

Review

The Baeyer–Villiger Oxidation of Cycloketones Using Hydrogen Peroxide as an Oxidant

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Abstract: Baeyer–Villiger oxidation can synthesize a series of esters or lactones that have essential application value but are difficult to be synthesized by other methods. Cycloketones can be oxidized to lactones using molecular oxygen, peroxy acids, or hydrogen peroxide as an oxidant. Hydrogen peroxide is one of the environmental oxidants. Because of the weak oxidation ability of hydrogen peroxide, Bronsted acids and Lewis acids are used as catalysts to activate hydrogen peroxide or the carbonyl of ketones to increase the nucleophilic performance of hydrogen peroxide. The catalytic mechanisms of Bronsted acids and Lewis acids differ in the Baeyer–Villiger oxidation of cyclohexanone with an aqueous solution of hydrogen peroxide as an oxidant.

Keywords: Bronsted acid; Lewis acid; cycloketone; lactone; hydrogen peroxide

1. Introduction

The oxidation of ketones to lactones using KHSO_5 as an oxidant was first reported in 1899 by Adolf Baeyer and Victor Villiger [1]. Lactones have significant commercial magnetism in the pharma, food, cosmetics, and perfumery industries [2,3]. The Baeyer–Villiger (BV) reaction can synthesize a series of esters or lactones that have essential application value but are difficult to be synthesized by other methods [4,5]. The BV reaction has been widely used in perfumes, pesticides, medicines, sterols, antibiotics, and pheromones, and for the synthesis of polymerized monomers, etc. [6–9].

Various oxidants and catalysts have been developed to improve BV oxidation. Peroxy benzoic acid, 3-chloroperbenzoic acid, pentafluoroperbenzoic acid, and trifluoroperacetic acid were the oxidants in traditional BV oxidation [10,11]. Peroxy acids produce one molecule of organic acid, the atom utilization rate is low, and the waste acid produced is difficult to handle and pollutes the environment. Current researches are focusing more attention on the replacement of the organic peroxy acids by more atom-efficient and environmental oxidants to overcome the problems. Molecular oxygen and hydrogen peroxide are more environmentally friendly oxidants, and they are used as substitutes for organic peroxy acids [12–14]. Although molecular oxygen and hydrogen peroxide have environmental advantages, their oxidation capacity is weak. To achieve a high conversion of ketones and high selectivity of esters or lactones, catalysts are required to catalyze the occurrence of the BV reaction of ketones [15–18]. The O–O bond in molecular oxygen is so stable that it is difficult to transfer oxygen atoms directly to ketones to form esters. Aldehydes were added as co-oxidants. Aldehydes were first oxidized by molecular oxygen to the corresponding peroxy acid, which oxidizes ketones to esters [19–22]. Although the O_2 /aldehydes system could avoid using peroxy acids for BV oxidation, large amounts of aldehydes were required as pro-oxidants for the oxidation of ketones, leading to the production of large amounts of organic acid [23,24]. The usage of alcohol and aldehydes is still the main drawback [25]. Developing highly efficient catalysts and green oxidants is an important issue. Hydrogen peroxide is one of the environmental oxidants. The product of



Citation: Ma, Q.; Xue, Y.; Guo, J.; Peng, X. The Baeyer–Villiger Oxidation of Cycloketones Using Hydrogen Peroxide as an Oxidant. *Catalysts* **2023**, *13*, 21. <https://doi.org/10.3390/catal13010021>

Academic Editor: Eric M. Gaigneaux

Received: 31 October 2022
Revised: 19 December 2022
Accepted: 19 December 2022
Published: 23 December 2022



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hydrogen peroxide after the oxidation reaction is water. The hydrogen peroxide that does not participate in the oxidation reaction can be decomposed into water and oxygen. The oxidation ability of hydrogen peroxide is weak. It is difficult to directly oxidize ketones into esters with a high conversion rate. A high catalytic activity catalyst is required to activate hydrogen peroxide and the carbonyl of ketones to increase the nucleophilic performance of hydrogen peroxide.

The development of environmental chemical processes is required. For recyclable and high catalytic activity catalysts, Lewis acids and Bronsted acids with high catalytic activity were used as catalysts in the oxidation of cycloketones to lactones.

2. The Lewis Acid System

2.1. Homogeneous Systems

Markiton M. studied a range of metal triflates in the BV oxidation of 2-adamantanone. The results showed activity of $\text{Sn}(\text{OTf})_2$ was higher than other metal triflates. Both the conversion of 2-adamantanone and the yield of lactone were higher than 99% (0.67 mmol 2-adamantanone, 1.34 mmol 30 wt% H_2O_2 , 10 mol% $\text{Sn}(\text{OTf})_2$, 6 mL toluene, 70 °C, 30 min). To increase the catalytic activity of $\text{Sn}(\text{OTf})_2$, it was immobilized on multi-walled carbon nanotubes (MWCNTs), and then hydrolyzed to triflic acid in the BV oxidation. The catalytic activity of the recycled catalyst decreased. The participation of both Lewis and Bronsted acid sites in the conversion of the ketone was postulated [26].

Ionic liquids were easily leached from porous solids during the reaction. The supported ionic liquid catalyst was prepared by a ship-in-a-bottle technique or organic-additive-instant seed technology. Modi [27] synthesized $[\text{BMIM}]\text{BF}_4@Co/ZSM-5$ and $[\text{BMIM}]\text{BF}_4@Co/HY$. They were tested in the BV oxidation of cyclohexanone using 30% H_2O_2 as an oxidant under solvent-free conditions. $[\text{BMIM}]\text{BF}_4@Co/HY$ showed high catalytic activity with the conversion of cyclohexanone being 54.88%, and the ϵ -caprolactone selectivity 86.36% (50 mg $[\text{BMIM}]\text{BF}_4@Co/HY$, 0.03 mol cyclohexanone, 0.06 mol 30 wt% H_2O_2 , 75 °C, 6 h). $[\text{BMIM}]\text{BF}_4@Co/HY$ interacts with carbonyl and hydrogen peroxide simultaneously. The nucleophile BF_4^- plays an essential role in the catalytic reaction. The supported ionic liquid catalysts prepared by the ship-in-a-bottle technique or organic additive-instant seed methods were unstable [28,29]. Although the selectivity of ϵ -caprolactone was maintained at about 80%, the activity loss is considerable after six recycling cycles.

A series of oxo-rhenium complexes were prepared by reacting with Re_2O_7 using PTA, mPTA, HMT, Tpm, and $\text{Li}(\text{Tpm})_3$ as raw materials, respectively (Figure 1) [30]. These oxo-rhenium complexes' catalytic activity was studied toward the BV oxidation of cyclic and linear ketones. These prepared oxo-rhenium complexes exhibit higher catalytic activity in the oxidation of ketones with H_2O_2 than the simple rhenium oxides $\text{K}[\text{ReO}_4]$ and Re_2O_7 . The catalytic performances of oxo-rhenium complexes are shown Table 1. Although the oxo-rhenium complexes have good water solubility and are stable in an aqueous solution, the selectivity of the corresponding product ester is poor (<36%) when catalyzing the BV reaction of ketones.

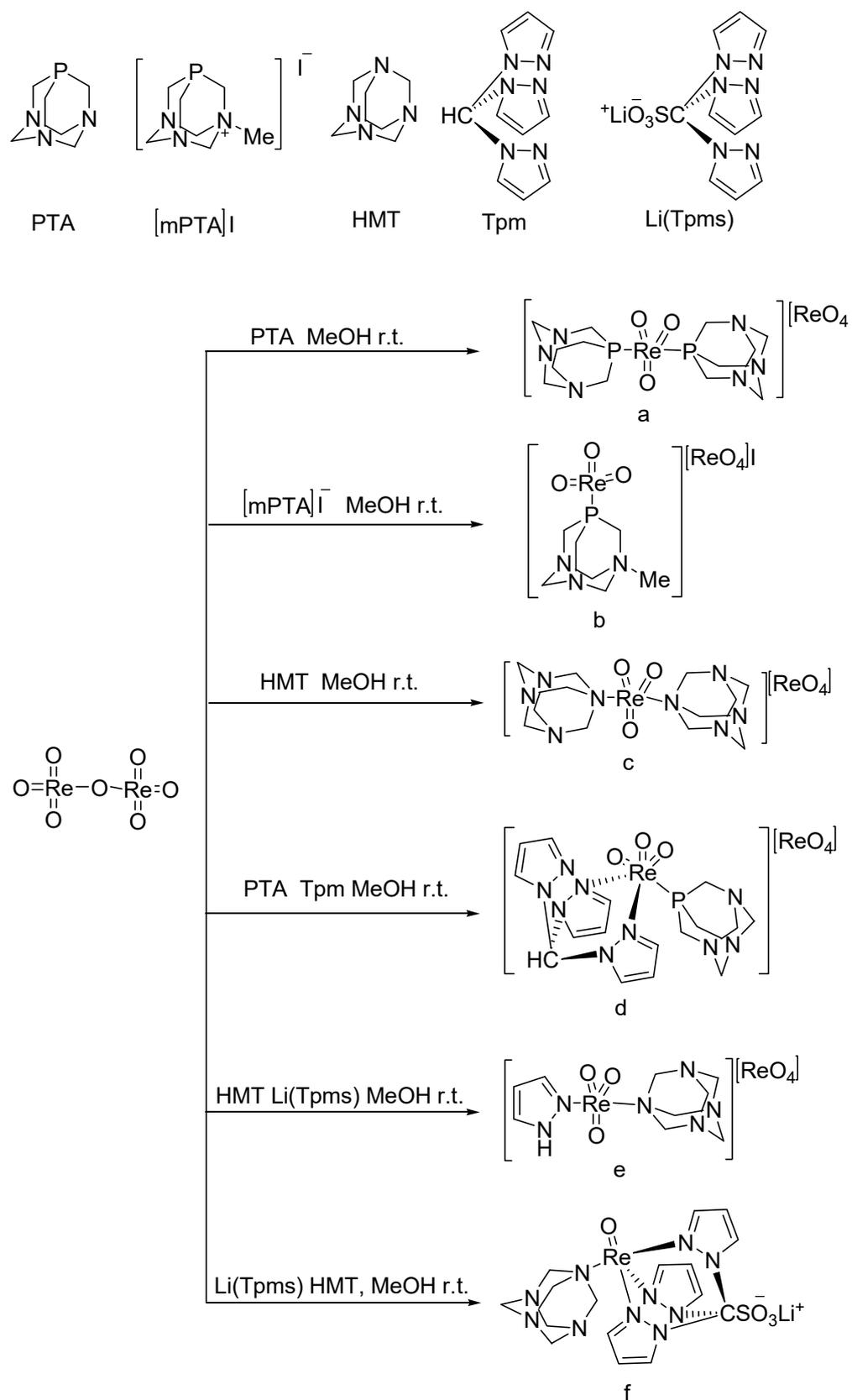
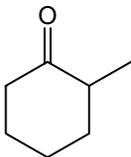
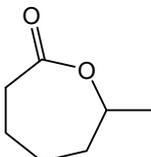
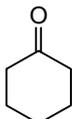
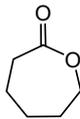
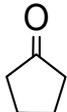
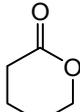


Figure 1. Preparation of rhenium complexes [30].

Table 1. Catalytic performance of Re complexes for the oxidation of cyclic ketones to lactones.

Ketone	Product	Catalyst	Conversion (%)	Selectivity (%)
		a	66	45
		b	85	36
		c	68	22
		d	75	21
		e	67	16
		f	70	10
		Re ₂ O ₇	60	11
		a	59	20
		b	37	43
		d	38	26
		Re ₂ O ₇	55	5
		a	63	37
		b	58	41
		d	67	51

1.7 μmol catalyst (The structures of catalysts a, b, c, d, e, and f are shown in Figure 1), $n(\text{ketone})/n(\text{H}_2\text{O}_2) = 1.7 \text{ mmol}/1.7 \text{ mmol}$, 3 mL 1,2-dichloroethane, 70 °C, 6 h.

Frisone studied the BV oxidation of cyclic ketones with H₂O₂ catalyzed by platinum (II) complexes (Figure 2) [31]. (P-P)Pt(CF₃)X (P-P = diphosphine; X = solvent, –OH) showed high activity for the BV oxidation of ketones using a commercial 32 wt% H₂O₂ solution. The conversion of cyclic ketones to the corresponding lactones is shown in Table 2. The solubility of the bis-cationic PtII catalyst in water led to hydrolysis with the release of one equivalent of H⁺. For more acid-sensitive lactones, the formation of the corresponding organic acid was increased because of H⁺-catalyzed hydrolysis of the intermediate lactone in water, higher temperatures, and the high catalyst loading result in lower yields of lactones.

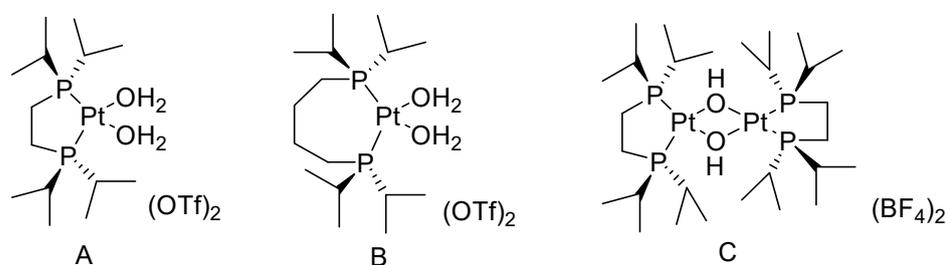
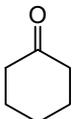
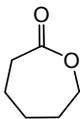
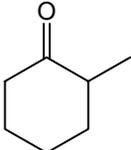
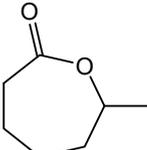
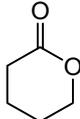
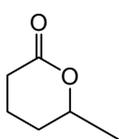
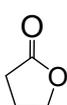


Figure 2. Structure of the PtII water-soluble catalysts ((A): (P-P)Pt(H₂O)(OTf)₂ (P-P = 1,2-Bis(di-i-propylphosphino)ethane); (B): (P-P)Pt(H₂O)(OTf)₂ (P-P = 1,4-Bis(di-i-propylphosphino)butane); (C): (P-P)₂Pt₂(OH)₂(BF₄)₂ (P-P = 1,2-Bis(di-i-propylphosphino)ethane)) [31].

Table 2. Catalytic performance of (P-P)Pt(CF₃)X for the oxidation of cyclic ketones to lactones.

Ketone	Product	Yield (mmol)	Time	Solvent
		1.94	35 min	-
		1.47	25 min	CH ₂ Cl ₂
		2.88	2.8 h	CH ₂ Cl ₂
		1.98	10 min	-
		2.7	49 min	-
		4.84	4 h	CH ₂ Cl ₂
		3.05	1.8 h	-
		1.62	5 h	THF
		0.77	51 min	-
		15.0	8 min	-
		37.1	2.75 h	-

Reaction conditions: 0.045 mmol Pt; 45 mmol ketone; 22.5 mmol H₂O₂; N₂ 1 atm; 1 mL solvent (where present).

2.2. Heterogeneous Systems

Sn-containing materials were extensively used as a highly active Lewis acid heterogeneous catalyst [32–35]. The catalytic performances of Sn-containing materials for the oxidation of cyclic ketones are shown Tables 3 and 4. Because of the large specific surface area and various channel structures, mesoporous materials have attracted much attention in the field of catalysis. Corma A. synthesized a catalyst (Sn-zeolite beta) that had discrete and isolated Lewis sites [36]. Sn was incorporated into the zeolite framework as tetrahedrally coordinated Sn. The chemoselectivity of Sn-zeolite beta in the BV oxidation of ketones was high when using H₂O₂ as an oxidant. The selectivity for lactones was 100%. The mechanism of the BV reaction of cyclohexanone catalyzed by Sn-zeolite beta using aqueous hydrogen peroxide as an oxidant is shown in Figure 3. The oxygen atom in the ketone is coordinated with the Sn (Lewis acid center). Then it was easy for the oxygen atom of hydrogen peroxide to attack the carbon atom of carbonyl. The catalytic activity of Sn-zeolite beta in the BV oxidation of adamantanone and cyclohexanone was higher than the best homogeneous catalytic system. In addition, Sn-zeolite beta was filtered out and reused four times without special treatment, and its activity did not decrease in the BV oxidation of adamantanone and cyclohexanone. However, the preparation of Sn-zeolite beta was complex. The crystallization of Sn-zeolite beta takes 20 days at 140 °C in a stainless steel autoclave.

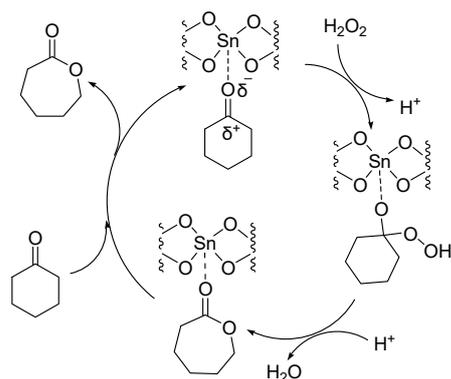


Figure 3. Mechanism of BV reaction catalyzed by Sn-zeolite beta using aqueous hydrogen peroxide as oxidant [36].

Different tin contents of Sn-Beta zeolites were synthesized by aerosol-seed-assisted hydrothermal methods. This method reduced the amount of template and mineralizer and the reaction time. The optimal condition was obtained through several synthesis parameters (1SiO₂: 0.4TEAOH: 0.4HF: 5.6H₂O with 3 wt% of seeds, 423 k, 6–9 days). The synthesized catalyst of Sn-Beta zeolite was tested in the BV oxidation of cyclohexanone using H₂O₂ as an oxidant. With the increase in tin content, the conversion of ketone increased, and the selectivity of ϵ -caprolactone decreased. The amount of the extra framework Sn sites increased with the increase in tin content, which may cause the oxidation of ϵ -caprolactone to acid [37].

Different Sn-zeolites (Sn-MCM-68, Sn-BEA, Sn-MWW, Sn-MFI) were synthesized and evaluated in the BV oxidation of 2-adamantanone. By comparison, Sn-MCM-68 possesses more catalytic activity because of its three-dimensional channels and relatively higher hydrophobicity [38]. After the reaction, Sn-MCM-68 and Sn-BEA were separated, washed with chlorobenzene, and calcined. The catalytic activity of the regenerated catalyst was comparable to the fresh catalyst.

Han Y. synthesized a series of Mg-Sn-W composite oxides with different W contents. These catalysts were tested in the BV oxidation of cyclohexanone. The tests of BV oxidation with Mg-Sn-W oxide catalysts showed high activity, and the selectivity of caprolactone approached 90%. The tungsten oxide was the main active component. Mg-Sn-W oxide was separated by filtration and used again immediately. The catalytic activity decreased significantly (conversion of cyclohexanone is 37%, selectivity of ϵ -caprolactone is 75%). Mg-Sn-W oxide was separated, washed with water and ethanol, and calcined at 400 °C. Although the structure of the recycled catalyst was not destroyed, the catalytic activity was still slightly worse than the fresh catalysts. (conversion: 59% (second), 55% (third), 50% (fourth); selectivity: 83% (second), 80% (third), 76% (fourth)) [39]. A series of magnesium–aluminum hydrotalcite-like compounds were prepared to catalyze the BV oxidation of cyclohexanone using H₂O₂ as oxidation. The results showed that the crystal size affected the catalytic activity. Enhanced hydrophilicity of poorly crystalline HT samples facilitates the approach and activation of H₂O₂ on basic surface centers. The catalytic activities of HT samples were different. The conversion of cyclohexanone increased from 30 to 37%, while the selectivity of ϵ -caprolactone decreased from 100 to 70% [40]. In addition, a series of tin-containing compounds of Sn-MCM-56 [41], Sn/HT [42], Sn-MCM-41 [43], Sn-palygorskite [44], P-PAMAM-HBA-Sn [45], Sn[N(SO₂C₈F₁₇)₂]₄ [46], and Sn (salen)-NaY [47] were prepared. The catalytic activity tested in the BV reaction showed as being high. They are all heterogeneous catalysts and can be regenerated. Sn-MCM-56 was separated, washed with chlorobenzene, and calcined at 500 °C for 6 h. The catalytic activity of the regenerated catalyst was almost back to the initial level (conversion of 2-adamantanone: 40% (fresh), 38% (fifth)) (0.04 g Sn-MCM-56, n(adamantanone)/n(H₂O₂) = 2 mol/4 mol, 56 wt% H₂O₂, 4.5 g chlorobenzene, 90 °C, 2 h) [41]. Sn/HT was separated, and calcined at 400 °C for 2 h. The catalytic activity of the recycled Sn/HT was the same as that of the

fresh one [42]. The catalytic activity of the regenerated P-PAMAM-HBA-Sn was lower than the fresh one (conversion of 2-adamantanone: 100% (fresh), 95 (second), 90 (third), 85 (fourth), 80% (fifth)) [45]. The catalytic activity of the regenerated Sn[N(SO₂C₈F₁₇)₂]₄ was almost back to the initial level (conversion of 2-adamantanone: 93% (fresh), 92% (second), 90% (third), 90% (fourth)) [46]. Sn (salen)-NaY was separated by filtration and washed with 1,4-dioxane. The catalytic activity of the recycled Sn (salen)-NaY was the same as that of the fresh one (conversion of cyclohexanone: 75% (fresh), 74% (second), 75% (third)) [47]. The catalytic activity of Sn-bentonite formed by a simple procedure is low. It is necessary to add additives to improve the yield of lactones [48]. In addition, the toxicity of organotin compounds and tin chloride is high, and can induce DNA lesions. Although the toxicity of inorganic tin is low, its preparation uses tin chloride as a raw material [49]. Therefore new active, selective, and recyclable catalysts are still required, and a heterogeneous catalyst is an excellent option.

Table 3. Catalytic performances of Sn-containing materials for the oxidation of cyclohexanone and adamantanone.

Ketone	Product	Catalyst	Reaction Conditions	Conversion (%)	Yield (%)	Selectivity (%)	Ref.
		Sn-zeolite beta	n(cyclohexanone)/n(H ₂ O ₂) = 1.5 mol/1 mol, 35 wt% H ₂ O ₂ , 90 °C, 3 h	-	52	98	[36]
		Sn-Beta-166 (Si/Sn = 166)	50 mg catalyst; n(cyclohexanone)/n(H ₂ O ₂) = 2 mol/3 mol, 30 wt% H ₂ O ₂ , 8 mL 1,4-dioxane, 80 °C, 3 h.	29	-	68	[37]
		Sn-Beta-125 (Si/Sn = 125)	50 mg catalyst; n(cyclohexanone)/n(H ₂ O ₂) = 2 mol/3 mol, 30 wt% H ₂ O ₂ , 8 mL 1,4-dioxane, 80 °C, 3 h.	36	-	66	[37]
		Sn-Beta-100 (Si/Sn = 100)	50 mg catalyst; n(cyclohexanone)/n(H ₂ O ₂) = 2 mol/3 mol, 30 wt% H ₂ O ₂ , 8 mL 1,4-dioxane, 80 °C, 3 h.	39	-	62	[37]
		Mg-Sn-W	96 g acetic acid, 75 g butyl acetate, 57 g cyclohexane, 54 g H ₂ O ₂ (50 wt%), 60 °C—0.05 MPa, 5 h	90	-	90	[39]
		Sn-zeolite beta	n(adamantanone)/n(H ₂ O ₂) = 1 mol/1 mol, 35 wt% H ₂ O ₂ , 56 °C, 6 h	-	94	98	[36]
		Sn-MCM-68	0.05 g catalyst; n(adamantanone)/n(H ₂ O ₂) = 2 mol/4 mol, 30 wt% H ₂ O ₂ , 90 °C, 1 h	78.1	-	99	[38]
		Sn-BEA	0.05 g catalyst; n(adamantanone)/n(H ₂ O ₂) = 2 mol/4 mol, 30 wt% H ₂ O ₂ , 90 °C, 1 h	65.2	-	99	[38]
		Sn-MWW	0.05 g catalyst; n(adamantanone)/n(H ₂ O ₂) = 2 mol/4 mol, 30 wt% H ₂ O ₂ , 90 °C, 1 h	32	-	99	[38]
		Sn-MFI	0.05 g catalyst; n(adamantanone)/n(H ₂ O ₂) = 2 mol/4 mol, 30 wt% H ₂ O ₂ , 90 °C, 1 h	20.1	-	99	[38]
		Sn-MCM-56	0.04 g Sn-MCM-56, n(adamantanone)/n(H ₂ O ₂) = 2 mol/4 mol, 56 wt% H ₂ O ₂ , 4.5 g chlorobenzene, 90 °C, 4 h	55	-	-	[41]

Table 4. Catalytic performances of Sn-containing materials for the oxidation of cycloketones.

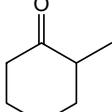
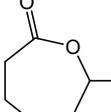
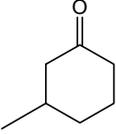
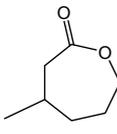
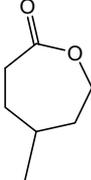
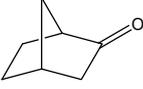
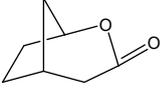
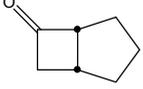
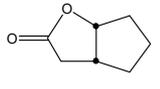
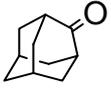
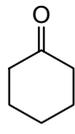
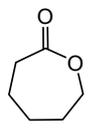
Ketone	Product	Reaction Conditions	Conversion (%)	Selectivity (%)
		0.25 g catalyst; n(ketone)/n(H ₂ O ₂) = 12.5 mol/50 mol, 30 wt% H ₂ O ₂ , 10 mL acetonitrile, 70 °C, 4 h [42].	100 [42]	16 [42]
		3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.15 mmol, 30% H ₂ O ₂ , 3 mL 1,4-dioxane, 70 °C, 24 h [44].	81 [44]	100 [44]
		3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.2 mmol, 30% H ₂ O ₂ , 3 mL 1,2-dichloroethane, 70 °C, 15 h [45].	99 [45]	100 [45]
		0.03 mol catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/2 mmol, 35% H ₂ O ₂ , 3 mL 1,2-dichloroethane, 50 °C, 5 h [46].	70 [46]	82 [46]
		50 mg catalyst, 1 g ketone, 2 mL tert-BuOOH; 5 mL 1,4-dioxane, 70 °C, 12 h [47].	100 [47]	99 [47]
		0.25 g catalyst; n(ketone)/n(H ₂ O ₂) = 12.5 mol/50 mol, 30 wt% H ₂ O ₂ , 10 mL acetonitrile, 70 °C, 4 h [42].	100 [42]	42 [42]
		3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.15 mmol, 30% H ₂ O ₂ , 3 mL 1,4-dioxane, 90 °C, 24 h [44].	80 [44]	100 [44]
		50 mg catalyst, 1 g ketone, 2 mL tert-BuOOH; 5 mL 1,4-dioxane, 90 °C, 24 h [47].	80 [47]	99 [47]

Table 4. Cont.

Ketone	Product	Reaction Conditions	Conversion (%)	Selectivity (%)
		0.25 g catalyst; n(ketone)/n(H ₂ O ₂) = 12.5 mol/50 mol, 30 wt% H ₂ O ₂ , 10 mL acetonitrile, 70 °C, 4 h [42].	100 [42]	32 [42]
		0.25 g catalyst; n(ketone)/n(H ₂ O ₂) = 12.5 mol/50 mol, 30 wt% H ₂ O ₂ , 10 mL acetonitrile, 70 °C, 4 h [42]. 3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.15 mmol, 30% H ₂ O ₂ , 3 mL 1,4-dioxane, 90 °C, 24 h [44]. 3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.2 mmol, 30% H ₂ O ₂ , 3 mL ethanol, 70 °C, 15 h [45]. 50 mg catalyst, 1 g ketone, 2 mL tert-BuOOH; 5 mL 1,4-dioxane, 90 °C, 24 h [47].	100 [42] 44 [44] 85 [45] 85 [47]	26 [42] 100 [44] 100 [45] 99 [47]
		50 mg catalyst, n(ketone)/n(H ₂ O ₂) = 1.0 mmol/1.5 mmol, 35 wt% H ₂ O ₂ , 3.00 g dioxane, 90 °C, 7 h [43].	71 [43]	98 [43]
		50 mg catalyst, 250 mg ketone, 150 mg H ₂ O ₂ , 50 wt% H ₂ O ₂ , 3.00 g dioxane, 40 °C, 7 h [43].	62 [43]	98 [43]
		3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.15 mmol, 30% H ₂ O ₂ , 3 mL nitrobenzene, 90 °C, 24 h [44]. 3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.2 mmol, 30% H ₂ O ₂ , 3 mL 1,4-dioxane, 90 °C, 15 h [45]. 0.01 mol catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/2 mmol, 35% H ₂ O ₂ , 3 mL 1,2-dichloroethane, 25 °C, 2 h [46]. 50 mg catalyst, 1 g ketone, 2 mL tert-BuOOH; 5 mL 1,4-dioxane, 90 °C, 20 h [47].	100 [44] 99 [45] 94 [46] 100 [47]	100 [44] 100 [45] 99 [46] 99 [47]
		3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.15 mmol, 30% H ₂ O ₂ , 3 mL 1,4-dioxane, 70 °C, 24 h [44]. 3 mg catalyst, n(ketone)/n(H ₂ O ₂) = 0.1 mmol/0.2 mmol, 30% H ₂ O ₂ , 3 mL 1,2-dichloroethane, 70 °C, 15 h [45]. 0.01 mol catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/2 mmol, 35% H ₂ O ₂ , 3 mL 1,2-dichloroethane, 25 °C, 4 h [46]. 50 mg catalyst, 1 g ketone, 2 mL tert-BuOOH; 5 mL 1,4-dioxane, 70 °C, 24 h [47].	16 [44] 70 [45] 73 [46] 75 [47]	90 [44] 100 [45] 66 [46] 90 [47]

The synthesis of pyridinium perrhenate is shown in Figure 4 [50]. PyHReO₄ was used to catalyze the BV oxidation of 2-adamantanone using 30% H₂O₂ as an oxidant, and the catalytic activity was high (yield: 90.02%; selectivity > 99%). PyHReO₄ was separated by silica gel column chromatography. The catalytic activity of PyHReO₄ in the oxidation of 2-adamantanone is attributed to the interaction between Re and hydrogen peroxide (Figure 5).

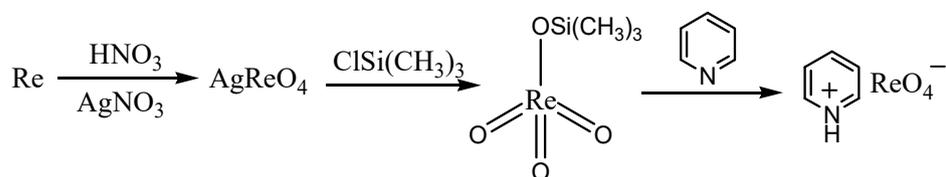


Figure 4. Synthesis of pyridinium perrhenate [50].

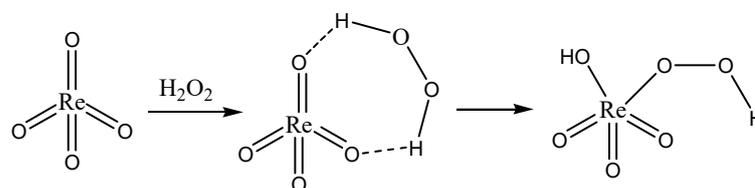


Figure 5. Interaction between Re and hydrogen peroxide [50].

Silver supported on montmorillonite clay (Ag-NPs@mont) was synthesized and used as active catalysts in the BV oxidation of ketones with hydrogen peroxide as an oxidant under the solvent-free condition at room temperature [51]. The Ag-NPs@mont nanocatalyst was separated by filtration, washed with acetone, and dried. The recycled Ag-NPs@mont nanocatalyst was reused four times without significant loss of catalytic activity under the same conditions. The conversion of cyclohexanone was 99% under solvent-free conditions. The results in the oxidation of various ketones showed that the conversion of cyclic ketones was higher than aromatic ketones because aromatic ketones are more stable than cycloketones.

The magnetic composite Fe_3O_4 @I-SR was prepared by loading Fe_3O_4 nanoparticles onto a porous illite silicon slag (I-SR) [52]. Fe_3O_4 nanoparticles were evenly distributed over the I-SR. Fe_3O_4 @I-SR showed high catalytic activity in the oxidation of cyclohexanone. The conversion of cyclohexanone and the selectivity of ϵ -caprolactone were higher than 99%. Fe_3O_4 @I-SR was separated, washed with acetone and ethanol, and dried. The catalytic activity of the recovered Fe_3O_4 @I-SR was almost the same as that of the fresh one (conversion of cyclohexanone: 99% (fifth); selectivity of ϵ -caprolactone: 99% (fifth)). Fe_3O_4 @I-SR can activate both the ketone group and H_2O_2 , which can be used as catalysts to improve oxidation efficiency. Fe_3O_4 @GO also showed high catalytic activity and selectivity for the BV oxidation of cyclohexanone without solvent [53].

Priya prepared mixed oxides of MoLaCeSm-Si [54]. MoLaCeSm-Si catalyst showed good activity and selectivity simultaneously in the oxidation of cyclohexanone to ϵ -caprolactone at room temperature. MoLaCeSm-Si was washed with acetone, dried, and activated at 400 °C for 1 h. The activity of the recovered MoLaCeSm-Si was not lost after six cycles. The conversion of cyclohexanone in the first cycle was 83.1%, and the selectivity of ϵ -caprolactone was 88.9%. The conversion of cyclohexanone was 79.1%, and the selectivity of ϵ -caprolactone was 81.2%, with the catalyst of MoLaCeSm-Si recovered from the sixth cycle. MoO_3 , La_2O_3 , CeO_2 , and Sm_2O_3 in MoLaCeSm-Si each contribute their characteristic properties to increase the catalytic activity towards the oxidation of cyclohexanone at room temperature. Mo^{6+} in MoLaCeSm-Si provides the Lewis acidic center, [55] lanthanum induces primary sites on MoLaCeSm-Si [56], and ceriasamarium increases the oxygen vacancies [57] and performs the role of oxygen carrier between H_2O_2 and cyclohexanone.

Furia [58] studied the BV reaction of ketones catalyzed by transition metals. They used a 70% hydrogen peroxide solution as an oxidant and a molybdenum peroxy complex as a catalyst to oxidize cyclopentanone to δ -valerolactone (Figure 6). The maximum conversion of cyclopentanone is 65%, and the maximum yield of δ -valerolactone is 54%. (0.09 M catalyst, 1.4 M cyclopentanone, 2.2 M H_2O_2 , 70 °C, 6 h)

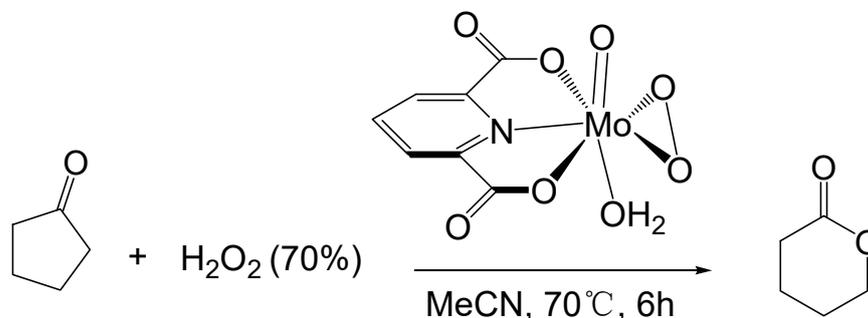
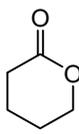
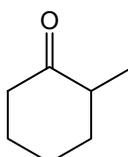
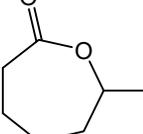
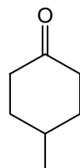
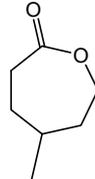
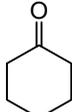
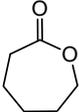


Figure 6. Oxidation of cyclic ketones catalyzed by molybdenum peroxy complex [58].

MoO_3 , WO_3 , and $[\{\gamma\text{-SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\mu\text{-O})_2]^{4-}$ have high catalytic activity and selectivity in the BV oxidation of cyclic ketones [59,60]. The catalytic activity of the recycled $[\{\gamma\text{-SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\mu\text{-O})_2]^{4-}$ was the same as that of the fresh one (yields of lactone: 99% (third run)). The conversion of cyclic ketones and the yields of corresponding lactones are shown in Table 5. Cyclic ketones with tertiary carbon atoms adjacent to the ketone carbonyl

group are more likely to undergo the BV reaction than cyclic ketones with secondary carbon atoms adjacent to the ketone carbonyl group, and the selectivity for the formation of corresponding lactones is also higher.

Table 5. Catalytic performances of different catalysts for the oxidation of cyclic ketones to lactones.

Ketone	Product	Reaction Conditions	Conversion (%)	Selectivity (%)
		25 mg catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/20 mmol, 30% H ₂ O ₂ , 25 °C, 4 h [51].	90 [51]	100 [51]
		catalyst/substrate = 20 wt%, n(ketone)/n(H ₂ O ₂) = 2.5 mmol/6.25 mmol, 50% H ₂ O ₂ , 3.5 mL dioxane, 40 °C, 12 h [59].	83 [59]	15 [59]
		1.25 μmol catalyst, n(ketone)/n(H ₂ O ₂) = 1.25 mmol/2.5 mmol, 80% H ₂ O ₂ , 1.0 mL MeNO ₂ , 60 °C, 45 min [60].	99 [60]	99 [60]
		25 mg catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/20 mmol, 30% H ₂ O ₂ , 25 °C, 4 h [51].	89 [51]	94 [51]
		0.02 g Fe ₃ O ₄ @GO, n(ketone)/n(H ₂ O ₂) = 2 mmol/12 mmol, 30% H ₂ O ₂ , solvent free, 25 °C, 5 h [53].	89 [53]	84 [53]
		catalyst/substrate = 20 wt%, n(ketone)/n(H ₂ O ₂) = 2.5 mmol/6.25 mmol, 50% H ₂ O ₂ , 3.5 mL dioxane, 40 °C, 12 h [59].	99 [59]	96 [59]
		25 mg catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/20 mmol, 30% H ₂ O ₂ , 25 °C, 4 h [51].	90 [51]	96 [51]
		0.02 g Fe ₃ O ₄ @GO, n(ketone)/n(H ₂ O ₂) = 2 mmol/12 mmol, 30% H ₂ O ₂ , solvent free, 25 °C, 5 h [53].	97 [53]	95 [53]
		catalyst/substrate = 20 wt%, n(ketone)/n(H ₂ O ₂) = 2.5 mmol/6.25 mmol, 50% H ₂ O ₂ , 3.5 mL dioxane, 40 °C, 12 h [59].	99 [59]	93 [59]
		1.25 μmol catalyst, n(ketone)/n(H ₂ O ₂) = 1.25 mmol/2.5 mmol, 80% H ₂ O ₂ , 1.0 mL MeNO ₂ , 60 °C, 15 min [60].	99 [60]	99 [60]
		0.04 g catalyst, n(ketone)/n(H ₂ O ₂) = 0.05 mol/0.18 mol, 30% H ₂ O ₂ , 25 °C, 4 h [51].	99 [51]	100 [51]
		25 mg catalyst, n(ketone)/n(H ₂ O ₂) = 2 mmol/20 mmol, 30% H ₂ O ₂ , 25 °C, 45 min [51].	99 [51]	99 [51]
		0.02 g Fe ₃ O ₄ @GO, n(ketone)/n(H ₂ O ₂) = 2 mmol/12 mmol, 30% H ₂ O ₂ , solvent free, 25 °C, 5 h [53].	90 [53]	52 [53]
		catalyst/substrate = 20 wt%, n(ketone)/n(H ₂ O ₂) = 2.5 mmol/6.25 mmol, 50% H ₂ O ₂ , 3.5 mL dioxane, 40 °C, 12 h [59].	92 [59]	22 [59]

The high catalytic activity of MoO₃ is due to its reaction with hydrogen peroxide to form peroxy acids. The possible reaction process is shown in Figure 7.

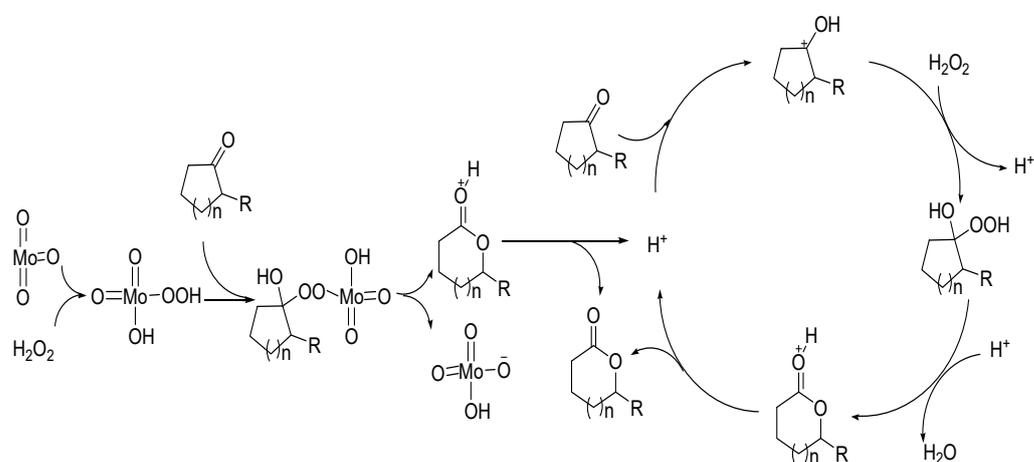


Figure 7. A possible mechanism for Baeyer–Villiger oxidation over transition metal oxides [59].

The catalytic mechanisms of Bronsted acids and Lewis acids are different. The good catalytic performance of transition metal oxides can be attributed to the coordination of the Lewis acid center of metal with carbonyl oxygen, and the reaction with hydrogen peroxide to form peroxy acids.

3. The Bronsted Acid System

3.1. Homogeneous Systems

Bronsted acid showed high catalytic activity in the BV oxidation. The conversion of 2-heptylcyclopentanone to δ -dodecalactone was catalyzed by different Bronsted acids (CH_3COOH , CF_3COOH , $\text{CH}_3\text{SO}_3\text{H}$, TsOH , $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$) using aqueous hydrogen peroxide (30 wt%) as oxidant [61]. The catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was higher than the other acids. Although the catalytic activity was affected by acid strength, it was not the only factor. Although the conversion of cyclopentanone, cyclohexanone, and cycloheptanone was high, the selectivity for the corresponding lactones was very poor. The low selectivity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was ascribed to its acid sites, which catalyzed the hydrolysis and oxidation of lactones, leading to the formation of acids. It is difficult to separate $\text{H}_3\text{PW}_{12}\text{O}_{40}$ from the reaction system.

The study by Mouheb L. found the Keggin-type polyoxometalates $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_{2.98}\text{Sn}_{0.1}\text{PMo}_{12}\text{O}_{40}$, $\text{Cs}_{1.5}\text{Sn}_{0.75}\text{PMo}_{12}\text{O}_{40}$, $\text{Cs}_{2.14}\text{Sn}_{0.43}\text{PMo}_{12}\text{O}_{40}$, and $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ involve acidic sites of the Bronsted and Lewis type [62]. The catalytic activity of POMs was tested in the homogenous oxidation of cyclohexanone using hydrogen peroxide as an oxidant. The products of the reaction are adipic (AA), glutaric (GA), succinic (SA) acids, butane-1,3-diol (Diol), and ϵ -caprolactone (ϵ -CL). The results showed that the whole Keggin-type polyoxometalates have a high catalytic activity (conversion of cyclohexanone is 98–100%) (Table 6) [62]. The substrate was activated by the Bronsted acidity [63]. $\text{H}_3\text{PMo}_{12}$ was oxidized to $\{\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4\}_3^-$, $\{\text{PMo}_3\text{O}_m\}_n^-$ and $\{\text{PO}_4[\text{MoO}(\text{O}_2)_2]_2\}_2^-$, peroxy species in the presence of H_2O_2 [64]. POM oxygen atoms were replaced by the “peroxy” (O_2^{2-}) from the hydrogen peroxide, Peroxy ions are distributed in the Keggin anion without disturbing its structure. The good catalytic performance of POMs was attributed to the formation of Peroxy-POM.

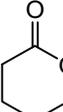
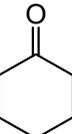
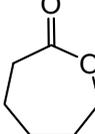
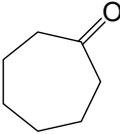
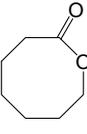
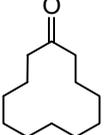
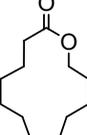
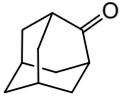
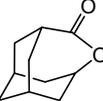
Table 6. Catalytic performances of POMs for cyclohexanone oxidation.

Catalysts	Conversion (mol%)	Selectivities (Yields) (%)			
		Adipic Acid	Glutaric Acid	Succinic Acid	ϵ -Caprolactone
$\text{H}_3\text{PMo}_{12}$	100	31	7	1	7
$\text{Cs}_3\text{PMo}_{12}$	98	09	5	1	11
CsSnPMo_{12}	100	50	9	2	18
HSnPMo_{12}	100	59	13	4	13
$\text{Cs}_2\text{Sn}_{0.5}\text{PMo}_{12}$	100	55	16	3	14

3.2. Heterogeneous Systems

KHPW was prepared with a potassium content of 1.3 wt%. Although the chemical structure of KHPW was similar to that of HPW, it has better thermal stability and can be separated from the reaction solution by filtration. After repeated use three times in the oxidation of 2-heptylcyclopentanone, the catalytic activity of KHPW did not decrease significantly. In the BV oxidation of 2-adamantanone and cyclododecanone, the corresponding lactones are obtained in good yields [65]. The oxidation of cyclic ketones to corresponding lactones with 30% H_2O_2 in the presence of HPW and KHPW is shown in Table 7.

Table 7. Catalytic performances of HPW and KHPW for the oxidation of cyclic ketones to lactones.

Ketone	Product	Catalysts	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)
		HPW	25	12	42	56
		HPW	40	12	97	15
		KHPW	15	24	91	42
		HPW	40	12	97	17
		KHPW	40	24	95	46
		HPW	40	12	98	11
		KHPW	55	24	89	37
		HPW	40	12	45	35
		KHPW	55	24	93	82
		HPW	40	12	98	93
		KHPW	40	12	98	95

Reaction conditions: substrate (2.5 mmol), catalyst/substrate = 20 wt%, H₂O₂ (30 wt%) (6.25 mmol).

Keggin-type heteropolyacids (HPAs) always show higher catalytic activity than common acids. HPAs have strong acidity and redox capacity, and their crystal structures are adjustable [66]. HPAs have been used in many reactions such as hydrations [67], isomerization [68,69], esterification [70], Fries rearrangement [71], Friedel–Crafts acylation [72], and etherification [73], etc. Three mesoporous materials were prepared by loading silicotungstic acids on SBA-15, MCM-41, and MCM-48 [66]. These prepared materials can be recycled and showed excellent catalytic activity in the BV oxidation of cyclic ketones using 30% H₂O₂ aqueous solution as oxidant. The conversion of cyclic ketones to the corresponding lactones was up to 90% under the optimum reaction conditions. Cyclic ketones were easily introduced into the hole of MCM-41 and SBA-15, so the catalytic activity of HSiW/MCM-41 and HSiW/SBA-15 was higher than HSiW/MCM-48 in the BV oxidation.

Ionic liquids are often used as green solvents or catalysts because of their low volatility, good thermal stability, good solubility, and convenient separation at room temperature. Bronsted acidic heteropolyanion-based ionic liquid ([MIMPS]₃PW₁₂O₄₀) exhibited higher catalytic activity in the BV reaction of cyclohexanone to produce ε-caprolactone. The phosphotungstic anion (PW₁₂O₄₀³⁻) was successfully modified by the organic precursor MIMPS, and SO₃H was introduced into the catalyst ([MIMPS]₃PW₁₂O₄₀). [MIMPS]₃PW₁₂O₄₀ could be dissolved in the reaction system as a liquid, then precipitated after the reaction [74]. The conversion of cyclohexanone was 93.51%, the yield of ε-caprolactone was 93.26%, and the selectivity of ε-caprolactone was 99.73% under optimum reaction conditions (0.8 g [MIMPS]₃PW₁₂O₄₀, n (H₂O₂): n (cyclohexanone) = 6: 1, 25 g cyclohexane, 70 °C, 1 h). Tungsten and SO₃H play a very crucial role in promoting the yield of ε-caprolactone because tungsten and SO₃H are oxidized to peroxyacid in the existence of H₂O₂. The W element in [MIMPS]₃PW₁₂O₄₀ showed a noticeable loss after several cycle tests. This leads to catalyst deactivation. Stabilizing the active components of the catalyst is a critical problem to be solved in catalyst preparation.

Yu F.L. synthesized a series of amino-acid-based ionic liquids. (Figure 8) [75] They were used as catalysts for the BV oxidation of cyclopentanone. The proline-based ionic liquid [ProH]CF₃SO₃ showed the best catalytic activity. Under the optimum conditions (n(cyclopentanone):n(catalyst):n(H₂O₂) = 1:0.06:4, 60 °C, 6 h), the conversion of cyclopentanone was 96.57%, and the selectivity for δ -valerolactone was 73.01%. The catalytic activity of [ProH]CF₃SO₃ in the BV oxidation of cyclopentanone increases with increasing acidity, but the increase in acidity can lead to the hydrolysis of δ -valerolactone. The carbonyl was activated by H⁺ to facilitate the oxidation of hydrogen peroxide. The possible reaction process is shown in Figure 9.

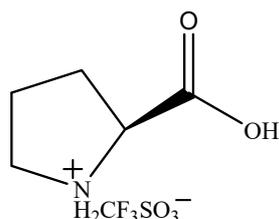


Figure 8. Structure of [ProH]CF₃SO₃ [75].

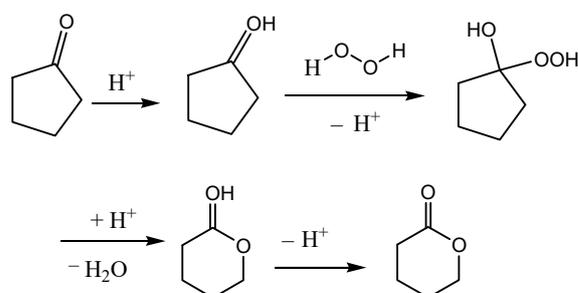


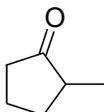
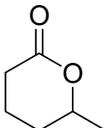
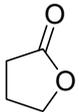
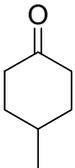
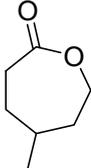
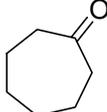
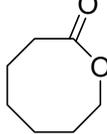
Figure 9. A possible mechanism for Baeyer–Villiger oxidation over Bronsted acid [75].

Bronsted acid catalysts of silica/A153–SO₃H [76], silica-VTMO–OSO₃H [77], and Fe–Co/SPS [78] were prepared. The acidity of silica/A153–SO₃H was 2.34 mmol g^{−1}. The acidity of silica-VTMO–OSO₃H was 1.39 mmol g^{−1}. The catalytic activity of [ProH]CF₃SO₃, silica/A153–SO₃H, silica-VTMO–OSO₃H, and Fe–Co/SPS in the BV oxidation of various cyclic ketones with 30% H₂O₂ is shown in Table 8.

Table 8. Oxidation of cyclic ketones to lactones.

Entry	Ketone	Product	Conversion (%)	Yield (%)
1			95 [75]	73 [75]
			53 [76]	45 [76]
			55 [77]	43 [77]
			53 [75]	34 [75]
2			61 [76]	55 [76]
			64 [77]	52 [77]
			90 [78]	52 [78]
			98 [75]	91 [75]
3			99 [76]	96 [76]
			99 [77]	96 [77]
			97 [78]	95 [78]
4			97 [76]	93 [76]
			95 [77]	91 [77]
			89 [78]	84 [78]

Table 8. Cont.

Entry	Ketone	Product	Conversion (%)	Yield (%)
5			82 [75]	64 [75]
6			96 [75]	92 [75]
7			57 [75]	30 [75]
8			34 [75]	18 [75]
			15 [76]	8 [76]
			17 [77]	10 [77]

4. Conclusions

The BV oxidation of cycloketones could be catalyzed by Bronsted acids and Lewis acids. The obtained catalysts have different catalytic activities in the BV oxidation of cycloketones using hydrogen peroxide as the oxidant. The catalytic mechanisms of Bronsted acids and Lewis acids are different. The excellent catalytic performance of Lewis acids can be attributed to the coordination of the Lewis acid center of metal with carbonyl oxygen. The high catalytic activity of Bronsted acids is due to their reaction with hydrogen peroxide to form peroxy acids. The carbonyl was also activated by H^+ to facilitate oxidation.

In the oxidation of cyclohexanone, the catalytic activity and selectivity of Lewis acids are higher than those of Bronsted acids. The low selectivity of Bronsted acids is ascribed to their acid sites, which catalyzed the hydrolysis and oxidation of ϵ -caprolactone. Among the Lewis acid catalysts mentioned in this paper, the catalytic activity and selectivity of the heterogeneous catalysts are higher than those of the homogeneous catalysts. In particular, the heterogeneous catalysts can be easily recycled and reused, and the catalytic activity and the selectivity of the recycled catalysts are almost the same as those of the fresh catalysts. The catalytic activity and the selectivity of Ag-NPs@montnano, $Fe_3O_4@I-SR$, and Mg-Sn-W are higher than those of other catalysts, but the preparation of Mg-Sn-W uses the toxic tin chloride, the preparation is complex, and it is not economical to use Ag-NPs@montnano as a catalyst. $Fe_3O_4@I-SR$ is a better choice in the BV oxidation of cyclohexanone.

Author Contributions: Conceptualization, X.P.; writing—original draft preparation, Q.M.; writing—review and editing, Y.X. and J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi, grant number 2019L0919. This work was also supported by the Fund for Shanxi “1331 Project” and the National Natural Science Fund of China (grant number 22072105).

Conflicts of Interest: The authors declare no conflict of interest.

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