



Short Communication

MgO/SnO₂/WO₃ as catalysts for synthesis of ε-caprolactone over oxidation of cyclohexanone with peracetic acid

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ABSTRACT

Different Mg/Sn/W mixed oxides prepared by precipitation were used as catalysts in the Baeyer–Villiger oxidation of cyclohexanone with a mixture of 50% hydrogen peroxide and acetic acid as oxidant. The Mg/Sn/W oxide obtained by precipitation from NH₃·H₂O was found to be the catalyst providing the highest yield of ε-caprolactone and initial catalytic activity among all samples.

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1. Introduction

The Baeyer–Villiger (BV) reaction which converts ketones to esters was first reported by Baeyer and Villiger in 1899 [1]. The corresponding ε-caprolactone is an important synthetic intermediate to produce polyesters [2,3]. Since then, the BV reaction has become a fine organic synthesis method, which has been reported by large numbers of books and papers [4,5].

The BV reaction only takes place in the presence of catalysts, and the reaction gives a high yield especially in the presence of heterogeneous catalysts [6,7]. So various heterogeneous catalysts such as zeolites [8], solid acid [9], clays [10,11], As [12], titanium silicalite [13], Sn-incorporated zeolites [14], silica-incorporated transition metal ions [15], and metal complexes [16] have also been proved effective in the past decade. In recent years, hydrotalcites supported Sn or Al/Mg were found to be effective catalysts for the BV oxidation of cyclohexanone with H₂O₂ [17,18].

The discovery of Ti-silicalite (TS-1) came into the revolution in the use of heterogeneous catalysts in oxidation processes, and it revealed that Ti-peroxide species could activate H₂O₂ in various oxidation reactions [19]. Above all the researches, metal ions especially Sn and Mg were found to be effective in the BV reaction. In general, different new catalysts were developed by using hydrogen peroxide which is more

benign and environmental friendly than organic oxidants in the BV reaction.

Recently our lab reported the synthesis of ε-caprolactone by oxidation of cyclohexanone with monoperoxy succinic acid. The results were excellent [20]. In this work, we optimized the operating conditions and used peracetic acid instead of monoperoxy succinic acid to oxidize cyclohexanone. We reported the oxidation of cyclohexanone by using Mg/Sn/W oxides as a catalyst and 50% hydrogen peroxide/acetic acid mixture as oxidant. We creatively put forward a new catalyst that added W ions into the Mg/Sn oxides in the BV reaction. A series of MgO/SnO₂/WO₃ catalysts which were respectively precipitated by NH₃·H₂O, Na₂CO₃, NaHCO₃, NaOH, (NH₄)₂CO₃ were comparatively characterized for their structural and textural properties.

2. Experimental

2.1. Preparation of catalysts

All the substrate materials, MgCl₂·6H₂O, SnCl₄·5H₂O and H₂WO₄ were obtained from Sinopharm Chemical Reagent Co., Ltd.

A solution containing 112.5 g MgCl₂·6H₂O and 28 g SnCl₄·5H₂O in 200 mL of deionized water was used. Then five different precipitants in 200 mL of deionized water were dropped into the above solution respectively at pH 9.5 at 30 °C under mechanical agitation. The five solutions were added with 9.5 g H₂WO₄ and kept stirring until its color becomes white respectively during precipitation. The solids were

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Table 1

Nomenclature of the Mg/Sn/W mixed oxides used as catalysts.

Samples	Precipitants
1#	NH ₃ ·H ₂ O
2#	Na ₂ CO ₃
3#	NaHCO ₃
4#	NaOH
5#	(NH ₄) ₂ CO ₃

dried at 100 °C for 12 h, after which the suspensions were filtered and washed with deionized water. Then the catalysts of Mg/Sn/W oxides were obtained, followed by calcination in air at 600 °C for 3 h. Table 1 showed their nomenclature.

2.2. Characterization of the catalysts

X-ray diffraction (XRD) analysis was performed to study the phase structure and crystallinity of all catalysts. All samples were recorded on Bruker D8-ADVANCE in the 2θ range of 5–70° using Cu Kα radiation.

Fourier transform infrared (FTIR) spectra for the oxides were recorded over the wavenumber range 400–4000 cm⁻¹ on the TENSOR 27 spectrophotometer.

N₂ adsorption and desorption isotherms were carried out using Micromeritics ASAP 2000 system by N₂ physisorption at 77.35 K. The Brunauer–Emmett–Teller (BET) surface area was calculated on the basis of the BET treatment of the isotherms. The pore volume and the pore distribution were achieved by using the Barrett–Joyner–Halenda (BJH) method.

Transmission electron micrographs (TEM) were performed on a JXA-8230/INCAX-ACT electron microscope. Scanning electron microscopy (SEM) was performed digitally on a JSM-5610LV microscope operating at 30 kV.

2.3. Activity tests

BV oxidation reaction was completed in two steps.

In a typical synthesis, 52.5 g acetic acid, 35.5 g cyclohexane and 1.5 g catalyst were mixed in a 250 ml three-neck flask at 50 °C. The middle flask neck was fitted with an oil–water segregator which was used for removing water from the reflux condenser, and the condenser was connected with a U type pressure-difference valve which was linked with a vacuum pump. The left flask neck was used for testing temperature by fitting a thermometer and the right one was matched with an isobaric funnel to drop hydrogen peroxide. 25 g H₂O₂ (50%) was added into the solution in ten minutes. The system was under stirring throughout the progress and the pressure was kept at –0.6 Mpa. Then the peracetic acid solution was obtained after a 3 h reaction.

The peracetic acid solution was slowly added into the three-neck flask containing 28 g cyclohexanone in 20 min. The oxidation reaction was at atmospheric pressure at 50 °C with magnetic stirring. Products were identified after 3 h which was carried out by an Agilent 6890N GC–MS instrument with a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm).

3. Results and discussion

3.1. XRD

The XRD patterns for the five samples are shown in Fig. 1. The variable crystallinity of the oxides was exhibited in the 2θ range of 5–70°. According to the X-ray powder diffraction file, the diffraction peak of MgO around 42.9° (2θ) and 62.3° (2θ) can be observed in all samples except sample 1# [21]. The peak of sample 5# showed the highest intensity, so it was used as a reference. The peak intensity and thus the

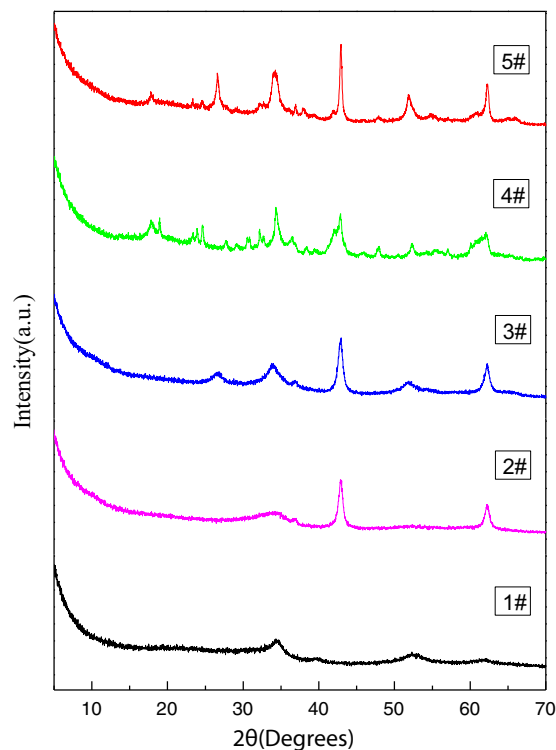


Fig. 1. XRD patterns for the MgO/SnO₂/WO₃ catalysts.

crystallinity of other three samples decreased as the number of the samples was 3#, 2#, 4#. The peak of MgSnO₃ around 36.7° (2θ) could be observed in all samples. The diffraction peak of SnO₂ around 26.6° (2θ) only could be observed in samples 3# and 5#. The diffraction peak of WO₃ was not shown in any samples, it indicated that the WO₃ might incorporate into the Mg and Sn oxides.

3.2. FT-IR spectroscopy

All the FT-IR spectra for MgO/SnO₂/WO₃ catalysts are shown in Fig. 2. They all exhibited a strong band at ca. 3420 cm⁻¹ due to stretching vibrations in hydroxyl groups [22]. There were bands at 1637 cm⁻¹ typical of torsional vibrations in physisorbed water [23]. The absorptions at 594 and 800 cm⁻¹ were corresponding to

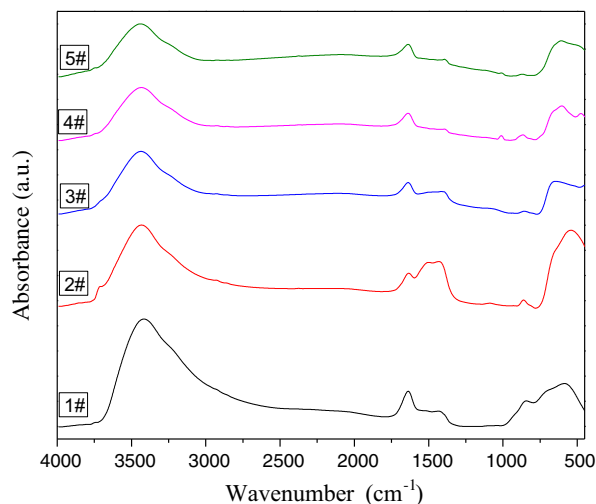


Fig. 2. FT-IR spectra for the MgO/SnO₂/WO₃ catalysts.

Table 2
Textural properties of MgO/SnO₂/WO₃ catalysts.

Sample	Precipitant	$S_{\text{BET}}(\text{m}^2/\text{g})^{\text{a}}$	$V_{\text{a}}(\text{cm}^3/\text{g})^{\text{b}}$	$r_{\text{p}}(\text{\AA})^{\text{c}}$
1#	NH ₃ ·H ₂ O	117.1	0.29	175
2#	Na ₂ CO ₃	75.9	0.41	190
3#	NaHCO ₃	75.6	0.37	1123
4#	NaOH	28.0	0.22	1129
5#	(NH ₄) ₂ CO ₃	30.6	0.15	793

^a Specific surface area.

^b Pore volume.

^c Average pore diameter.

W–O–O–W peroxide groups, and the peak near 644 cm⁻¹ might be attributed to stretching vibrations in W–O–W groups [24]. The bands in the 595–667 cm⁻¹ region of the spectra might be ascribed to Sn–O groups. The spectrum was similar in all samples except the differences

in intensity between some bands. These phenomena were attributed to the fact that the bands of metal oxides appeared in all the samples.

3.3. Surface area and porosity

Table 2 lists the specific surface areas, cumulative pore volumes and average pore diameter of the catalysts. Sample 1# which was obtained by using NH₃·H₂O as precipitant showed the bigger BET surface areas of 117.1 m²/g than 28.0 m²/g that of sample 4# which was precipitated from NaOH. The pore diameters of these samples were around 0.3 cm³/g except sample 5# which was obtained by using (NH₄)₂CO₃ as precipitant. Due to the change of precipitant, the variation range of pore diameter was very large. As shown in Table 2, the pore diameter of sample 3# and sample 4# was almost 10 times than that of samples 1# and 2#. Obviously, the use of different precipitants was related to the structure of

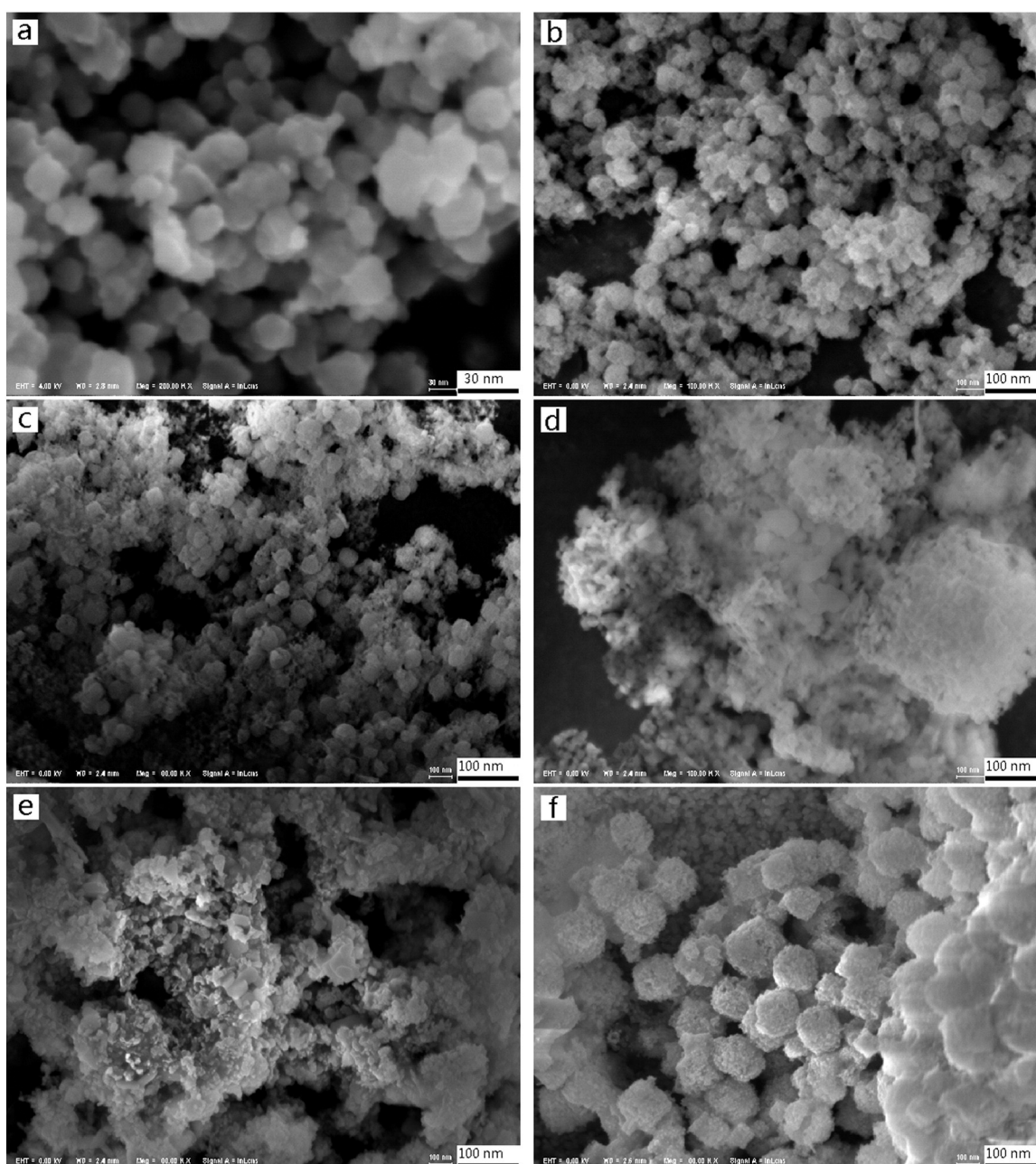


Fig. 3. SEM images of MgO/SnO₂/WO₃ catalysts.

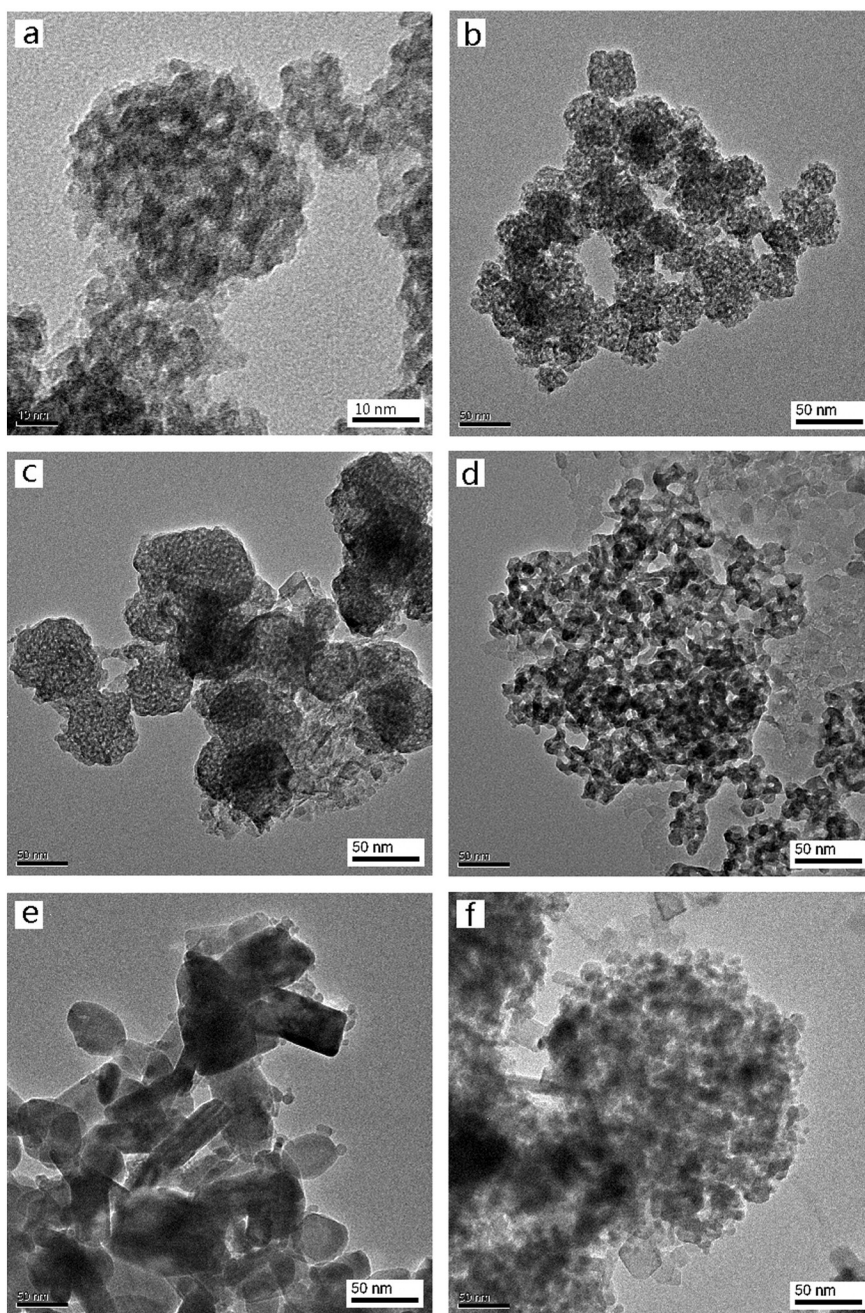


Fig. 4. TEM images of MgO/SnO₂/WO₃ catalysts.

the catalysts, which was in consistent with the results of XRD and FT-IR spectra.

3.4. Morphology

The SEM images of the five samples are shown in Fig. 3. The structure and morphology of all the samples which were prepared by different precipitants showed big differences. SEM image of sample 1# which showed the biggest BET surface areas revealed uniform particles composed of disordered platelets gathered into spherical structures (Fig. 3a, b). SEM image of sample 2# was similar to that of sample 1#, but trivial particles in other shapes could be observed (Fig. 3c). Sample 3# showed an extensive agglomeration of particles into large oxide particles (Fig. 3d). Irregular channels and agglomerated particles could be identified in sample 4# (Fig. 3e). Larger particles were identified in sample 5# compared with sample 1#. Sample 1# might show the highest

catalytic activity among all the samples due to the SEM images, which was in consistent with the catalytic behaviors tests.

The metal particles size and particle distribution in five samples were investigated by TEM (Fig. 4). Sample 5# showed an extensive agglomeration of metal species into large metal oxide particles of a certain size distribution (Fig. 4f). Many clear channels and relatively small particles with a homogeneous distribution could be easily identified in sample 1# (Fig. 4a, b). Irregular particles could be observed in sample 4#. Sintering would be seen in sample 2# as well as 3# which contained smaller particles than sample 2#. The results of TEM images were in consistent with that of N₂ adsorption–desorption and SEM images.

4. Catalytic experiments

The BV oxidation of cyclohexanone with hydrogen peroxide is a complex process in this work. Thus, to identify the role played by the

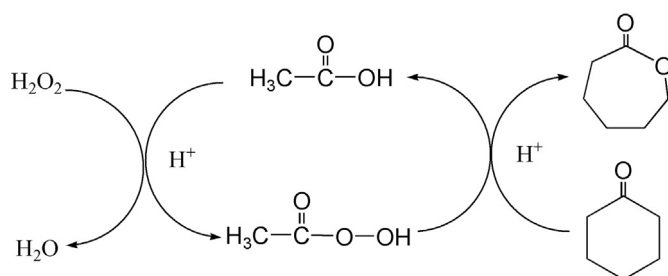


Fig. 5. The Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide/acetic acid as oxidant.

reactants was crucial. Series of tests were conducted by using hydrogen peroxide/acetic acid in the BV oxidation of cyclohexanone (Fig. 5) to identify the most active catalyst among the five samples. The conversion of cyclohexanone and the yield and selectivity of ϵ -caprolactone were studied in the BV reaction using the five different catalysts, and the results were shown in Table 3.

The crystallinity, the structure and thus the selectivity and activity of catalysts were influenced by precipitants shown in Table 3. NH_4^+ , CO_3^{2-} and HCO_3^- were respectively conducive to produce more active sites during the preparation of the catalyst. The presence of NH_4^+ and CO_3^{2-} might show bad effects on the resultant structure of the catalysts, but there were still many active sites exposed on the surface of the particles rather than in the pores, which was in accordance with the images of SEM and TEM. The NH_4^+ of sample 1# precipitated from $\text{NH}_3 \cdot \text{H}_2\text{O}$ could be converted to NO or NO_2 in calcination and the precipitate from $\text{NH}_3 \cdot \text{H}_2\text{O}$ was the easiest to be filtered and washed compared with other catalysts. It might indicate that a proper precipitant in the preparation of catalyst was an important factor to determine the activity of the catalyst and the influence of washing and filter conditions was also crucial to the industrial scale. In summary, the catalyst precipitated by $\text{NH}_3 \cdot \text{H}_2\text{O}$ at pH 9.5 at 30 °C was used in our pilot study.

5. Conclusion

In this work, we synthesized five Mg/Sn/W precipitates and calcined them in air at 600 °C for 3 h to obtain oxides as catalysts in the BV oxidation of cyclohexanone. The method used in this work to prepare $\text{MgO}/\text{SnO}_2/\text{WO}_3$ mixed oxides allowed the metal to be incorporated into the structure as confirmed by the XRD patterns. All catalysts provided excellent conversion and selectivity towards ϵ -caprolactone; however, the catalyst obtained by using $\text{NH}_3 \cdot \text{H}_2\text{O}$ as precipitant proved to be more active than other oxides in the BV oxidation of cyclohexanone with hydrogen peroxide. Further work to explore the nature of these novel catalysts is still continuing in our lab.

Table 3

The conversion of cyclohexanone and the yield and selectivity of ϵ -caprolactone in BV reaction.

Samples	Precipitants	Conversion ^a /%	Yield ^b /%	Selectivity ^c /%
1#	$\text{NH}_3 \cdot \text{H}_2\text{O}$	91	86	94
2#	Na_2CO_3	90	83	92
3#	NaHCO_3	89	73	82
4#	NaOH	87	64	74
5#	$(\text{NH}_4)_2\text{CO}_3$	89	79	90

^a Conversion of cyclohexanone.

^b Yield of ϵ -caprolactone.

^c Selectivity of ϵ -caprolactone.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.08.031>. These data include MOL files and InChIKeys of the most important compounds described in this article.

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