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Baeyer–Villiger oxidation of ketones with hydrogen peroxide catalyzed by Sn-palygorskite

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Abstract—Palygorskite-supported Sn complexes were prepared by a simple procedure. Cyclic ketones and acyclic ketones were oxidized by hydrogen peroxide in a reaction catalyzed by palygorskite-supported Sn complexes, affording corresponding lactones or esters with selectivity for the product of 90–100%. The catalysts can be recycled for several times without significant decline in catalytic activity.

The Baeyer–Villiger oxidation was first reported by Baeyer and Villiger in 1899 when they converted menthone, camphor, and carvone into the corresponding lactones with Caro's acid as an oxidant.[1] The reaction can be applied in the synthesis of a wide variety of chemicals, ranging from simple monomers used in the polyester industry to the more complex molecules that were applied for the synthesis of pharmaceutical products.[2] However, the oxidants used in the traditional Baeyer–Villiger oxidation are organic peroxy acids which potentially produce large amounts of harmful wastes. Much recent effort has been devoted to find chemically green oxidants along with the recyclable catalysts.

Supported catalysis, in particular, accord with green chemistry by allowing easy separation of the products and permitting the recycling and reuse of the catalyst with operational and economical advantages. Polymer-anchored metal complexes,[3–5] solid acids,[6] Sn-MCM-41,[7] sulfonated resins,[8] titanium silicalites,[9] transition metal-functionalized hydrotalcites,[10] and Sn-synthesized hydrotalcites[11] are examples of some of the heterogeneous catalysts used to perform the Baeyer–Villiger reaction. The best catalytic system for the Baeyer–Villiger reaction was reported recently by Corma and his colleagues.[12,13] They found that Sn-Zeolite beta was a very active and selective catalyst for the Baeyer–Villiger oxidation of cycloketones with environmentally benign hydrogen peroxide as an alternative to organic peroxy acids. The Sn-zeolite beta was synthesized using dealuminated nanocrystalline (20 nm) zeolite as seeds and a crystallization procedure was performed in Teflon-lined stainless steel autoclaves, which were heated to 140 °C and rotated over a period of 20 days.

We report here the catalytic Baeyer–Villiger oxidation of ketones with a recyclable catalytic system using palygorskite as a catalytic support and 30% hydrogen peroxide as oxidant. The catalyst and the catalytic system we used are similar to those of Corma's, but the procedure for the preparation of the Sn-palygorskite is much simpler. Furthermore, palygorskite is a biocompatible and environmentally friendly natural mineral abundant in deposits all over the world. The catalyst can be prepared in large scale and can be recycled.

Palygorskite is a natural clay mineral characterized by a porous crystalline structure containing tetrahedral layers alloyed together by longitudinal sideline chains. A typical unit cell consists of $(Mg,Al)_5Si_8O_{20}(OH)_2(H_2O)_4{\cdot}4H_2O$, with Mg preferentially located in octahedral sites. These mineral clays possess Mg^{2+} and Al^{3+} cations that can be easily exchanged.[14] Due to its sorptive and rheological properties, palygorskite is widely used in different industrial fields. In spite of numerous studies on the catalytic properties of palygorskite, organic reactions catalyzed by palygorskite-supported

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Keywords: Baeyer–Villiger oxidation; Palygorskite; Ketone oxidation.

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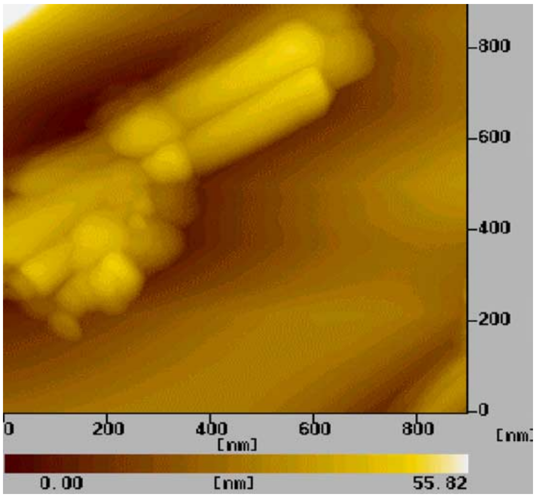


Figure 1. AFM pattern of palygorskite used for the preparation of Sn-palygorskite catalyst. The palygorskite particle is about 650 × 350 nm with the thickness of 25–50 nm.

catalyst, especially for the oxidation reactions, have been scarcely reported. We show that upon incorporation of 2.41 wt% of tin into the framework of palygorskite (Fig. 1), Sn-palygorskite was obtained. This material acts as an efficient and stable heterogeneous catalyst for the Baeyer–Villiger oxidation of ketones by 30% hydrogen peroxide.

Sn-palygorskite was prepared according to the following procedure.

Palygorskite (1 g) (received from Gansu Kaixi Ecological Environment Material Company, powdered to 0.26–2.93 μm) was leached with 1 N HCl (20 mL) at room temperature for 1 h. $SnCl_2 \cdot 4H_2O$ (2 g) was then added to the mixture and the resultant slurry was stirred at room temperature for 24 h. The products were collected by filtration, washed with copious amounts of ethanol and water, dried at 333 K under vacuum for 24 h. The content of Sn in the Sn-palygorskite is 2.41 wt% according to chemical analysis.

Figure 2 shows the infrared spectra of natural palygorskite and Sn-palygorskite. The bands at 1026 and 469 cm^{-1} were attributed to in-layered Si–O–Si bonds. The band near 800 cm $^{-1}$ may correspond to the Al–O–Si bond. The Lewis and Bronsted acid sites were situated at 1653 and 1448 cm^{-1}, respectively, as identified by the adsorption of an *n*-butylamine probe molecule.[15] There are obvious changes in the IR spectra of Sn-palygorskite compared to that of palygorskite. In the IR spectra of Sn-palygorskite, the peak near 1448 cm^{-1} almost disappears. The strong absorption at 469 cm^{-1} is shifted to 539 cm^{-1}. These may be attributed to the palygorskite inlaid with tin.

Oxidation of ketones was carried out in a 25 mL glass reactor. A typical procedure for the Baeyer–Villiger oxidation is as follows: 2-adamantone (15 mg, 0.1 mmol) and 30% hydrogen peroxide (1.5 equiv) were dissolved in nitrobenzene or 1,4-dioxane (3 mL). Sn-palygorskite (3 mg) was added, the mixture was heated to 90 °C and stirred for 24 h. The products were identified by GC–MS analysis. Other cyclic ketones and acyclic ketones were also oxidized in this oxidation system to give the corresponding lactones or esters. The results are summarized in Table 1.

We confirmed that the oxidation reaction did not occur in the absence of the catalyst. Moreover, the reaction did not proceed in the presence of $SnCl_2$, or untreated palygorskite was used.

Sn-palygorskite possesses high catalytic activity for the Baeyer–Villiger oxidation of cyclic ketones and acyclic ketones. In particular, 2-adamantanone, 3-methyl-2-pentanone and 4-methyl-2-pentanone were converted into the corresponding lactone or ester almost quantitatively. In the case of adamantanone, it is noteworthy that Sn-palygorskite as heterogeneous catalyst can be recycled at least four times without significant decline in catalytic activity.

A possible reaction mechanism using Sn-palygorskite as catalyst for the Baeyer–Villiger oxidation is shown in

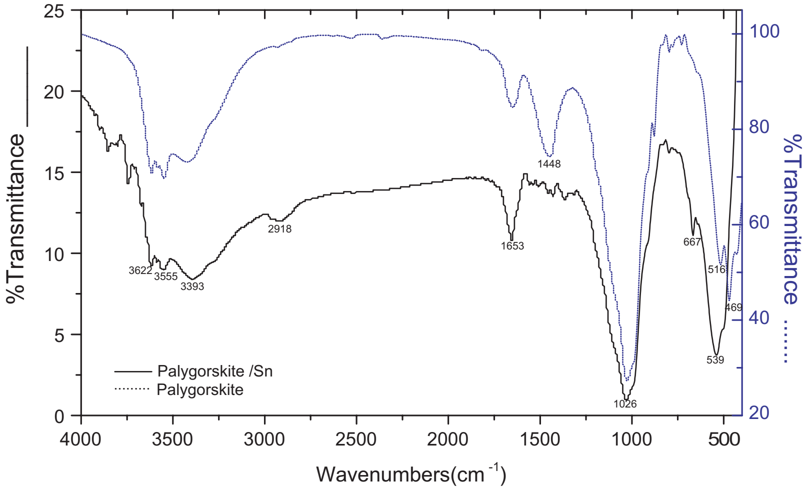
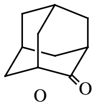
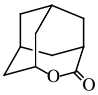
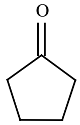
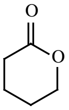
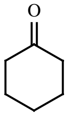
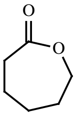
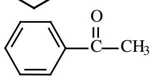
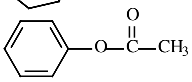
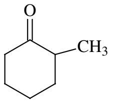
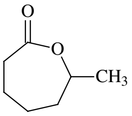
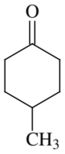
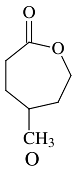
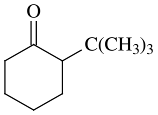
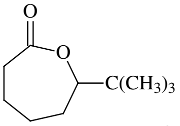
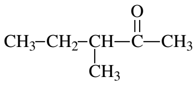
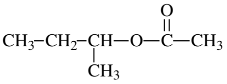
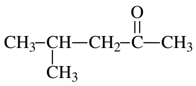
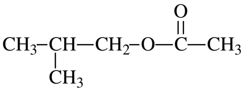


Figure 2. The IR spectra of palygorskite and Sn-palygorskite.

Table 1. Baeyer–Villiger oxidation of several ketones catalyzed by Sn-palygorskite

Substrate	Temp (°C)	H_2O_2 (equiv) (30%)	Solvent	Conversion (%)	Selectivity[a] (%)	Turnover number	Product
	90	1.5	Nitrobenzene	100	100	164	
	70	1.5	1,4-Dioxane	81	100	132	
	70	1.5	1,4-Dioxane	16	90	26	
	70	1.5	1,4-Dioxane	37	100	61	
	90	1.5	1,4-Dioxane	80	100	197	
	90	1.5	1,4-Dioxane	44	100	108	
	90	1.5	1,4-Dioxane	25	100	31	
 $CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}{-}CH_3$	90	1.5	1,4-Dioxane	100	100	123	 $CH_3{-}CH_2{-}\underset{CH_3}{CH}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$
 $CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$	90	1.5	1,4-Dioxane	100	100	123	 $CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

Reaction condition: substrate 0.1 mmol, 30% H_2O_2 (1.5 equiv to the ketones), Sn-palygorskite 3 mg, 24 h.

[a] Selectivity to the mentioned product listed in the last column.

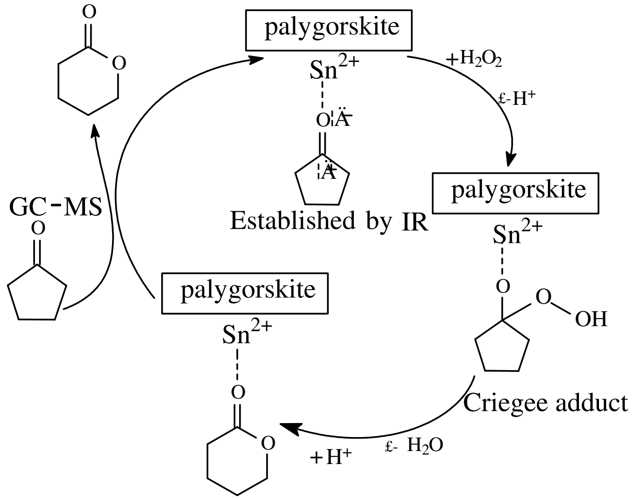


Figure 3. Catalytic mechanism for the Baeyer–Villiger oxidation catalyzed by Sn-palygorskite.

Figure 3. Firstly, the ketone is coordinated to the Lewis-acid tin center, and thereby, the carbonyl group is activated. Hydrogen peroxide subsequently attacks the electrophilic carbonyl carbon atom. After the rearrangement, the lactone product is replaced by a new substrate molecule. This mechanism is analogous to that for peracids, which Corma et al.[12] have confirmed by means of an ^{18}O labeling experiment, infrared spectroscopy and gas chromatography–mass spectrometry.

In summary, Sn-palygorskite was prepared by a simple procedure and shown to act as a highly active catalyst for the Baeyer–Villiger oxidation of ketones using environmentally friendly 30% hydrogen peroxide as oxidant. The catalyst can also be recycled. Further work exploring the utility of these novel catalysts is on-going in our laboratory.

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