific area and high structural charge (up to 1000 meq kg^{-1}), which endow them with excellent adsorption properties [86–88]. MMT supported Sn catalyst Sn-MMT, prepared by ion-exchanging method in the presence of HCl, exhibited an efficient and very cost-effective catalyst for the BV oxidation reactions [89], showing the similar catalytic mechanism to that

of the Sn-beta-zeolites [40].

While for the BV oxidation of 2-heptylcyclopentanone to δ -dodecalactone, the tin ion-exchanged bentonite (Sn-bentonite) seems to be a rather efficient and highly selective catalyst, as shown in Table 6, the conversion of 2-heptylcyclopentanone to δ -dodecalactone in high yield (81%) could be obtained at the Sn-bentonite catalyst with methanesulfonic acid (MSA) and sodium dodecyl sulfate (SDS) as the additives [90]. The possible reactions are shown in Scheme 2, in which the cycloketone is coordinated to the Lewis acid tin center to activate the carbonyl group first, similar to Sn-beta-zeolites [40], and then the peroxy acid resulting from the interaction between hydrogen peroxide and MSA attacks the electrophilic carbonyl carbon, thus, leading to the excellent results of the BV oxidation over Sn-bentonite [90]. These Sn incorporated cationic clay materials are prospective catalysts for the wide applications in industry for BV oxidation of ketones for its low cost and facile synthesis.

Sn-based anionic clay catalysts

Anionic clays as another kind of important catalyst minerals are widely used in the fields such as base catalysis, hydrogenation, polymerization, condensation, alcohol transformation, which show high catalytic activity and good chemoselectivity [91–94]. Anionic clays are also named as “layered double hydroxides” or simply “hydrotalcites”, which can be generically formulated as $[\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^{x+}[\text{A}_{n/x}]^{n-} \cdot m\text{H}_2\text{O}$, where M(II) and M(III) are divalent and trivalent metal, respectively, lying at octahedral positions of Mg^{2+} in brucite-like layers and A is the interlayer anion, which can vary widely in nature and be either inorganic or organic. x , which represents the

Figure 12 Structure schematics of brucite montmorillonite.

Table 6 Catalytic performances of Sn-bentonite catalysts for the BV oxidation of 2-heptylcyclopentanone to δ -dodecalactone [90]

Entry	Catalyst	Additive	Time (h)	Conversion ^{a)} (%)	Yield ^{a)} (%)
1	-	-	24	15	9
2	Sn-bentonite	-	24	38	30
3	-	MSA	24	21	17
4	-	MSA, SDS	24	18	12
5	Sn-bentonite	MSA, SDS	7	95	75
6 ^{b)}	Sn-bentonite	MSA, SDS	14	76	52
7 ^{c)}	Sn-bentonite	MSA, SDS	7	92	69
8	Sn-bentonite	MSA, SDS	7	95	75
9 ^{d)}	Sn-bentonite	MSA, SDS	7	83	62
10	Sn-bentonite	MSA, SDS	7	95	75
11 ^{e)}	Sn-bentonite	MSA, SDS	7	95	81
12 ^{f)}	Sn-bentonite	MSA, SDS	7	83	69
13 ^{g)}	Sn-bentonite	MSA, SDS	7	67	53
12 ^{h)}	Sn-bentonite	MSA, SDS	7	88	68
13 ^{e)}	Sn-bentonite	MSA, SDS	10	99	77
14 ^{e), i)}	Sn-bentonite	MSA, SDS	7	4	2
15 ^{e), i)}	Sn-bentonite	MSA, SDS	7	82	68

Reaction conditions: 2-heptylcyclopentanone (50 mmol), 35 wt.% H₂O₂ (200 mmol), Sn-bentonite (1.50 g), MSA (2.60 mmol), SDS (0.92 mmol), toluene 10 mL, 70°C. a) Calculated by GC based on the internal standard (nonane); b) MSA (1.04 mmol), SDS (0.37 mmol); c) toluene 20 mL; d) toluene 5 mL; e) 2-heptylcyclopentanone (50 mmol), 35 wt.% H₂O₂ (150 mmol); f) 1st recycled Sn-bentonite; g) 2nd recycled Sn-bentonite; h) 2-heptylcyclopentanone (50 mmol), 35 wt.% H₂O₂ (100 mmol); i) 50°C; j) 90°C.

Scheme 2 Possible catalytic pathway for BV oxidation over Sn-bentonite. Reprinted with permission from Ref. [90], Copyright 2015, Springer.

ratio $M(II)/[M(II) + M(III)]$, usually ranges from 0.17 to 0.33 [95,96].

The structure of hydrotalcites is similar to brucite, $Mg(OH)_2$, which consists of positively charged layers of double hydroxides and interlayer spacing filled with anions that offset the positive charge of the layers and water molecules (as shown in Fig. 13). Tin oxide catalyst supported on an Mg/Al hydrotalcite (Sn/HT), such as 1.5

Figure 13 Structure schematics of brucite (a) and Mg/Al hydrotalcite (b).

wt.% Sn/HT, are active and highly selective for the BV oxidation of a variety of cyclic ketones at 70°C, and the TONs obtained are generally encouraging by using an H₂O₂/acetonitrile system, since the acetonitrile has a comparatively high dissolving power for both the organic substrate and aqueous H₂O₂ as well [97]. The high lactone selectivity can be attributed to the operation of a different mechanism of oxidation from the traditional peroxide catalyzed oxidations. First, acetonitrile is known to activate H₂O₂ by forming a perhydroxyl anion (OOH⁻),

which nucleophilically attacks the nitrile group to generate a peroxy-carboximidic acid intermediate [98,99]. The intermediate is an effective oxygen transfer agent. In the meantime, the carbonyl group of the ketone is activated by coordinating to the Lewis acid center (Sn) on the catalyst, in which the electrophilicity of carbonyl carbon is increased. This is followed by a nucleophilic attack by the active peroxide species (peroxy-carboximidic acid in this case) to form a “Criegee” adduct which rearranges to give a lactone. The second step of the mechanism is similar with the oxidation mechanism for the reaction over Sn-beta zeolite catalyst reported by Corma *et al.* [40]. However, the catalyst is apparently not active for the oxidation of aliphatic and acyclic ketones, such as 2-hexanone and acetophenone, because the methyl group has the lowest migrating mobility [100]. In addition, as hydrotalcite is also an excellent epoxidation catalyst [98,99], thus, the Sn/HT catalyst system is not selective for the lactone formation in the case of olefinic ketones.

Among the hydrotalcites of variable metal composition, such as Mg/Al, Mg/Al/Sn and Mg/Al/Zr, the tin-containing catalyst were the most active and provided better results for the BV oxidation of cyclohexanone with H_2O_2 as oxidant and benzonitrile as solvent [101]. This is due to the different two-step mechanism from that reported by Pillai *et al.* [97], H_2O_2 firstly attacks a Brønsted ba-

sic site at the catalyst surface to form a hydroperoxide species, which subsequently attacks benzonitrile to form a peroxy-carboximidic intermediate. In the second step, the previous formed intermediate attacks a cyclohexanone molecule adsorbed at Lewis acid site of the Sn/HT catalyst to form an intermediate resembling the “Criegee” adduct in homogeneous catalytic processes. Finally, the intermediate undergoes rearrangement to the corresponding lactone [102]. Though Sn-containing hydrotalcite catalyst is effective for the BV oxidation, the preparation method may lead to a different catalytic performance. Sn-hydrotalcite-like catalyst prepared by ion-exchanging method exhibits better catalytic performance for the liquid phase BV oxidation of adamantanone than the catalysts prepared by direct synthesis or grafting approaches when using H_2O_2 as the oxidant and acetonitrile as the solvent [103].

Recently, Hara *et al.* [104] successfully intercalated Sn species into lithium taeniolite (Li/TN) to form a novel clay catalyst (Sn(x)/TN) by a conventional cation-exchange method, and the kind of Sn(x)/TN catalysts showed extremely high performance in BV oxidation of various cyclic ketones with H_2O_2 as oxidant as shown in Table 7, e.g., the conversion rate of BV oxidation cyclopentanone can reach at 100% with a target product selectivity of >99%, and the value for adamantanone is 98% with a selectivity of >99%. The highly dispersed isolated Sn^{IV} species in the TN

Table 7 BV oxidations of ketones by using Sn(0.77)/TN as catalyst^{a)} [104]

Entry	Substrate	Time (h)	Product	Conversion ^{b)} (%)	Yield ^{b)} (%)
1		2		100	>99(89)
2 ^{c)}		2		99	98
3 ^{d)}		2		97	97
4		10		100	>99(78)
5		6		98	98(93)
6		6		98	>99(81)
7		6		77	72

a) Substrate (0.5 mmol), Sn(0.77)/TN catalyst (0.05 g, Sn: 7.7 mol%), 1,2-DCE (1.5 mL), 30 wt.% H_2O_2 (2 eq. relative to the ketone), reflux; b) determined by GC using an internal standard technique. Values in parentheses were isolated yields; c) 1st cycle; d) 2nd cycle.

interlayer has proven to be active species for selective and environmentally benign BV oxidation. It is satisfactory that no Sn leaching was observed during the oxidations, and the catalyst was recyclable.

Sn incorporated clay catalysts would be prospective in the application of BV oxidation of ketone or cyclic ketone owing to their high catalytic activity, good chemoselectivity and mild catalytic condition, though they are less active in the BV oxidation of aliphatic and acyclic ketones. Especially, the synthetic procedure of the Sn-based clay catalysts is simple and facile, which is desirable in broad catalytic applications. More importantly, the Sn-based clay catalysts are usually cost-effective, biocompatible and environmentally friendly, which are encouraging if used as catalysts for BV oxidations.

MO-SnO₂ metal oxide nanocomposite catalysts

As important solid acids, transition metal oxides are currently attracting considerable attention due to their unique properties and broad range of potential applications. These materials have been used in the isomerization of alkanes and other petrochemical processes such as alkylation of aromatics and hydrocarbon cracking [105]. Monometallic oxides such as MgO [106], SnO₂ [107], WO₃ [108], ZrO₂ [109], TiO₂ [110], Al₂O₃ [111], Nb₂O₅ [112], Ta₂O₅ [113], and bimetallic oxides such as Nb-Ta oxides [114,115], Mg-Ta oxides [116], Nb-W oxides [117], Sn-W oxides [118], Zr-W oxides [119], and WO₃-TiO₂ [120,121] have been extensively explored. The transition-metal centers in the inorganic frameworks of porous structures also possess variable oxidation states and empty d-orbitals, which allow electron transfer to occur between the reactants and active sites during the catalytic process [122].

Magnesium based oxides, such as MgO, Mg(OH)₂, HT, exhibit high catalytic activity for BV oxidations [123–125]. By a co-precipitation method, bimetal oxide including MgO/SnO₂, MgO/Al₂O₃, MgO/La₂O₃, MgO/TiO₂, MgO/ZnO, etc. can be successfully prepared. Among these oxides, MgO/SnO₂ showed the most excellent catalytic performance in the BV oxidation of cyclohexanone to ϵ -caprolactone with aqueous hydrogen peroxide as an oxidant [126]. Especially, under optimal reaction conditions, the as-prepared MgO/SnO₂ catalyst with the Mg/Sn molar ratio of 7:3 presented a cyclohexanone conversion rate of 90.5% and caprolactone selectivity of 100%. The catalytic mechanism of MgO/SnO₂ is much different from that reported by Corma *et al.* [40]. For MgO/SnO₂ catalyst, H₂O₂ firstly attack the Brønsted basic site on the catalyst

surface resulting in the formation of peroxide intermediate, and the formed peroxide intermediate is unstable and will react with benzonitrile to form intermediate similar with peracid, which is the same as the mechanism reported by Ruiz *et al.* [123]; secondly, as reported by Corma *et al.* [40], the coordination of cyclohexanone to the Lewis acid of Sn site results in the enhanced electrophilicity of carbonyl carbon, which facilitates the nucleophilic attack by activated H₂O₂. Thus, the bimetal oxides MgO/SnO₂ shows much higher catalytic activity than the single MgO or single SnO₂.

Sn/W mixed transition-metal oxides prepared by calcining corresponding Sn/W hydroxide precursors at different temperatures could act as effective heterogeneous catalysts for the BV oxidation of ketones [127], and many ketones such as adamantanone, cyclopentanone, cyclohexanone, as well as benzyl alcohol were transformed into the corresponding products with high conversion rates of 65%–100% and high selectivities of 82%–100%. Moreover, the catalysts can be easily separated from the reaction mixtures and reused for at least five cycles without significant loss of activity as known from the data shown in Table 8. Shortly afterwards, Fe-doped SO₄²⁻/SnO₂ (STF, with the Fe/Sn molar ratio of 0.5) solid acid catalysts were proved to be efficient and stable catalysts for the BV oxidation of cyclic ketones including adamantanone, cyclopentanone, cyclohexanone and benzyl alcohol with the corresponding conversion rates and target product selectivities of 77%–99% and 85%–99%, respectively [128]. Besides bimetal oxides, ternary metal oxides, such as Mg/Sn/W mixed oxides prepared via co-precipitation were found to be capable of providing the highest yield of ϵ -caprolactone when using a mixture of 50% hydrogen peroxide and acetic acid as co-oxidant [129]. For the same BV oxidation of cyclohexanone, Fe-Sn-O ternary metal oxide catalyst with a tetragonal structure showed a ϵ -caprolactone yield as high as 98.8%, and without any major decline in catalytic activity even cycled for five times [130].

Table 8 Recycling performances of Sn/W-2-800 catalyst in the BV oxidation of 2-adamantanone [127]

Entry	1	2	3	4	5
Conversion (%)	100	100	99	97	93
Selectivity (%)	100	99	99	99	97

Reaction conditions: 2-adamantanone 0.1 mmol, catalyst 6 mg, 30% H₂O₂ 2.0 eq., 1,2-dichloroethane 3 mL, 10 h, 75°C. Conversion rate and selectivity were determined by GC analysis.

Polymer based Sn catalysts

Organic polymer-supported reagents have been found widespread utility in organic synthesis [131]. The use of polymer-bound complexes in catalysis dates from about 30 years ago for meeting the need of separating soluble catalysts from the reaction mixtures [132,133]. For example, aminomethyl polystyrene resin-supported tin complex (PS-Sn) catalyst is an active and selective catalyst for the BV oxidation of cyclic and acyclic ketones including 2-adamantanone, 2-methylcyclohexanone, cyclohexanone, 2-tert-butylcyclohexanone, 4-tert-butylcyclohexanone, 4-methylcyclohexanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, and cyclopentanone using 30% H₂O₂ as oxidant. This new catalytic system with Sn content of 1.28 wt.% can be prepared in a simple procedure (shown in Scheme 3) and permits recycled use [134]. Through a solid phase synthesis method, dendritic Sn complexes can also be incorporated into chloromethyl polystyrene to obtain promising BV oxidation catalysts (P-PAMAM-HBA (1.0G)-Sn(II)), which exhibit high conversion rate of 63%–99% and 100% target product selectivity for the BV oxidation of cyclic and acyclic ketones [135]. Moreover, the catalysts can be prepared in a simple and large scale

Scheme 3 The synthesis scheme of aminomethyl polystyrene resin-supported tin complex (PS-Sn) catalyst. Reprinted with permission from Ref. [134], Copyright 2006, Elsevier.

manner without the utilization of any expensive materials and can be recycled as heterogeneous catalysts.

Shortly after this report, Li *et al.* [136] prepared another kind of dendritic Sn complex catalyst by using cellulose as support through employing a solid phase synthetic methodology as shown in Schemes 4 and 5, and the synthesized catalyst, P-PAMAM-HBA (2.0G)-Sn (II), is proved to be efficient for the BV oxidation of the cyclic ketones and acyclic ketones, such as 2-adamantanone, cyclohexanone, 4-methylcyclohexanone, 4-tert-butylcyclohexanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone and cyclopentanone with hydrogen peroxide as oxidant.

Scheme 4 The procedure for the preparation of the polymer-supported dendrimers. Reprinted with permission from Ref. [136], Copyright 2007, Elsevier.

Scheme 5 The procedure for the preparation of the ligand of first generation. Reprinted with permission from Ref. [136], Copyright 2007, Elsevier.

Especially, it is enviable that the cellulose-supported dendritic Sn complexes afford the corresponding lactones or esters with the conversion rate of 70%–99% and the product selectivity of 100%. Moreover, the catalyst P-PAMAM-HBA (2.0G)-Sn (II) can be recycled for several times without any significant decline in catalytic activity. For this catalyst, the mechanism is analogous to the mechanism reported by Corma *et al.* [40]. Also, the dendritic Sn complexes can be incorporated into chitosan, which also exhibit promising catalytic performance for the BV oxidation of ketones in the presence of H_2O_2 . Notably, the chitosan-supported dendritic Sn complex catalysts can be prepared in a simple and large scale manner with low-cost raw materials and also can be recycled [137].

Though use of H_2O_2 is a “green” process as water is the byproduct of this oxidation reaction, the main challenges to this process are the compatibility of solvent with aqueous H_2O_2 and finding the right catalyst which could activate peroxide in the presence of water. To overcome this problem, a new family of porous and layered Sn(IV) phenylphosphonates (SnPP) with high surface areas and 1–2 nm in pore diameters were developed [138,139], and these materials have been found to be extremely active for BV reaction of aromatic aldehydes using 30% aqueous H_2O_2 solution. When the SnPP catalysts were used to

catalyze the BV oxidation on 4-methoxybenzaldehyde, a maximum conversion rate of 88% was observed over Sn(IV)($\text{O}_3\text{PC}_6\text{H}_4\text{-C}_6\text{H}_4\text{PO}_3$) (SnPP-A) [140]. Table 9 gives the catalytic activity of different Sn catalysts for the BV oxidation of 4-methoxybenzaldehyde. It can be seen that the catalyst SnPP-A shows conversion rate of 98% and target selectivity of 100%, which are much higher than those of Sn-beta zeolite with conversion rate of 58% and target selectivity of 86%. Though the amount of Sn contained in SnPP-A is much higher than in the other Sn systems, SnPP-A exhibits much higher catalytic activity compared to other heterogeneous catalysts reported in the literatures [140].

The most fascinating part of the SnPP-A catalyst is that the BV reaction proceeds more efficiently in the absence of any organic solvents. This is a great progress in the BV oxidation by using H_2O_2 as oxidant, because various products can be formed depending on the catalyst and the solvent used in the BV oxidations of aromatic aldehydes.

CATALYTIC MECHANISM OF Sn-BASED CATALYSTS FOR BV OXIDATION BY USING H_2O_2

Generally, the catalytic mechanism of the Sn-based catalysts for the catalytic BV oxidation by using H_2O_2 as oxidant

Table 9 Comparisons of catalytic activity among three kinds of Sn catalysts in the BV oxidation of 4-methoxybenzaldehyde

Catalyst	Sn (wt.%)	Conversion (%)	Selectivity (phenol %)	Comments
Beta zeolite SnO ₂	~2	56	46	Acetonitrile 50% H_2O_2 [41]
Sn-beta Zeolite	~2	58	86	Toluene 35% H_2O_2 [43]
SnPP-A*	24.5	98	100	No solvent 30% H_2O_2 [140]

Reaction conditions: 0.05g catalyst (* 0.025g catalyst), 80°C, 7 h, 3.7 mmol of aldehyde and 4.5 mmol of H_2O_2 .

can be mainly divided into two catalogues, one is the activation of ketone carbonyl by catalysts facilitating the nucleophilicity attack by H_2O_2 , and the other is the co-activation of both H_2O_2 and ketone substrate, which will be discussed specifically as following.

Ketone carbonyl activation for increased carbonyl carbon electrophilicity

BV oxidation involves two principal steps: (1) addition of the hydrogen peroxide oxidant and the ketone substrate to form the “Criegee” intermediate and (2) BV rearrangement of the Criegee intermediate to the ester product. The Gibbs activation barriers for the addition and rearrangement steps in the non-catalyzed BV oxidation have been reported to be 39.8 and 41.7 kcal mol^{-1} , respectively [141,142], which makes the reaction difficult to proceed without catalyst. By employing specific Sn-containing catalysts, the Gibbs activation barriers for the addition and rearrangement steps will be much reduced due to the activation of ketone carbonyl by the Lewis acid of Sn sites on the catalysts. Specifically, as shown in Scheme 6, the ketone carbonyl molecule will firstly coordinate to the Sn site on the catalyst and then is activated by the Lewis acid site of Sn species, resulting in the increased electrophilicity of carbonyl carbon. Subsequently, the electrophilicity enhancement of the carbonyl carbon facilitates the nucleophilic attack by a H_2O_2 molecule to form a “Criegee” intermediate. Finally, the ester is formed following the intermediate rearrangement. This catalytic mechanism makes the BV oxidation of ketones possess not only high conversion rate but also high chemoselectivity. As a representative, the Sn-beta-zeolite catalysts follow this type catalytic mechanism which was firstly reported by Corma *et al.* [40], so does Sn-MFI-ns [46], Sn substituted de-

laminated zeolites (Sn-DZ-1) [48], and the Sn-based NaY zeolites [50]. In addition, this type of catalytic mechanism is also applicable for Sn-based mesoporous catalysts such as Sn-MCM-41 [59,60], Sn-SBA-15 [64], Sn-MCM-48 [65], Sn-SBA-16 [71], Sn-MWW [77]. Sn-based cationic clay catalysts such as Sn-palygorskite [84,85], Sn-MMT [89], Sn-bentonite [90], and Sn-based polymer catalysts such as aminomethyl polystyrene resin supported tin complex (PS-Sn) [134], chloromethyl polystyrene supported dendritic Sn complexes catalyst (P-PAMAM-HBA (1.0G)-Sn(II)) [135], cellulose supported dendritic Sn complexes catalyst (P-PAMAM-HBA (2.0G)-Sn (II)) [136], chitosan supported dendritic Sn complexes [137], porous Sn(IV) phenylphosphonates (SnPP) [140].

The homogeneous catalyst, Sn-based FBS catalyst, also follows this type of catalytic mechanism, such as tin(IV) bis(perfluorooctanesulfonyl)amide [31,32]. This is because that the high amount of fluorine in the $-\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_{24}$ ligand endows the catalyst with enhanced electrophilicity and the electropositivity of Sn metal active center as well, which in turn results in significantly elevated electrophilicity of carbonyl carbon atom of a ketone molecule once coordinated to the tin(IV) bis(perfluorooctanesulfonyl)amide catalyst, thus the nucleophilic attack by H_2O_2 will be intensified, leading to the accelerated BV oxidation of ketones.

Co-activation of oxidant H_2O_2 and carbonyl of ketone

In this type catalytic mechanism, not only the carbonyl carbon of ketone molecule, the oxidant H_2O_2 is also activated by solvent or catalyst. In principle, H_2O_2 may be basically activated in three ways [143], (1) hydroxy (OH^-) and hydroperoxy (HOO^-) radicals may be generated via a Haber-Weiss mechanistic scheme in the presence of metal

Scheme 6 The catalytic mechanism of ketone activation by Sn-based catalyst during the BV oxidation: ketone carbonyl is activated by coordinating to a Lewis acidic Sn site resulting in the electrophilicity enhancement of carbonyl carbon, which facilitates the nucleophilic attack by a H_2O_2 molecule.

compound catalysts. However, these radicals usually lead to nonselective transformations of organic substrates; (2) strong HOO^- nucleophile can be well created under basic conditions, which is active for the epoxidation of electrophilic alkenes such as β -unsaturated ketones or carboxylic acid derivatives; (3) heterolytic oxidation, which is probably the most important synthetic application of H_2O_2 in the area of as in the epoxidation of alkenes. In the case of Sn-based catalysts for BV oxidation of ketones, H_2O_2 can be most probably activated via the first and second pathway.

During the BV oxidation of ketones, the activations of H_2O_2 and carbonyl of ketone can be achieved in the following two routes. In route (I), H_2O_2 is activated by the organic solvent used (such as acetonitrile) or additive (such as methanesulfonic acid) as shown in Scheme 7a, to form a hydroperoxy (HOO^-), which is responsible for the nucleophilic attack on nitrile to generate a peroxycarboximide intermediate [98,99]. Such an intermediate is an efficient oxygen transfer agent ready to nucleophilically attack carbonyl carbon. Meanwhile, the carbonyl group on ketone is activated by coordinating to the Lewis acidic Sn center on the catalyst forming an electrophilic carbonyl carbon as shown in Scheme 7b, which further facilitates the nucleophilic attack by the active peroxide species (peroxycarboximide in this case) to form a “Criegee” adduct. Finally, the adduct intermediate rearranges to give lactone. Thus, a different mechanism of BV oxidation from the traditional peroxide catalyzed oxidation mechanism can be outlined, in which actually the second step of carbonyl carbon activation is principally the same as the BV oxidation mechanism over Sn-beta-zeolite catalyst reported by Corma *et al.* [40]. The catalytic mechanism of Sn-based cationic clay catalysts such as Sn-bentonite catalyst [90] and Sn-based anionic clay catalysts such as Sn-doped hydrotalcite (Sn/HT) catalyst [97], for BV oxidation of ketones follows this route (I) including two activation steps.

The route (II) of the co-activation is that both H_2O_2 and carbonyl of ketone are activated by the Sn-based catalysts. In the absence of solvent coordination, tin-based catalyst activates hydrogen peroxide to produce a tin hydroperoxo (SnOOH) intermediate with a moderate Gibbs activation barrier of $15.4 \text{ kcal mol}^{-1}$ [141,142]. Water molecules' coordinating to the tin active site facilitates the proton transfer and lower the Gibbs activation barrier for tin hydroperoxo intermediate formation by $3\text{--}7 \text{ kcal mol}^{-1}$, further favoring the activation of H_2O_2 by Sn-based catalyst [141,142]. Specifically, as shown in Scheme 8a, hydrogen peroxide firstly attacks a Brønsted basic site at the Sn-based catalyst surface to form a metal hydroperoxide (SnOOH), which is active species and subsequently attacks solvent, such as benzonitrile, to form a peroxycarboximide intermediate [101]. Secondly, the ketone molecule coordinates to the Lewis acid site of the Sn-based catalyst, which activates the carbonyl of ketone, resulting in the enhanced electrophilicity of the carbonyl carbon (Scheme 8b), which in turn intensifies the nucleophilic attack by previously formed peroxycarboximide intermediate to form an intermediate resembling the “Criegee” adduct in homogeneous catalytic processes. Finally, the intermediate undergoes rearrangement to the corresponding lactone product. In this route, the Sn-based catalyst plays a bifunctional role in activating both H_2O_2 molecules and carbonyl group of ketone. The catalytic process in the BV oxidation over a number of Sn-based catalysts, for example, Sn-incorporated anionic clay catalysts, such as Sn-doped hydrotalcite (Sn/HT) when using H_2O_2 as oxidant and benzonitrile as solvent [97], and MO-SnO₂ metal oxide catalysts, such as MgO/SnO₂ [126], follow the route (II) of the co-activation of H_2O_2 molecules and carbonyl group of ketone.

In fact, the Sn-based zeolite beta is also bifunctional because of the existence of Sn-OH specie in the form of $\text{Sn}(\text{OSiH}_3)_3\text{OH}$ cluster. Both the quantum-chemical results and the kinetic study indicate that the catalytically active

Scheme 7 The catalytic mechanism of H_2O_2 and carbonyl group co-activation via route I: H_2O_2 is activated by solvent and ketone activated by Sn-based catalyst during Baeyer-Villiger oxidation.

Scheme 8 The catalytic mechanism of H_2O_2 and carbonyl group co-activation via route II: both H_2O_2 and carbonyl on ketone are activated by Sn-based catalyst during the BV oxidation.

sites in Sn-based zeolite beta can be divided into two types: the Lewis acid Sn atom to which ketone molecule tends to coordinate, and the oxygen atom of the Sn-OH group that interacts with H_2O_2 forming a hydrogen bond [144,145]. The effect of Lewis acidic Sn center is strong and therefore is believed to play a dominating role in the catalytic reaction of BV oxidation of ketones [142].

Tin-containing redox molecular sieves and clay catalysts, such as Sn-supported hydrotalcite composites, are environmentally advantageous catalysts not only because they can activate hydrogen peroxide but also because their heterogeneous nature enables facile catalyst recovery and recycling. Furthermore, any leached tin from these catalysts will probably in the form of inorganic tin oxides that will arouse negligible environmental threat. Tin-containing redox molecular sieves clearly demonstrate great potentials as industrial catalysts for accomplishing environmentally friendly BV oxidations with H_2O_2 as environmentally friendly oxidant.

CONCLUSIONS AND OUTLOOK

In this review, we first discussed very briefly the features of BV oxidation reaction, the catalytic mechanism, and the corresponding oxidants conventionally used, in which the catalytic BV oxidation by using H_2O_2 as oxidant should be applicable because of avoiding of waste and harmful product in traditional oxidants. The main content is then focused on the Sn-based catalysts for the BV oxidation of ketones by using cost-effective and less polluting H_2O_2 as oxidant. The catalytic performances and the catalytic mechanisms of most kinds of Sn-based catalysts reported so far were reviewed and discussed, including the homogeneous catalysts (such as Sn-based FBS), and heterogeneous catalysts (such as Sn-based zeolite catalyst, Sn-based mesoporous composites, Sn incorporated clay catalyst, tin-based metal oxide composites, and polymer supported Sn cata-

lyst). Two types of catalytic mechanisms of Sn-based catalysts have been proposed, namely, 1) ketone carbonyl activation by the coordination to the Lewis acid Sn site of the catalyst leading to the intensified electrophilicity of carbon which facilitates the nucleophilic attack by H_2O_2 molecule; 2) both oxidant H_2O_2 and carbonyl of ketone are activated, resulting in much accelerated BV oxidation. In the second type of catalytic mechanism, the co-activation of H_2O_2 and carbonyl of ketone are accomplished via two different routes: in route (I), the oxidant H_2O_2 is activated by organic solvent or additive used, such as acetonitrile, to form peroxycarboxymidic intermediate, and in the meantime, the carbonyl of ketone is activated by Lewis acidic Sn site resulting in the intensified electrophilicity of the carbonyl carbon, which facilitates the nucleophilic attack by the peroxycarboxymidic intermediate formed previously; Comparatively, the route (II) is featured with the co-activation of both of H_2O_2 and ketone substrate by specific Sn-based catalysts, in which the H_2O_2 is activated to form peroxycarboxymidic intermediate and then nucleophilically attacks the carbonyl carbon of ketone which has been activated by the coordination to Sn-based catalyst. The Sn-based catalyst in route (II) is bifunctional—Brønsted basic site at the Sn-based catalyst surface activate H_2O_2 and the coordination to Sn species can activate the carbonyl carbon of ketone.

Among the Sn-based BV oxidation catalysts reported, the catalytic processes of Sn cooperated FBS catalyst, Sn-based zeolite catalyst, Sn-based mesoporous composites, Sn incorporated cationic clay catalyst, such as palygorskite supported Sn(II) complexes and SnCl_2 incorporated MMT, Sn-bentonite and polymer supported Sn catalyst are proposed to follow the first type of mechanism of single carbonyl of ketone activation. Differently, that of Sn incorporated anionic clay catalyst, such as tin oxide supported on an Mg/Al hydrotalcite most probably follows

the second type of oxidant H_2O_2 and carbonyl co-activation via route (I), i.e., H_2O_2 and carbonyl are activated respectively by the solvent used and the Sn active sites on Sn-based catalyst; comparatively, those of hydrotalcites contained variable metal composition (Mg/Al, Mg/Al/Sn and Mg/Al/Zr) and the Sn-based metal oxide composites, such as MgO/SnO_2 also proceed according to the second type of the catalytic mechanisms but via route (II), in which both H_2O_2 and carbonyl are activated by the Sn active sites on Sn-based catalyst. We expect that the above catalytic mechanism discussions and proposals will be helpful for understanding the catalytic performance of Sn-based catalysts in the BV oxidation reaction, and for searching even better catalysts as well for the practical application of the catalytic BV oxidation of ketones.

Tin-based catalysts, owing to their strong Lewis acidic site character, exhibit high catalytic performance for the catalytic BV oxidation of ketone or cyclic ketone by using cost-effective and environmentally friendly H_2O_2 as oxidant. It should be pointed out that among many kinds of catalysts, heterogeneous Sn-containing catalysts are becoming increasingly attractive due to their unique characters of simple operation, nontoxicity, easy separation, acceptable recoverability, etc. Though the overall catalytic activity of homogeneous Sn-containing organic catalysts is comparable to that of heterogeneous catalysts, the practical applications of the former during the BV oxidation has been limited because of their toxicity and possible pollution to water and air. Comparatively, Sn-based heterogeneous catalyst is a much better option for catalyzing BV oxidation reactions.

Among various Sn-based heterogeneous catalysts, Sn-based zeolite molecular sieves, featuring the extraordinarily high conversion rates and chemoselectivities, are superior to other kinds of Sn-containing catalysts. Especially, in the BV oxidations of unsaturated ketone, the chemoselectivity is extraordinarily high by using Sn-based zeolite molecular sieves as catalyst with the aim product being frequently 100% ester or lactone. More attractively, after the introduction of mesopore structure into the zeolite crystals, the obtained Sn-containing mesoporous zeolite presents a substantially enhanced catalytic performance in the BV oxidations of bulky cycle ketones with large molecular weights. However, the synthesis of Sn-based zeolites is still not simple, and usually long synthetic periods and careful controls over the hierarchically porous structure are necessary. Comparatively, Sn-incorporated clay catalysts are characteristic of simple synthesis, abundance in nature and therefore much more

cost-effective, which make the catalyst highly promising for the large-scale industrial applications. Unfortunately, compared to other Sn-based catalysts, the product yields of BV oxidations by employing Sn-incorporated clays, such as Sn-palygorskite as catalyst, is relatively low, and much longer reaction time periods will be needed. In addition, Sn-incorporated clay catalysts, such as Sn-hydrotalcite, are not active enough for the BV oxidation of aliphatic and acyclic ketones.

In spite of the significant progresses made in the past decades, the overall performance of Sn-containing catalysts in BV oxidation reactions, when employed in the practical applications, is still not as perfect as expected, and therefore there is still rooms for improvement. First, the recyclability of Sn-based heterogeneous catalyst should be substantially enhanced by developing novel catalysts or modifying the reported ones, that is to say, the problems of metal active species falling off and activity loss should be resolved before industrial applications to guarantee the recycled use and long enough catalytic lifetime of the catalysts. Secondly, Sn-based catalysts of crystalline architectures are expected to possess tunable and large enough pore structures for the free accesses of bulky ketone or cycle ketone molecules to the active catalytic sites in the inner framework of the catalysts. Additionally, further detailed fundamental investigations should be engaged in understanding the origin and nature of the catalytic activity in the BV oxidations on atomic levels, which are not only dependent on the metal ions incorporated, but also on the atomic environments around the metal ions. The differences in catalytic activity between external and internal active sites of the Sn-based catalysts are also fundamentally interesting. Finally but even more challengingly, the development of novel catalysts, including Sn-based heterogeneous catalysts for catalyzing the organic co-solvent-free BV oxidation reactions using oxygen or air as oxidant, will become a great breakthrough in the field. The success in finding this kind of novel catalysts will further remarkably enhance the atom economy of the reaction, and reduce the reaction cost and potential harms to environments, which may greatly promote the more extensive industrializations of various BV oxidation reactions from fine chemical engineering to the syntheses of general chemicals, and finally benefit the sustained development of the industry production of useful chemicals.

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Sn基Baeyer-Villiger氧化反应催化剂

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摘要 Baeyer-Villiger (BV) 反应是有机化学合成中的一个重要反应. 特别是催化型的BV反应不仅能够简化反应过程还能够降低反应物的消耗量和减少副产物的生成量, 因此更加具有实际应用价值. 其中最为有利的催化型BV反应是使用低成本、环境友好的过氧化氢(H_2O_2)作为氧化剂, 来取代传统的氧化剂过酸. 本综述首先简要阐述了以 H_2O_2 为氧化剂的BV氧化反应的特点以及传统使用的氧化剂类型, 然后重点综述了Sn基催化剂材料在以 H_2O_2 为氧化剂的催化型BV反应中的催化性能以及相应的催化机理, 具体包含了Sn基均相催化剂材料(例如Sn基含氟双相体系催化剂), Sn基异相催化剂材料(例如Sn基沸石, Sn基介孔复合物, Sn基粘土, Sn基金属氧化物, 以及Sn基聚合物催化剂). 最后, 对以 H_2O_2 为氧化剂的BV反应的Sn基催化剂的实际应用进行了评论和展望, 讨论了它们在提高BV氧化反应催化活性方面可能的改进和发展的方向.