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Baeyer–Villiger oxidation of cyclohexanone by molecular oxygen with Fe–Sn–O mixed oxides as catalysts

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Fe–Sn–O mixed oxides were synthesized and used as catalysts for Baeyer–Villiger oxidation of cyclohexanone, which showed both high catalytic activity and selectivity. X-ray powder diffraction and scanning electron microscopy suggested that the Fe–Sn–O catalysts had a tetragonal structure with a grain size of 29.3 nm. An ε -caprolactone yield as high as 98.8% was obtained in a small-scale experiment (5 mmol of cyclohexanone). In a scale-up test (20 mmol of cyclohexanone), the cyclohexanone conversion and ε -caprolactone yield were 96.7 and 96.5%, respectively. In addition, the catalysts can be reused five times without any major decline in catalytic activity. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: Baeyer–Villiger oxidation; molecular oxygen; cyclohexanone; Fe–Sn–O mixed oxides

Introduction

The Baeyer–Villiger (B-V) oxidation reaction, originating from the 1890s, provides a method for converting ketones to the corresponding lactones or esters, which are important intermediates in the chemical and drug industries.^[1-7] However, traditional oxidants used in B-V oxidation are generally peroxonitrates which might erode the reaction equipment and pollute the environment.^[6,8-10] Therefore, environmentally friendly oxidants have attracted considerable attention.^[11,12]

With water being the only by-product, hydrogen peroxide has been widely used as an environmentally friendly oxidant in organic synthesis research. Lei *et al.*^[13] reported that cyclohexanone could be oxidized using hydrogen peroxide through a reaction catalyzed by palygorskite-supported Sn complexes, affording the corresponding ester with selectivity for the product of 90–99%. Corma *et al.*^[14] reported that tin–zeolite with 1.6 wt% tin incorporated into the framework showed high selectivity for the B-V oxidation of cyclohexanone by hydrogen peroxide. Both palygorskite (Mg, Al) sites which are octahedrally coordinated can be easily exchanged. Sn-exchanged palygorskite and Sn-exchanged Mg–Al hydrotalcite are active and selective for the B-V oxidation of cyclic ketones with H₂O₂.^[15] However, H₂O₂ is not stable and the oxidizing capacity is weak at low concentration, while at high concentration H₂O₂ is dangerous and hard to obtain.

Another environmentally friendly oxidant is molecular oxygen, with the advantages of safe, cheap, faster kinetics, higher yield, higher active oxygen content, better reproducibility,^[1,16-24] and so on. The oxygen–aldehyde system with heterogeneous catalysis has been extensively studied since 1990 by Kaneda *et al.*,^[17] with the oxidative cleavage of alkenes into carbonyl compounds on RuO₂–CH₃CHO–O₂. Zhou and co-workers^[25] also reported that cyclohexanone can be converted to the corresponding ester with a yield of 71% over iron(III) *meso*-tetraphenylporphyrin chloride, but the procedures for preparing the catalyst were complicated.

In the study reported here, we prepared Fe–Sn–O mixed oxides using a simple procedure. And the Fe–Sn–O catalysts were easily separated from the reaction system. Further, the catalyst showed good reusability and high catalytic ability for several other ketones. It has been reported that the Fe–Sn–O catalyst has a higher activity but a shorter lifetime.^[26] But the Fe–Sn–O catalyst prepared in our study can be reused five times without significant loss in activity and selectivity.

Experimental

Materials and Instrumentation

Tin(IV) chloride pentahydrate, iron(III) nitratenonahydrate, anhydrous sodium carbonate, 1,2-dichloroethane, benzaldehyde, chloroform, cyclohexanone, cyclopentanone, phenylmethylketone, butanone, methylisobutylketone and 4-methylcyclohexanone (all of AR grade) were used as received without further purification. A GC-9800 gas chromatograph equipped with a 30 m × 0.53 mm SE-54 column was used to monitor and analyze the reaction process. X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8-Advance with monochromated high-intensity Cu K α radiation (λ = 0.15418). The scanning was performed from 10° to 80° at a rate of 12° min⁻¹. Scanning electron microscopy (SEM) images were obtained using a JSM1500F microscope. The samples were treated by spraying with gold before observation.

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A mixed solution of $SnCl_4 \cdot 5H_2O$ (0.03 mol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.03 mol) was added slowly into aqueous sodium carbonate (2 M) and sodium hydroxide (1 M) with vigorous stirring at 333 K. Then the precipitation solution was stirred for another 2 h after the dripping operation. Right after stirring the crystals were aged for 40 h at 333 K. Next, the precipitates were filtered and washed extensively with deionized water to neutral. Then the brick-red precipitates were dried at 373 K in an air oven for 24 h, ground finely and subsequently calcined at 1123 K for 5 h at a heating rate of 7 K min⁻¹ in a muffle furnace. After the calcination, the mixed oxides were cooled to room temperature in a vacuum desiccator and thoroughly ground. Finally, the mixed oxides were treated using ultrasound for 2 h. The resultant mixed oxides were designated as Fe-Sn-*x*-*T*₁-*t*₁ (*x*: molar ratio of Fe to Sn; *T*₁: calcination temperature; *t*₁: calcination time).

Catalytic Experiments

The B-V oxidation reactions were carried out at 50 °C in a fournecked flask containing 5 mmol of cyclohexanone, 15 mmol of benzaldehyde and 20 ml of 1,2-dichloroethane. An amount of 90 mg of catalyst was added into the catalytic system. Dioxygen was bubbled into the solution through a purpose-made glass tube throughout the process. The reaction mixture was stirred for 4 h, and then the catalysts were removed by filtration. The product was determined using GC (GC-9800, 30 m \times 0.32 mm SE-54 capillary column) internal standard method, using toluene as the internal standard, programmed heating and a flame ionization detector. The temperatures of gasify room, column and detector were 260, 90 and 230 °C, respectively.

Results and Discussion

Characterization of Catalyst

The catalysts were analyzed using optical microscopy, SEM and XRD methods. The diffraction patterns were identified by comparing with the Joint Committee of Power Diffraction Standards (JCPP) database.

XRD patterns of Fe₂O₃, SnO₂ and the fresh catalyst are shown in Fig. 1. Several typical peaks ($2\theta = 26.6^{\circ}$, 33.9°, 37.9°) of Fe–Sn–O mixed oxides conform with the peaks of SnO₂ in JCPP (PDF no. 71–0652). Another two typical peaks ($2\theta = 24.2^{\circ}$, 33.2°) correspond to the peaks of Fe₂O₃ in JCPP (PDF no. 85–0987). Collectively, these results suggest that the mixed oxides are composed of SnO₂ and Fe₂O₃. Furthermore, the typical peaks at $2\theta = 26.6^{\circ}$ and 33.9° are assigned to the 110 and 101 planes of tetragonal SnO₂.^[27] According to the Scherrer equation,^[28,29] $L = K\lambda/\beta \cos \theta$ (K = 0.89, $\lambda = 0.15418$ nm), the size of the nanocrystallites ranges from 15.1 to 51.1 nm. And the mean size (L) of nanocrystallites is 29.3 nm. The SEM images of the fresh catalyst (Fig. 2(a)) and the recycled catalyst after five cycles (Fig. 2(b)) show that the catalysts have a granular structure. And after five cycles, the main granular morphology remains unchanged.

Catalytic Activities of Fe-Sn-O Mixed Oxides

Experiments were conducted to compare the activity of Fe–Sn–O to those of other catalysts prepared using the same method. As evident from Table 1, Fe-Sn-1:1-850-5 exhibits high activity (conversion of 99.9%) and excellent selectivity (yield of 98.8%) (entry 2).



Figure 1. (A) XRD patterns of (a) Fe_2O_{3r} (b) fresh catalyst and (c) SnO_2 . (B) XRD patterns of (a) catalyst after using five times and (b) fresh catalyst.



Figure 2. SEM images: (a) sample of fresh catalyst; (b) sample of catalyst after using five times.

By comparison, without the presence of any catalyst, the cyclohexanone conversion and ε -caprolactone yield are only 79.0 and 74.7%, respectively (entry 12). Also, the yield obtained using Fe₂O₃ is higher than that using SnO₂, a possible reason being that the valence state of the metal has an effect on the catalytic results. When mixing different metal ions into the process of catalyst preparation, the Fe–Sn–O mixed oxides result in a higher yield of ε -caprolactone than other different mixed oxides (entries 2, 8, 9, 11). Thus, Fe-Sn–1:1-850-5 is a suitable catalyst.

Table 1. B-V oxidation of cyclohexanone catalyzed by heterogeneous catalysts ^a				
	O O ₂ / Be Cat.,55°C	nzaldehyde		
Entry	Catalyst	Conversion (%) ^b	Yield (%) ^b	
1	Fe-Sn-1:1-600-5	93.5	91.0	
2	Fe-Sn-1:1-850-5	99.9	98.8	
3	Fe-Sn-1:1-900-5	94.5	86.7	
4	Fe-Sn-1:2-850-5	95.3	90.3	
5	Fe-Sn-1:3-850-5	94.5	91.2	
6	Fe-Sn-2:1-850-5	96.7	89.7	
7	Fe ₂ O ₃	97.3	89.9	
8	Fe-Mg-1:1-850-5	91.2	90.8	
9	Sn-Mg-1:1-850-5	90.0	87.6	
10	SnO ₂	89.8	86.8	
11	Al-Mg-1:1-850-5	67.8	41.3	
12	Blank	79.0	74.7	
^a Reaction conditions: cyclohexanone (5 mmol), benzaldehyde (3 eq.), catalyst (90 mg), 1,2-dichloroethane (20 ml), O ₂ (20 ml min ⁻¹ , 25 °C, 0 1 MPa)				

^bConversion and yield determined by GC.

Table 2 summarizes the results of B-V oxidation of various ketones over Fe-Sn-1:1-850-5. The catalyst shows excellent activity in the oxidation of cyclic ketones, with yields of 98.8, 97.2 and 99.3% (entries 1–3). But the catalyst shows poorer performances in the oxidation of aliphatic ketones, resulting in yilds of only 38.5 and 29.3% (entries 4, 5). This indicates that the size, shape and the electron cloud distribution have a significant impact on lactone yield. A trace of phenylmethylketone is obtained. It is possible that the conjugation effect between the benzene ring and the carbonyl makes the structure stable and not easy to attack.

Scale-up Experiments

Scale-up experiments were conducted in a 100 ml glass flask. In a typical reaction, 20 mmol of cyclohexanone and benzaldehyde (3 eq.) were dissolved into a mixture of 40 ml of 1,2-dichloroethane and 140 mg of catalyst was added. Afterwards dioxygen was bubbled into the stirred solution at a steady rate of 30 ml min⁻¹. The mixture was heated to 55 °C and stirred for 5 h. As evident from

Table 2. B-V oxidation of various ketones over Fe-Sn-1:1-850-5 ^a				
$R \xrightarrow{O_2 / \text{Benzaldehyde}} R \xrightarrow{O_1 / \text{Benzaldehyde}} R \xrightarrow{O_2 / \text{Benzaldehyde}} R \xrightarrow{O_1 / \text{Corr}} R'$				
Entry	R	R'	Conversion (%) ^b	Yield (%) ^b
1	(CH ₂) ₂	(CH ₂) ₃	99.8	98.8
2	(CH ₂₎₂	(CH ₂) ₂	97.2	97.2
3	$(CH_2)_2(CH)CH_3$	(CH ₂) ₂	99.8	99.3
4	(CH ₃)	$(CH_2)_2CH(CH_3)_2$	44.8	38.5
5	CH ₃ (CH ₂)	(CH ₂)CH ₃	32.1	29.8
6	(CH)₅C	(CH ₃)	11.3	7.6
^a Reaction conditions: ketone (5 mmol) benzaldehyde (3 eg.) catalyst				

(90 mg), 1,2-dichloroethane (20 ml), O_2 (20 ml min⁻¹, 25 °C, 0.1 MPa). bConversion and yield determined by GC. Table 3, cyclohexanone conversion of 94.9% and ε -caprolactone yield of 93.4% (entry 2) are obtained. Further, the effects of various factors on the reaction were investigated using single-factor tests.

Effects of solvent

Several organic solvents were used to analyze the influence of the solvent. Results in Table 4 show that 1,2-dichloroethane gives the best performance (entry 3) with the yield of ε -caprolactone being 95.3%, followed by acetonitrile (entry 2). The yields are only 13.4, 14.9 and 70.3% with 1,4-dioxane (entry 1), n-butyl alcohol (entry 5) and dichloromethane (entry 4), respectively. It is speculated that the formation of hydrogen bonds between the oxygen atom of 1,4-dioxane and the hydrogen atom of benzoic acid that is produced through the oxidation of benzaldehyde influences the first step of the formation of protonated ligand of cyclohexanone. The boiling point of dichloromethane is only 39.9 °C, which cannot reach the desired temperature required for the activation of molecules. And when *n*-butyl alcohol is used as solvent, GC analysis shows many peaks of by-products. It is possibly that the *n*-butyl alcohol is oxidized by the oxygen primarily, and then oxidations of the cyclohexanone cannot proceed without solvent. So the best solvent is 1,2-dichloroethane.

Effects of solvent volume

To investigate the effect of the solvent volume, several experiments were conducted with different volumes of 1,2-dichloroethane. As evident from Table 5, the yield increases firstly and then reaches an approximate constant with an increase of solvent volume (entries 1–4). These results might be caused by the fluctuation of the oxygen flow rate. In the reaction process, the benzaldehyde is oxidized to benzoic acid. The benzoic acid, with a high melting point of 122.13 °C, is easily crystallized in a small amount of solvent. The oxygen vent might be plugged by the precipitate,

Table 3. Results of scale-up experiments ^a			
Entry	Catalyst	Conversion (%) ^b	Yield (%) ^b
1	Fe-Sn-1:1-850-5	94.7	93.4
2	Fe-Sn-1:1-850-5	94.9	93.4
3	Fe-Sn-1:1-850-5	94.6	93.3
^a Departies and itiana, avalabely and (20 mmal), becarded by de (2 ea.)			

^aReaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), catalyst (140 mg), 1,2-dichloroethane (40 ml), O₂ (30 ml min⁻¹, 25 °C, 0.1 MPa), $T_2 = 55$ °C, 5 h.

^bConversion and yield determined by GC.

Table 4. B-V oxidation of cyclohexanone in various solvents ^a			
Entry	Solvent	Conversion (%) ^b	Yield (%) ^b
1	1,4-Dioxane	15.0	13.4
2	Acetonitrile	85.6	84.3
3	1,2-Dichloroethane	95.6	95.3
4	Dichloromethane ^c	80.1	70.3
5	n-Butyl alcohol	15.1	14.9

^aReaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), catalyst (140 mg), O₂ (30 ml min⁻¹, 25 °C, 0.1 MPa), solvent (40 ml).
^bConversion and yield determined by GC.

 $^{\rm c}T_2 = 39.9 \,^{\circ}{\rm C}.$

Table 5. B-V oxidation of cyclohexanone using various volumes of solvent ^a				
Entry	Solvent (ml)	Conversion (%) ^b	Yield (%) ^b	
1	0	Trace	Trace	
2	20	89.6	86.3	
3	25	94.7	94.3	
4	30	95.7	95.6	
5	35	93.4	93.0	
6	40	92.3	92.0	
^a Reaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), catalyst (140 mg), O ₂ (30 ml min ⁻¹ , 25 °C, 0.1 MPa), 1,2-dichloroethane, $T_2 = 55$ °C, 5 h.				

and then the yield decreases. Table 5 shows that the yield reaches a maximization of 95.6% (entry 4) with a solvent volume of 30 ml.

Effects of catalyst dosage

Table 6 summarizes the effect of catalyst dosage on yield. It is clear that the yield increases as the catalyst dosage increases from 80 to 120 mg (entries 1–4), reaching a maximum of 95.9%. Then the yield remains about the same as the catalyst dosage increases further (entries 4–6). This is because a certain amount of substrate requires a proper amount of catalyst. Initially the contact between the reactant molecules and the active centers of the catalyst is insufficient. With an increase of the catalyst dosage, the amount of the active centers are obtained with 120 mg of catalyst. Accordingly, the optimum catalyst dosage is 120 mg.

Effects of dioxygen rate

The oxygen flow was adjusted from 15 to 35 ml min^{-1} to investigate the effect of the oxygen flow rate. The results in Table 7 show that the conversion increases from 75.7% (entry 1) to 96.7% (entry 3) as the oxygen flow increases from 15 to 25 ml min^{-1} . Then the conversion displays little variation as the oxygen flow increases continually from 25 ml min^{-1} (entries 3–5). The yield of ε -caprolactone reaches a maximum of 96.3% (entry 3). Therefore, the optimum dioxygen rate is 25 ml min^{-1} .

Table 6. dosages ^a	B-V oxidation of cycl	lohexanone using va	rious catalyst
Entry	Catalyst dosage (g)	Conversion (%) ^b	Yield (%) ^b
1	80	85.6	85.4
2	100	90.1	89.8
3	110	94.7	94.3
4	120	96.0	95.9
5	130	95.9	95.6
6	140	95.9	95.7

^aReaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), O₂ (30 ml min⁻¹, 25 °C, 0.1 MPa), 1,2-dichloroethane (30 ml), $T_2 = 55$ °C, 5 h.

^bConversion and yield determined by GC.

Table 7. B-V oxidation of cyclohexanone using various rates of dioxygen ^a				
Entry	Dioxygen rate (ml min ⁻¹)	Conversion (%) ^b	Yield (%) ^b	
1	15	75.7	75.4	
2	20	89.9	89.5	
3	25	96.7	96.3	
4	30	96.5	96.4	
5	35	96.6	96.4	
^a Reaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), O ₂ (25 °C, 0.1 MPa), 1,2-dichloroethane (30 ml), catalyst (120 mg), $T_2 = 55$ °C, 5 h. ^b Conversion and yield determined by GC.				

Effects of temperature and reaction time

The relationship between the temperature and the ε -caprolactone yield was investigated using a series of B-V oxidation reactions, which were carried out in 1,2-dichloroethane solvent with reaction temperature (T_2) varied from 45 to 65 °C, while the reaction time (t_2) ranged from 1 h to 5 h. The results are shown in Fig. 3. It is obvious that initially the yield increases rapidly with reaction time. However, the yield does not apparently increase after 4 h. Furthermore, Fig. 3 also shows that the yield increases firstly as T_2 increases from 45 to 55 °C. The highest yield of 95.9% is obtained at 55 °C for a reaction time of 4 h. However, as T_2 increases from 55 °C, the yield tends to decrease. It is possible that the solubility of oxygen in the solvent decreases as the reaction temperature increases, consistent with Henry's law.^[30] Therefore, the appropriate reaction time and temperature are 4 h and 55 °C, respectively.

Effects of molar ratio of benzaldehyde to cyclohexanone

To investigate the effect of the benzaldehyde in the reaction system, several experiments were carried out with the molar ratio of benzaldehyde to cyclohexanone ranging from 0:1 to 5:1. As shown in Fig. 4, it is obvious that the ε -caprolactone yield increases initially with the molar ratio and reaches a maximum yield of 96.3% at 3:1. When the molar ratio increases from 3:1, the yield falls slightly. It is evident that the appropriate molar ratio of benzaldehyde to cyclohexanone is 3:1.



Figure 3. Effect of temperature on B-V oxidation of cyclohexanone.



Figure 4. Effect of molar ratio of benzaldehyde to cyclohexanone on B-V oxidation of cyclohexanone.

Experiments Using Optimum Reaction Conditions

Several experiments were performed using the optimum conditions. As evident from Table 8, a conversion of 96.7% and a yield of 96.5% are obtained (entry 1). The similarly of results for the several experiments indicated that the catalyst features a good repeatability. Additionally, owing to the scale-up effect, the yield of the scale-up experiment was lower than the yield of 98.8% of the small-scale experiment. The temperature distribution, residence time distribution and concentration distribution of a 100 ml glass flask are different from those of a 50 ml glass flask. Also, the difference among the various experimental results data for the optimum reaction conditions is within experimental errors.^[31]

B-V Oxidation with Recycled Catalyst

To investigate the catalytic activity of regenerated catalysts, we removed the catalysts by filtration, followed by washing with 1,2dichloroethane and calcining at 573 K for 3 h, and then ultrasonic treatment. Table 9 summarizes the results of B-V oxidation over regenerated catalysts. It can be clearly seen that there is little loss in catalytic activity of the regenerated catalysts. A conversion of 96.7% and a yield of 96.5% are obtained using the fresh catalyst (entry 1). After four cycles, a yield of 94.0% is obtained (entry 4), and a yield of 93.4% after five cycles (entry 5). Moreover, as the XRD patterns show in Fig. 1(B), the typical peaks ($2\theta = 26.6^\circ$, 33.9°) of the fresh catalyst and the regenerated catalyst are identical. And from the SEM images of catalysts before and after use (five times), the morphology of the catalysts basically remains

Table 8.	Table 8. Results obtained using optimum reaction conditions ^a		
Entry	Catalyst	Conversion (%) ^b	Yield (%) ^b
1	Fe-Sn-1:1-850-5	96.6	96.5
2	Fe-Sn-1:1-850-5	96.5	96.4
3	Fe-Sn-1:1-850-5	96.7	96.5
4	Fe-Sn-1:1-850-5	96.6	96.4
30		(22))	

^aReaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), catalyst (120 mg), O₂ (25 ml min⁻¹, 25 °C, 0.1 MPa), 1,2dichloroethane (30 ml), $T_2 = 55$ °C, 4 h.

^bConversion and yield determined by GC.

Table 9.	Results of B-V oxidation over recycled catalyst ^a	
Run	Conversion (%) ^b	Yield (%) ^b
1	96.6	96.5
2	95.9	95.3
3	94.6	94.1
4	94.7	94.0
5	93.5	93.4

^aReaction conditions: cyclohexanone (20 mmol), benzaldehyde (3 eq.), catalyst (120 mg), $T_2 = 55$ °C, 4 h, O₂ (25 ml min⁻¹, 25 °C, 0.1 MPa), 1,2-dichloroethane (30 ml).

^bConversion and yield determined by GC.



Scheme 1. Mechanism of B-V oxidation of cyclohexanone and benzaldehyde.

unchanged. So the results indicate that the catalysts are not damaged in the reaction process.

Possible Mechanism

Scheme. 1 depicts a plausible mechanism of the B-V oxidation of cyclohexanone in the oxygen–benzaldehyde system. In the first step, molecular oxygen is transferred through the catalysts to oxidize the benzaldehyde into peroxybenzoic acid. In the second step, the cyclohexanone adsorbed at an acid site of the catalyst is attacked by PhCOOO⁻, and then a Criegee adduct is obtained after the nucleophilic addition reaction. Finally, ε -caprolactone is formed after the rearrangement of the Criegee adduct; simultaneously benzoic acid is produced.

Conclusions

In summary, novel Fe-Sn-1:1-850-5 was facilely prepared using inexpensive materials. The catalysts showed high catalytic activity for the B-V oxidation of cyclohexanone in an oxygen–benzaldehyde system. In the small-scale experiments (5 mmol of cyclohexanone), high catalytic activity (conversion of 99.9%) and selectivity (yield of 98.8%) were obtained; in the scale-up tests (20 mmol of cyclohexanone), the conversion and the yield were 96.7 and 96.5%, respectively. The effects of factors were investigated through single-factor experiments, and the optimum reaction conditions were found to be as follows: molar ratio of benzalde-hyde to cyclohexanone, 3:1 (based on 20 mmol of cyclohexanone);

dosage of Fe-Sn-1:1-850-5, 120 mg; oxygen flow, 25 ml min⁻¹; volume of 1,2-dichloroethane, 30 ml; reaction time, 4 h; reaction temperature, 55 °C. From analysis of catalysts using XRD and SEM, it was concluded that the original pattern of the catalysts was basically unchanged. And the catalysts can be reused five times with only 3.1% loss of the yield, which decreased from 96.5 to 93.3%.

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