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Magnesium Oxide-Supported Polytitazane Copper(II) Complex Catalyzed Aerobic Baeyer-Villiger Oxidation of Ketones and Cyclohexanol in the Presence of Benzaldehyde

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MAGNESIUM OXIDE-SUPPORTED POLYTITAZANE COPPER(II) COMPLEX CATALYZED AEROBIC BAEYER-VILLIGER OXIDATION OF KETONES AND CYCLOHEXANOL IN THE PRESENCE OF BENZALDEHYDE

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ABSTRACT

Magnesium oxide-supported polytitazane copper complex is prepared and found to be a very effective catalyst for the Baeyer-Villiger oxidation of ketones and cyclohexanol in the presence of an aldehyde as a reductant under an atmospheric pressure of oxygen at room temperature. The δ-valerolactone and ε-caprolactone can be obtained in high than 97% yield. The reactivity of ketones decreases as fellow: cycloketones > acetophenone > aliphatic ketone. It is found that cyclohexanol is selectively oxidized to ε-caprolactone in 77% yield and 89% selectivity by the above combined catalytic system. The catalyst is also very stable and can be reused at least six times without loss of its activity.

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INTRODUCTION

Baeyer-Villiger oxidation of ketones to esters or lactones is one of the most reliable reactions in synthetic chemistry[1]. Lactones occur in nature and also are important reaction intermediates in organic syntheses. Since *Mukaiyama et al.* found that aerobic Baeyer-Villiger oxidation can be achieved by using a catalytic system consisting of a metal diketonato complex and a sacrificial aldehyde[2,3] much efforts have been concentrated on the potentialities of this catalytic system[4,5]. However, such a homogeneous catalyst is not easily recovered and reused. In the previous papers[6,7], we have reported that a combination system of inorganic polymer supported transition metal complexes and an aldehyde was an efficient catalytic system for the aerobic epoxidation of olefins. The present research demonstrates that a copper(II) complex of magnesium oxide-supported polytitazane could be used in aerobic Baeyer-Villiger oxidation of ketones and cyclohexanol.

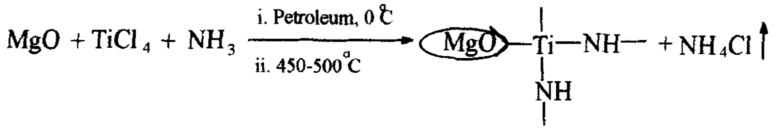
EXPERIMENTAL

Materials and Analyses

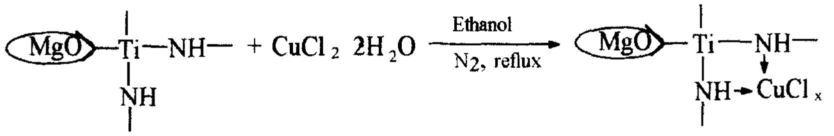
All reagents and solvents were AR grade. Magnesium oxide, titanium(IV) chloride and copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) were supplied by Beijing Chemicals Co. All the ketones and cyclohexanol were commercial chemicals and were used without further purification; their purities were checked by GC analyses just before use. All solvents were distilled before use. The reaction mixture was analyzed by a Shanghai GC 103 using a 2 m stainless column of PEG, then was washed with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and filtered. Evaporation followed gave pure lactone, which was identified by ^1H NMR and ^{13}C NMR.

Preparation of magnesium oxide-supported polytitazane copper complex (MgO>-Ti-N-Cu)

The preparation of magnesium oxide-supported polytitazane (Abbr. as MgO>-Ti-N) was similar to the previous method [6]. Several magnesium oxide-supported polytitazane copper complexes (Abbr. as MgO>-Ti-N-Cu(II)) with different amount of supported copper were prepared. For a typical example, $CuCl_2 \cdot 2H_2O$ (0.4 mmol) was dissolved in ethanol (20 mL) in a 50 mL flask, then MgO>-Ti-N (1.0 g) was added. The mixture was refluxed with stirring for 12 h until the solution became transparent and the solid became light green. After filtration and dried, the copper complex of magnesium oxide-supported polytitazane was ready for use. The synthetic routes for magnesium oxide-supported polytitazane copper complexes are shown as follows:

(I) 

(MgO>-Ti-N)

(II) 

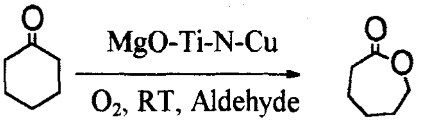
(MgO>-Ti-N) (MgO-Ti-N-Cu)

Baeyer-Villiger oxidation of ketones and cyclohexanol

A typical procedure for ketones and cyclohexanol Baeyer-Villiger oxidation was as follows: In a 50 mL flask equipped with a condenser and a magnetic stirring bar were placed cyclohexanone (1 mmol), benzaldehyde (3 mmol), MgO>-Ti-N-Cu (17 mg, Cu 5×10^{-3} mmol) in of 1,2-dichloroethane (4 mL). The mixture was stirred at room temperature under an atmospheric pressure of oxygen for 15 h. After the reaction, the catalyst was filtered off and the reaction products were detected by GC based on ketones used.

RESULTS AND DISCUSSION

In order to examine the effect of magnesium oxide-supported polytitazane copper (II) (MgO>-Ti-N-Cu) complex for aerobic Baeyer-Villiger oxidation, cyclohexanone was taken as a model substrate and treated with combination of molecular oxygen and an aldehyde in 1, 2-dichloroethane at room temperature in the presence of a catalytic amount of MgO>-Ti-N-Cu.



The ligand to metal mole ratio generally influences the stereostructure of the complex and thus affects the catalytic behaviors of the complex. The influence of mole ratio of N/Cu in the magnesium oxide supported polytitazane copper(II) complex on the Baeyer-Villiger oxidation of cyclohexanone is illustrated in FIG. 1. The 97% yield of ε-caprolactone is obtained at the

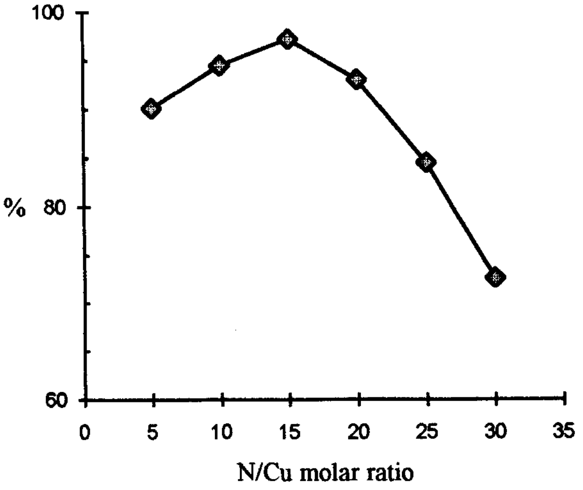


FIG. 1. Effect of N/Cu mole ratio on the Baeyer-Villiger oxidation of cyclohxanone.
Conditions: Cyclohexanone 1 mmol, Sub. / MgO-Ti-N-Cu =150/1, benzaldehyde 3 mmol, 1,2-dichloroethane 4 mL, 25°C, 15 hr.

TABLE 1. Effect of aldehyde on Baeyer-Villiger-type oxidation

Entry	Aldehyde	Yield of ε-caprolactone (%)
1-1	isobutyraldehyde	7
1-2	valeraldehyde	0
1-3	heptaldehyde	0
1-4	benzaldehyde	99
1-5	3-chlorobenzaldehyde	79
1-6	4-nitrobenzaldehyde	0
1-7	crotonaldehyde	64
1-8	2-hydroxybenzaldehyde	30

Conditions: Cyclohexanone 1 mmol, sub./cat. 150/1, MgO-Ti-N-Cu (metal 5×10^{-3} mmol), aldehyde 3mmol, 1,2-dichloroethane 4 mL, 25°C, 15 hr.

N/Cu mole ratio of 15. Both the lower and the higher N/Cu mole ratios may not facilitate the formation and stabilization of the unsaturated coordinated copper intermediate, so the yields of ε-caprolactone are lower.

Reports on the interpretation of the mechanism of activating molecular oxygen by transition metal complexes under *Mukaiyama* conditions suggested that the coordination of aldehyde to the metal ion was the most important process for the formation of an active oxygen species[8,9] and simultaneously the aldehyde as an oxygen carrier transferred monooxygen to the substrate molecule[10]. With the MgO-Ti-N-Cu(II) complex, the effect of aldehydes on the Baeyer-Villiger oxidation of cyclohexanone are examined in TABLE 1. The benzaldehyde works best with the ε-caprolactone obtained in 99% yield within 15 hr. When Aliphatic aldehydes such as isobutyraldehyde which has high reactivities for the epoxidation[11] were employed, both conversion of cyclohexanone and yield of ε-caprolactone were low.

Furthermore, the Baeyer-Villiger oxidation of cyclohexanone is greatly affected by the molar ratio of benzaldehyde / cyclohexanone. FIG. 2. shows the influence of benzaldehyde / cyclohexanone molar ratio on the oxidation of cyclohexanone. It can be seen that the highest yield of ε-caprolactone presents at the benzaldehyde / cyclohexanone molar ratio of 3/1. A further increase in the benzaldehyde / cyclohexanone molar ratio causes a decrease in the yield of ε-caprolactone.

In the scrutiny of solvents in the Baeyer-Villiger oxidation of cyclohexanone with benzaldehyde, it was found that 1,2-dichloroethane and dichloromethane were the best solvents. Carbon tetrachloride and ethyl acetate were good solvents while methanol is poor solvent for the Baeyer-Villiger oxidation.

The stability of the MgO-Ti-N-Cu(II) catalyst was studied by the following method. After each reaction, the catalyst was separated by filtration from the products, washed with 1,2-dichloroethane and dried under vacuum, then added to the reaction mixture to catalyze the reaction for the next time. From TABLE 3., it can be seen that MgO-Ti-N-Cu(II) can be reused six times without any remarkable change in the catalytic activity, but the yield of ε-caprolactone decreased from 100% to 91%.

The above procedure was also successfully applied in the oxidation of other cyclic or acyclic ketones. As shown in TABLE 4, cyclic ketones were oxidized into the corresponding lactones in high yields without any over oxidation products. Oxidation of acyclic ketones proceeded insufficiently and the yield of desired ester was not high (entry 6 and 7). A similar observation had been reported by *Kaneda* et al. in the oxidation of ketones[5].

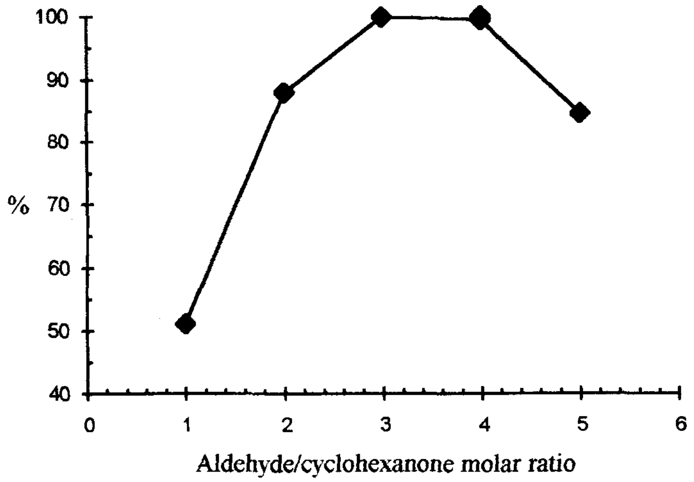


FIG. 2. Effect of benzaldehyde/cyclohexanone ratio on the Baeyer-Villiger oxidation.

Conditions: Cyclohexanone 1 mmol, sub./cat. 150/1, MgO-Ti-N-Cu (metal 5×10^{-3} mmol), benzaldehyde, 1,2-dichloroethane 4 mL, 25°C, 15 hr.

TABLE 2. Effect of solvent on Baeyer-Villiger-type oxidation

Entry	Solvent	Yield of ε-caprolactone (%)
2-1	dichloromethane	99
2-2	chloroform	76
2-3	carbon tetrachloride	85
2-4	1,2-dichloroethane	99
2-5	ethyl acetate	88
2-6	methanol	9

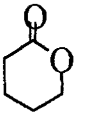
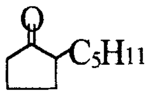
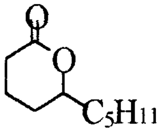
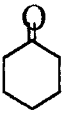
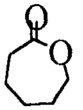
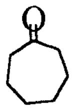
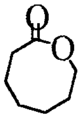
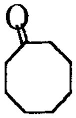
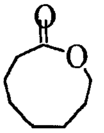
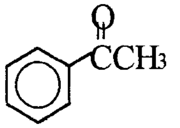
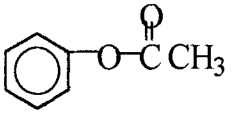
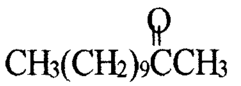
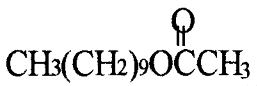
Conditions: Cyclohexanone 1 mmol, sub./cat. 150/1, benzaldehyde 3mmol, MgO-Ti-N-Cu (metal 5×10^{-3} mmol), solvent 4 mL, 25°C, 15 hr.

TABLE 3. Recycling of MgO-Ti-N-Cu complex in Baeyer-Villiger oxidation of cyclohexanone

Recycle number	1	2	3	4	6	6
Yield of ε-caprolactone (%)	100	99	99	96	94	91

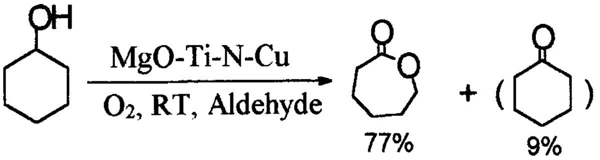
Conditions: Ketone 1 mmol, benzaldehyde 3 mmol, 1,2-dichloroethane 4 mL, MgO-Ti-N-Cu (metal 5×10^{-3} mmol), O_2(1atm), 25°C, 12 hr.

TABLE 4. MgO>-Ti-N-Cu catalyzed Baeyer-Villiger oxidation of various ketones

Entry	Ketone	Lactone(Ester)	Yield(%)
1			99
2			98
3			100
4			60
5			42
6			56
7	 $CH_3(CH_2)_9\overset{O}{\overset{\|}{C}}CH_3$	 $CH_3(CH_2)_9O\overset{O}{\overset{\|}{C}}CH_3$	15

Conditions: Ketone 1 mmol, benzaldehyde 3 mmol, 1,2-dichloroethane 4 mL, MgO-Ti-N-Cu (metal 5×10^{-3} mmol), O_2(1atm), 25°C, 12 hr.

It was noteworthy that cyclohexanol was also selectively oxidized to ε-caprolactone with 77% yield and 89% selectivity by the above combined catalytic system using 1,2-dichloroethane as solvent which is higher than the reference reports[12].



CONCLUSION

Magnesium oxide-supported polytitazane copper complex (MgO-Ti-N-Cu(II)) was prepared and found to be a highly active catalyst for the Baeyer-Villiger oxidation of cyclic ketones and their substituted derivatives and cyclohexanol in the presence of benzaldehyde under an atmospheric pressure of oxygen at room temperature. The catalyst could be recovered and reused at least six times without any remarkable loss in the catalytic activity .

REFERENCES

[1] G. R. Krow, *Org. React.*, **43,** 251 (1993)
[2] T. Yamada, K. Takahashi, K. Kato, T. Takai, S. Inoki, T. Mukaiyama, *Chem. Lett.*, 641 (1991)
[3] E. Hata, T. Takai, T. Yamada, T Mukaiyama, *Chem. Lett.*, 535 (1994)
[4] C. Bolm, G. Schlingloff, K. Weickhardt, *Tetrahedron Lett.*, **34,** 3405 (1993)
[5] K. Kaneda, S. Ueno, T. Imanaka, E. Shimotsuma, Y. Nishiyama, Y. Ishii, *J. Org. Chem.*, **59,** 2915 (1994)
[6] T-J. Wang, Z-H. Ma, Y-Y. Yan, M-Y. Huang, Y-Y. Jiang, *Polymer Bulletin*, **36,** 1 (1996)
[7] Y-Y. Yan, T-J. Wang, J-P Guo, M-Y. Huang, Y-Y. Jiang, *Chin. Chem. Lett.*, **7,** 749 (1996)
[8] P. Laszlo, and M. Levart, *Tetrahedron Lett., **34**(7), 1127(1993)*
[9] G. A. Barf, and R. A. Sheldon, *J. Mol. Catal. A: Chemical, **102**, 123(1995)*
[10] W. Nam, H. J. Kim, S. H. Kim, R.Y. N. Ho, and J. S. Valentine, *Inorg. Chem., **35**(4), 1045 (1996)*
[11] T. Yamada, T. Takai, O. Rhode, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **64,** 2109 (1991)
[12] J. A. Cella, J. A. Kelley, and E. F. Kenehan, *J. Org. Chem., **40**(12), 1860(1975)*