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

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Abstract

An environmentally benign and selective Baeyer–Villiger oxidation system is introduced. 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 90–99%. The influence of the solvents, reaction temperature, the amount of catalyst used and the reaction time on the catalytic activity and product selectivity were investigated in detail. The catalyst is cheap, easy to be prepared in large scale and can be recycled.
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Keywords: Baeyer–Villiger oxidation; Palygorskite; Ketone oxidation; Sn-palygorskite catalyst

1. Introduction

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]. Usually, this transformation is carried out by peroxy compounds such as peracids [2,3] and hydroperoxides [4–9]. Acids, bases, enzymes, and metal-containing reagents are known to catalyze Baeyer–Villiger oxidations [10–13].

Baeyer–Villiger oxidation is now a frequently used synthetic tool for the conversion of cycloalkanones to lactones. The reaction can also be applied in the synthesis of a wide variety of other chemicals, ranging from simple monomers used in the polyester industry to the more complex molecules that applied for the synthesis of pharmaceutical products [14]. However, the oxidants used in the traditional Baeyer–Villiger oxidation are organic peroxy acids which generally prepared by the utilization of excess hazardous concentration levels of hydrogen peroxide and potentially produce large amounts of harmful wastes. Much recent effort has been devoted to find the methods that use chemically green oxidants such as low concentration hydrogen peroxide and molecular oxygen along with the recyclable catalysts [15–18].

Supported catalysis, in particular, accorded with green chemistry by allowing easy separation of the products and permitting the recycling and reuse of the catalysts with operational and economical advantages. Polymer-anchored metal complexes [19–21], solid acids [4], Sn-MCM-41 [22], sulphonated resins [23], titanium silicalites [24], transition metal-functionalized hydrotalcites [25], hydrotalcite-supported Sb catalyst [26] and Sn-synthesized hydrotalcites [27] 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 by Corma and his colleagues (see Strukul's comment [28]). Corma et al. [29] 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

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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.

Low concentration of hydrogen peroxide (<30%) is a highly attractive oxidant for a number of reasons: it is a cheap, mild and an environmentally benign reagent with a high content of active oxygen, and water is formed as the only by-product. However, expensive catalysts are normally required to effect oxygen transfer from hydrogen peroxide to the substrate. Many transition metal complexes have been used for the activation of hydrogen peroxide [30–33].

In a previous article [34], we report the catalytic Baeyer–Villiger oxidation of ketones with a recyclable catalytic system using palygorskite as a catalytic supporter and 30% hydrogen peroxide as oxidant. We reported here the detailed experimental results of this interesting oxidation system. 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 [35]. 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 catalyst, especially for the oxidation reactions have been scarcely reported. We reported that cyclic ketones and acyclic ketones were oxidized by 30% hydrogen peroxide in a reaction catalyzed by palygorskite-supported Sn complexes. We showed that upon incorporation of 2.41% of tin into the framework of paly-gorskite (Fig. 1), Sn-palygorskite was obtained. This material acts as an efficient and stable heterogeneous catalyst for the Baeyer–Villiger oxidation. The effect of solvent, the reaction temperature, the amount of catalyst used and the reaction time on the catalytic activity and product selectivity were investigated.

2. Experimental

$SnCl_2 \cdot 2H_2O$, 2-adamantanone, cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-*tert*-butylcyclohexanone, 4-*tert*-butylcyclohexanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, and cyclopentone were obtained from commercial sources and used as received without further purification.

Sn-palygorskite was prepared according to the following procedure. Palygorskite (1 g) (received from Gansu Kaixi Ecological Environment Material Company Limited, powdered to 0.26–2.93 μm) was leached with 1N HCl (20 mL) at room temperature for 1 h. $SnCl_2 \cdot 2H_2O$ (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 ICP analysis.

Oxidation of ketones was carried out in a 25 mL glass reactor. A typical procedure for the Baeyer–Villiger oxidation is as follows: 2-adamantanone (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, 6.09×10^{-4} mmol) 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 Tables 1–6.
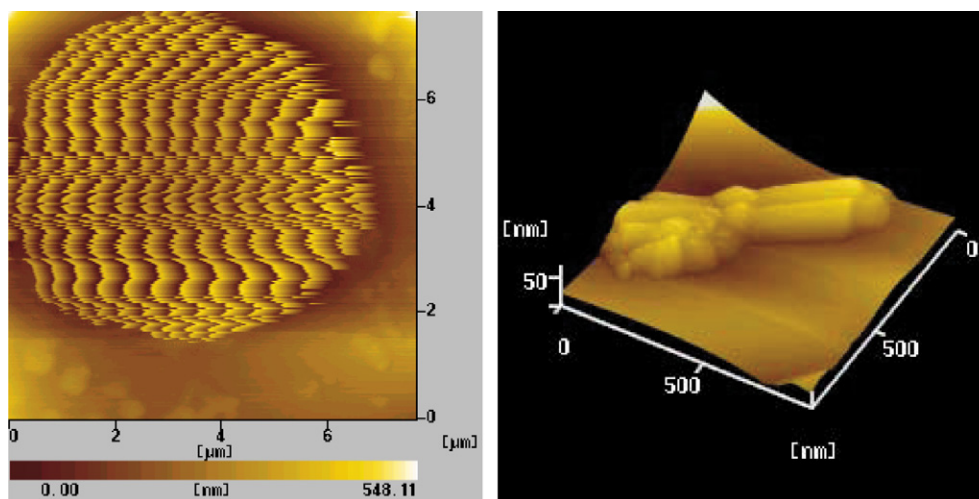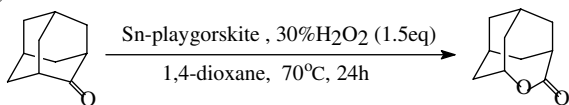

Fig. 1. AFM patterns of palygorskite used for the preparation of Sn-palygorskite catalyst. The palygorskite particle is about 0.3–6 μm × 0.2–5 μm with the thickness of 25–50 nm.

Table 1
Catalytic oxidation of 2-adamantanone with different amount of Sn-palygorskite

Entry	Cat (mmol)	Conv. (%)	Sele. (%)
1	2.03×10^{-4}	27	>99
2	4.06×10^{-4}	38	>99
3	6.09×10^{-4}	61	>99
4	8.12×10^{-4}	57	>99
5	10.15×10^{-4}	55	>99

Reaction conditions: 2-adamantanone 0.1 mmol, H_2O_2 (30%) 1.5 equiv. 1,4-dioxane 3 mL, 70 °C, 24 h.
Percentage of conversion and product selectivity were determined using GC analysis.

Table 2
Catalytic oxidation of 2-adamantanone catalyzed by Sn-palygorskite with different solvents
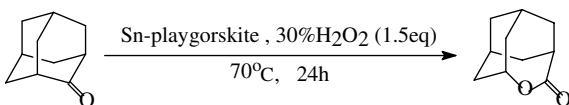
Entry	Solvent	Conv. (%)	Sele. (%)
1	CH_3CN	15	>99
2	C_6H_5Cl	17	>99
3	$C_6H_5NO_2$	71	>99
4	1,4-Dioxane	61	>99
5	C_6H_5F	31	>99

Reaction conditions: Sn-palygorskite 3 mg (6.09×10^{-4} mmol), 2-adamantanone 0.1 mmol, H_2O_2 (30%) 1.5 equiv. solvent 3 mL, 70 °C, 24 h.
Percentage of conversion and product selectivity were determined using GC analysis.

Table 3
Catalytic oxidation of 2-adamantanone catalyzed by Sn-palygorskite at different temperature using 4-dioxane as solvent
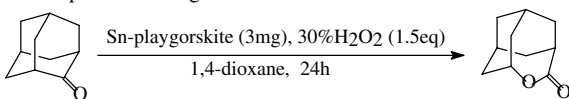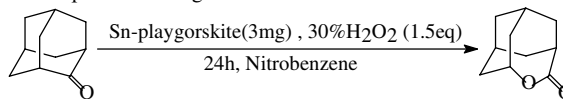

Entry	Temperature (°C)	Conv. (%)	Sele. (%)
1	30	–	–
2	50	27	>99
3	70	61	>99
4	90	85	53

Reaction conditions: Sn-palygorskite 3 mg (6.09×10^{-4} mmol), 2-adamantanone 0.1 mmol, H_2O_2 (30%) 1.5 equiv. 1,4-dioxane 3 mL, 24 h.
Percentage of conversion and product selectivity were determined using GC analysis.

FT-IR spectra were recorded on a Bio-Rad Win-IR spectrometer using KBr disks. GC/MS analyses were carried out on a trace HP GC6890/MS5973 equipped with a 25 m × 0.25 mm SE-54 column and a Shimadzu GC-16A gas chromatograph with a 3 m × 3 mm OV-17 column. The metal content of the Sn-palygorskite was determined

Table 4
Catalytic oxidation of 2-adamantanone catalyzed by Sn-palygorskite at different temperature using nitrobenzene as solvent


Entry	Temperature (°C)	Conv. (%)	Sele. (%)
1	30	28	>99
2	50	33	>99
3	70	71	>99
4	90	100	>99
5	110	62	>99
6	130	47	>99

Reaction conditions: Sn-palygorskite 3 mg (6.09×10^{-4} mmol), 2-adamantanone 0.1 mmol, H_2O_2 (30%) 1.5 equiv. nitrobenzene 3 mL, 24 h.
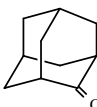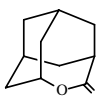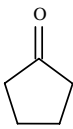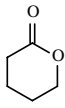Percentage of conversion and product selectivity were determined using GC analysis.

Table 5
Catalytic oxidation of 2-adamantanone by Sn-palygorskite with different time
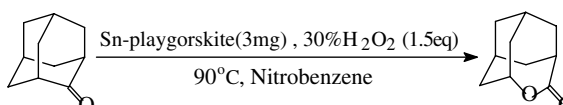
Entry	Time (h)	Conv. (%)	Sele. (%)
1	4	15	>99
2	6	35	>99
3	10	42	>99
4	14	49	>99
5	16	53	>99
6	20	74	>99
7	24	100	>99

Reaction conditions: Sn-palygorskite 3 mg (6.09×10^{-4} mmol), 2-andamantanone 0.1 mmol, H_2O_2 (30%) 1.5 equiv., nitrobenzene 3 mL, 90 °C.
Percentage of conversion and product selectivity were determined using GC analysis.
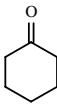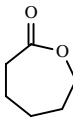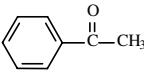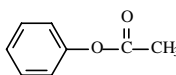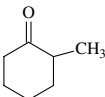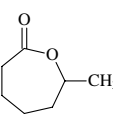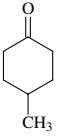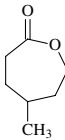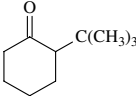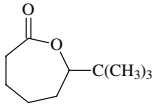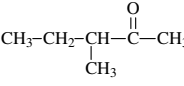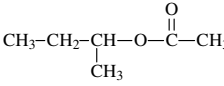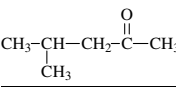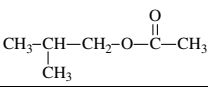
with a Shimadzu ICPV-5600 spectrophotometer under the standard conditions.

3. Results and discussion

3.1. Preparation and characterization of the catalyst

Fig. 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 [36]. There are obvious changes in the IR spectra of Sn-palygorskite compared to that of palygorskite. In the IR spectra of palygorskite-Sn, 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 through the formation of Sn–O bond.

Table 6
Baeyer–Villiger oxidation of several ketones catalyzed by Sn-palygorskite

Substrate	Temperature (°C)	H_2O_2 (30%)	Solvent	Conversion (%)	Selectivity (%)	Turnover number	Product
	90	1.5 equiv.	Nitrobenzene	100	>99	164	
	70	1.5 equiv.	1,4-Dioxane	81	>99	132	
	70	1.5 equiv.	1,4-Dioxane	16	90	26	
	70	1.5 equiv.	1,4-Dioxane	37	>99	61	
	90	1.5 equiv.	1,4-Dioxane	80	>99	197	
	90	1.5 equiv.	1,4-Dioxane	44	>99	108	
	90	1.5 equiv.	1,4-Dioxane	25	>99	31	
$CH_3-CH_2-CH(CH_3)-C(O)-CH_3$	90	1.5 equiv.	1,4-Dioxane	100	>99	123	$CH_3-CH_2-CH(CH_3)-O-C(O)-CH_3$
$CH_3-CH(CH_3)-CH_2-C(O)-CH_3$	90	1.5 equiv.	1,4-Dioxane	100	>99	123	$CH_3-CH(CH_3)-CH_2-O-C(O)-CH_3$

Reaction conditions: Sn-palygorskite 3 mg (6.09×10^{-4} mmol), ketone 0.1 mmol, H_2O_2 (30%) 1.5 equiv., solvent 3 mL.
Percentage of conversion and product selectivity were determined using GC analysis.

3.2. Catalytic oxidation properties of the Sn-palygorskite

Oxidation of ketones was carried out in a 25 mL glass reactor. We chose 2-adamantanone as a model compound for the investigation of catalytic activity and product selectivity. In most of the cases 15 mg of adamantanone and 1.5 equiv. hydrogen peroxide were used for each batch of the experiment. In order to investigate the effect of the temperature on the catalytic conversion and selectivity, both nitrobenzene and 1,4-dioxane were used as solvents. In other cases only 1,4-dioxane was used. Having established an effective oxidation protocol a series of ketones including
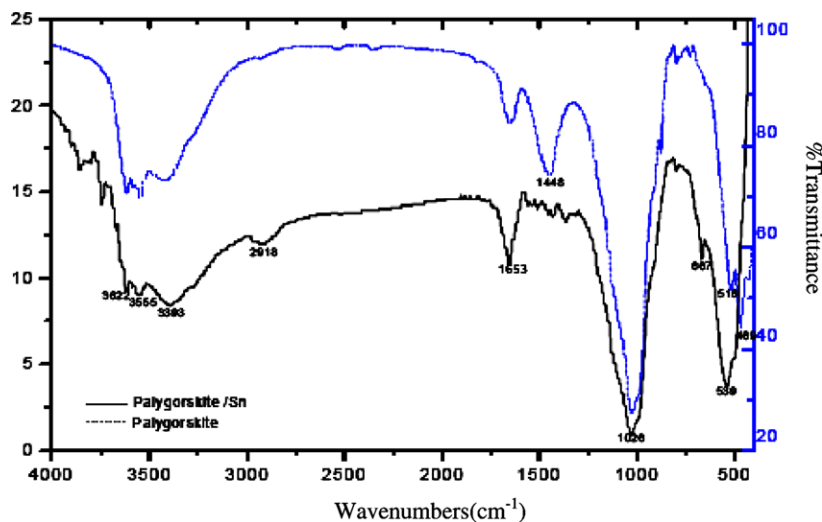
Fig. 2. The IR spectra of palygorskite and Sn-palygorskite.

2-adamantanone, acetophenone, cyclohexanone, 2-methyl-cyclohexanone, 2-tert-butylcyclohexanone, 4-methylcyclo-hexanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, and cyclopentanone were treated with Sn-palygorskite to give the corresponding lactones or esters. Formation of products and consumption of substrates were monitored by GC. The identity of products was determined either by comparison with authentic samples using gas chromatography or by GC/MS analysis. The conversion and product selectivity were determined using GC analysis. The results are summarized in Tables 1–6.

3.2.1. Effect of the ratios of catalyst to substrate

The reactions were carried out for 24 h at 70 °C to investigate the implications of the ratios of catalyst to substrate on the Baeyer–Villiger oxidation reactions, adamantanone was chosen as test substrate for the oxidation with hydrogen peroxide. Different ratios of catalyst to substrate were used to investigate the corresponding variations of the oxidation result. We stabilized the value of the substrate 2-adamantanone, and changed the milligram (mmol) of the catalyst. The oxidation results were changed with the ratio. The results are shown in Table 1.

It can be concluded from Table 1 that when the used amount of catalyst is in the range of 1.0 mg $(2.03 \times 10^{-4}$ mmol)–3.0 mg $(6.09 \times 10^{-4}$ mmol), the conversion increases with the amount of the catalyst. But when the amount of catalyst exceeds 3.0 mg $(6.09 \times 10^{-4}$ mmol), the volume of conversion decreases with the amount of catalyst. As we know, the numbers of the activity center of the catalyst generally increase with the amount of the catalyst used. The fact that when the amount of the catalyst used exceeds 3 mg $(6.09 \times 10^{-4}$ mmol) in this oxidation system, the conversion decreases with the amount. This may suggests that when the amount of the catalyst used is over certain amount, the catalyst catalyze the decomposition of the hydrogen peroxide which is not consumed for the substrate oxidation. The result

indicates that the optimum ratio of catalyst to substrates is 3.0 mg $(6.09 \times 10^{-4}$ mmol):0.1 mmol.

Also as shown in Table 1, the selectivity to the product is higher than 99% in all cases.

3.2.2. Effect of organic solvent

In order to investigate the effect of the solvents on the reaction, adamantanone was oxidized with hydrogen peroxide. The reactions were carried out at 70 °C for 24 h. Several organic solvents were examined for the oxidation of 2-adamantanone using Sn-palygorskite as catalyst. Table 2 shows that the reaction works in several organic medium such as acetonitrile, chlorobenzene, nitrobenzene, 1,4-dioxane and fluorobenzene. Although in all the examined solvents the product selectivity remains 100%, only in nitrobenzene and 1,4-dioxane, the conversion over 60% can be obtained. In the following experiments, we chose nitrobenzene or 1,4-dioxane as the organic medium to fulfill the oxidation.

3.2.3. Effect of temperature

The reactions were carried out for 24 h at different temperatures to investigate the influence of reaction temperature on the Baeyer–Villiger oxidation reactions, adamantanone was also chosen as test substrate for the oxidation with hydrogen peroxide. The effect of the reaction temperature is summarized in Tables 3 and 4. Table 3 shows that in 1,4-dioxane the conversion increased as the reaction temperature was increased from 30 to 90 °C Although relatively higher conversion can be obtained at higher temperatures, the selectivity to the product was decreased. In a different solvent such as in nitrobenzene, we obtain different results. Table 4 shows that increasing the reaction temperature from 30 to 90 °C obviously results in a significant increase in the conversion, but increasing the reaction temperature from 90 to 130 °C leads to a decrease in the conversion. Our experiment reveals that in nitrobenzene the oxidation will not

occur when we use hydrogen peroxide with the concentration of less than 20%. Although at higher temperature the oxidation will carried on in higher speed, at the same time hydrogen peroxide decomposes more quickly and this lead to the concentration of hydrogen peroxide become lower than needed concentration for the oxidation in a shorter period of time and thus result in the decrease of the conversion at temperature higher than 90 °C. The advantage of this catalytic system in nitrobenzene is that in all temperature range from 30 to 130 °C, the product selectivity is higher than 99%.

3.2.4. Effect of reaction time

The conversion is increased with the reaction time and the selectivity to the product is higher than 99% in all reaction time ranged from 2 to 24 h. Table 5 shows that the reactions generally begin with relatively fast rates in the first 4–6 h but tend to slow down in 10–16 h. After this time interval the reaction again turned fast until 24 h.
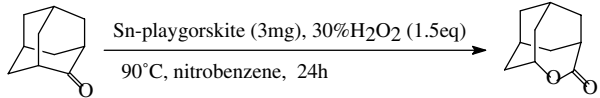
3.2.5. Oxidation of other ketones

A variety of cyclic and acyclic ketones were also oxidized using 3 mg (6.09×10^{-4} mmol) of Sn-palygorskite catalyst at 70–90 °C in this oxidation system. As shown in Table 6 Sn-palygorskite are active and highly selective for the Baeyer–Villiger oxidation of 2-adamantanone, 2-methylcyclohexanone, cyclopentone, 3-methyl-2-pentanone and 4-methyl-2-pentanone. The TONs obtained are generally encouraging for these five ketones. The outstanding of this catalytic system is that besides cyclo-ketones, the catalyst is also active for the oxidation of chain aliphatic ketones like 3-methyl-2-pentanone and 4-methyl-2-pentanone. For these two aliphatic ketones the TONs are over 100, the conversions are 100% and the selectivity to the corresponding esters remained higher than 99%. The results show that this oxidation procedure is promising for cyclic and acyclic ketones and much cleaner than the traditional BV oxidation as it gives relatively higher TON and involves no use of peracids which would produce harmful by-products. The catalyst preparation is very simple and does not involve the use of any expensive materials.

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 esters almost quantitatively. 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 untreated palygorskite.

3.3. Catalyst recycling

In order to investigate catalyst recycling, 2-adamantanone is still chosen as model compound. The reactions were carried out with 30% hydrogen peroxide in nitrobenzene at 90 °C for 24 h using 3 mg (6.09×10^{-4} mmol) of Sn-palygorskite as catalyst. When the catalyst is repeatedly filtered out and submitted to a new reaction batch without any fur-

Table 7
The recycling of Sn-palygorskite

Sn-playgorskite (3mg), 30%H$_2$O$_2$ (1.5eq)
90°C, nitrobenzene, 24h

Recycle times	Conv. (%)	Sele. (%)
1	100	>99
2	95	>99
3	85	>99
4	61	>99

Reaction conditions: Sn-palygorskite 3 mg (6.09×10^{-4} mmol), 2-andamtanone 0.1 mmol, H$_2$O$_2$ (30%) 1.5 equiv., nitrobenzene 3 mL. Percentage of conversion and product selectivity were determined using GC analysis.

ther treatment. The activity is lowered to 95%, 85% and 61% from the original 100% after 2, 3, and 4 cycles, respectively. As is shown in Table 7, Sn-palygorskite as heterogeneous catalyst can be recycled although the catalytic activity is lowered about 39% compared to that of the starting reactivity.

4. Conclusions

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 with high TONs and almost 100% selectivity using environmentally friendly 30% hydrogen peroxide as oxidant. 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. Sn-palygorskite is an efficient and relatively cheap catalysts for the BV oxidation reactions.

Acknowledgements

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