ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Green Oxidation Of Cyclohexene In Ultrasonic Irradiation Over Copper Supported Mixed Oxide Catalyst.

Deshmukh JM, and Gadale SR*.

Department of Chemistry, Yashwantrao Mohite College Pune-411 038 Bharati Vidyapeeth deemed University, Pune (India).

ABSTRACT

In the present article, oxidation of cyclohexene with hydrogen peroxide was performed using environmentally benign copper supported mixed oxide catalyst (CMS). The copper loading on molybdenum silica ($Cu/MoO_3/SiO_2$) mixed oxide was prepared by sol-gel method. It was found that, 15 wt.% CMS catalyst showed good catalytic activity and selectivity among prepared catalyst under solvent free reaction was carried out in ultra sonicator. A green method i.e ultrasonication plays an important role to give good catalytic activity and selectivity in solvent free reaction. The use of H_2O_2 oxidizing agent is an important feature of a green chemical reaction since it produces water, the only by-product. The effect of different reaction parameters such as different catalyst, effect of temperature, amount of oxidant, catalyst amount, influence of oxidant and methods of preparation of catalyst on the oxidation process was investigated and optimized.

Keywords: cyclohexene, mixed oxide catalyst, oxidation, hydrogen peroxide

**Corresponding author*

INTRODUCTION

In modern chemical industry, the selective oxidation of cyclohexene is an important chemical process, because its products of cyclohexanone and cyclohexanol are materials for the synthesis of adipic acid and caprolactam, which are intermediates of nylon-6 and nylon-66 polymers [1]. In the oxidation of cyclohexene, lot of homogeneous catalytic systems has been tried. Since heterogeneous catalysis has more efficient because of easier catalyst separation and recycling, various research groups were focused on development of oxidation of cyclohexene over heterogeneous catalyst with environmentally friendly oxidants. In synthetic organic chemistry, oxidation of olefin is an important transformation, because these products gave valuable, commercial intermediate and undergo further reaction [2-3]. Oxidation of cyclic hydrocarbon is one of the most widely used oxygenates producing industrial processes [4-6].

Oxidation of cyclohexene was carried out by using oxometal reagents as catalysts, such as ruthenium tetroxide [7] and permanganate [8]. The activity of these catalysts can be increased by addition of various oxygen donars such as per-acetic acid [9], NaOCl [10] and $NaIO_4$ [11].

The area of oxidation of cyclohexene has been widely investigated but several problems still remains. A search for simple oxidation of cycloalkenes to obtain high yield or conversion and selectivity under favourable economic and environmental conditions, is still a goal for current research field [12] and development of more selective and efficient catalyst for these reactions is an active area of research. Many researchers are interested for oxidation of cycloalkenes involved only substrate, catalyst and oxidizing agent H_2O_2 [13]. Hydrogen peroxide is most attractive oxidizing agent because it is quite, green, cheap and easy to handle [14-15].

Many studies have reported the epoxidation of cyclohexene using H_2O_2 over various microporous and mesoporous catalysts [16-18]. The catalytic activity of Ti-MCM-41 catalysts was studied over oxidation reaction of cyclohexene, but resulting a low catalytic activity [19-21]. In recent years, cyclohexene oxidation reaction was studied over to examine the catalytic performance of transition metal modified mesoporous materials [22-24].

In organic synthesis, ultrasound has increasingly been used in the last three decades. By using of ultrasound irradiation in organic reaction gave higher yields, shorter reaction time or milder conditions. Simple ultrasonic bath is widely available, safe, effective, cheapest sources of ultrasonic irradiation.

Here, oxidation of cyclohexene was carried out by using green oxidant over prepared catalysts in sonicator. The use of mixed oxide catalyst has afforded good conversions of cyclohexene with good selectivity to 2-cyclohexen-1-one and 2-cyclohexen-1-ol. This reaction was simple, greener and more efficient to cyclohexene oxidation.

MATERIALS AND METHOD

Material:

The entire reagents used for oxidation reaction were A. R. grade and obtained from Merck chemicals, India.

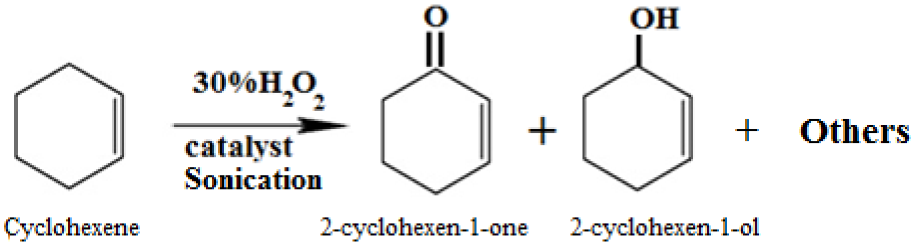
Method:

$Cu/MoO_3/SiO_2$ (CMS) catalysts with varying copper oxide molar concentrations (1, 5, 10, 15, 20 wt. %) were prepared. Copper acetate, ammonium heptamolybdate and tetra ethyl orthosilicate were used as copper, molybdenum and silica sources, respectively. In a typical procedure 10 wt.% CMS catalyst was synthesized by dissolving respective quantity of AHM in water at 80˚C. Copper acetate was dissolved in water. Then these two solutions were added to the dry isopropyl alcohol solution of TEOS with constant stirring. The resultant transparent greenish gel was air dried and calcined at 500˚C in air in a muffle furnace for 10 h. Similarly catalysts with 1, 5, 15, 20 wt. % copper oxide loadings were prepared.

Experimental:

Liquid phase oxidation of cyclohexene with aqueous hydrogen peroxide was carried out in two necked round bottom flask fitted with reflux condenser, kept in an ultra sonicator under solvent free condition. The solid acid catalyst was activated before its use in the catalytic reaction. To the mixture of cyclohexene (1mmol), 30% H_2O_2 (10 mmol) and $Cu/MoO_3/SiO_2$ catalyst (0.4 gm) was added in the flask. The reaction mixture was kept in ultra sonicator, after the desired time, the heterogeneous catalyst was recovered by simple filtration. Samples of the reaction mixture were determined on were withdrawn at regular time intervals. Finally products were analyzed by TLC and further confirmed by GC using a Shimadzu GC-2010 gas chromatograph system with a 30m RTX- column and nitrogen as carrier gas. Conversion and selectivity were calculate based on peak area of calibrated with an internal standard added to the organic phase. The validity of the identification and quantitation of the GC peaks was verified by comparison of the mass spectra and gas chromatographic retention times with those of the authentic compound. This catalyst was reactivated by washing subsequently with water and acetone and then reused without loss of reactivity.

Scheme

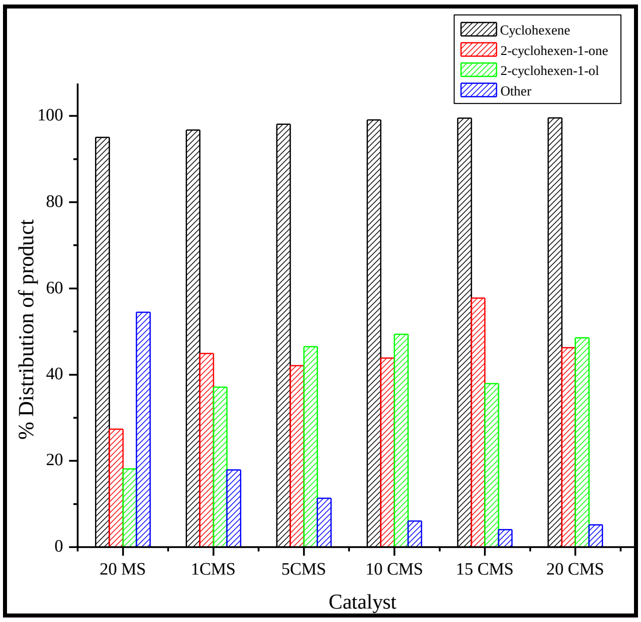


RESULT OF CATALYTIC ACTIVITY

The initial screening of the reaction systems provided very good conversions of the starting material with high selectivity to 2-cyclohexen-1-one, 2-cyclohexen-1-ol. Lower selectivity obtained to byproducts i. e cyclohexene oxide and cyclohexane diol. Blank reactions provided lower cyclohexene conversions due to absence of catalyst. We then decided to investigate the different parameters such as different loading of copper on MoO_3/SiO_2, concentration of oxidant, catalyst amount, methods of catalyst preparation and recyclability, which could influence the conversion and selectivity in the present cyclohexene reaction over CMS heterogeneous catalyst.

Effect of catalyst variation

The oxidation of cyclohexene using hydrogen peroxide is used as a test reaction in solvent free condition, for the catalytic evaluation of copper over MoO_3/SiO_2 with varying wt% concentration. The 15 wt.% CMS analogues displayed very high catalytic activity as presented. (fig 1). The conversion of reaction is in direct correlation with the concentration of the active metal sites in the materials. A maximum conversion of 98% was obtained with 15 wt. % CMS. Catalyst with different wt. % of copper content, increased cyclohexene conversions was observed with increased in metal content up to 15 wt% of CMS. In case of 10% CMS obtained higher conversion of cyclohexene, but it showed 2-cyclohexen-1-ol as major product and 2-cyclohexen-1-one as minor product. The 2-cyclohexen-1-one formation depends on the metal species in the samples and also on the surface acidity. With 20% MoO_3SiO_2 catalyst showed conversion up to 95% with lower selectivity of 2-cyclohexen-1-one (27.35%), 2-cyclohexen-1-ol (18.13%) and selectivity for other (54.45%) was increased. It indicated that amount of CuO played important role in getting higher conversion as well as selectivity. Selectivity of 2-cyclohexen-1-one was increased from 27-59.24 % as the concentration increased from 1 wt.% CMS to 15 wt.% CMS. And also selectivity for by-product was decreased from 54 to 4%. In case of 20 wt%. of CMS showed slight decrease in the selectivity of 2-cyclohexen-1-one with increase in selectivity of by-products. These results suggested that catalytic role of CuO in 15 wt.% CMS catalyst was important in oxidation reaction.



Reaction condition: Cyclohexene: 30%H_2O 1:10$_2$, 0.4gm, 2hr & sonication

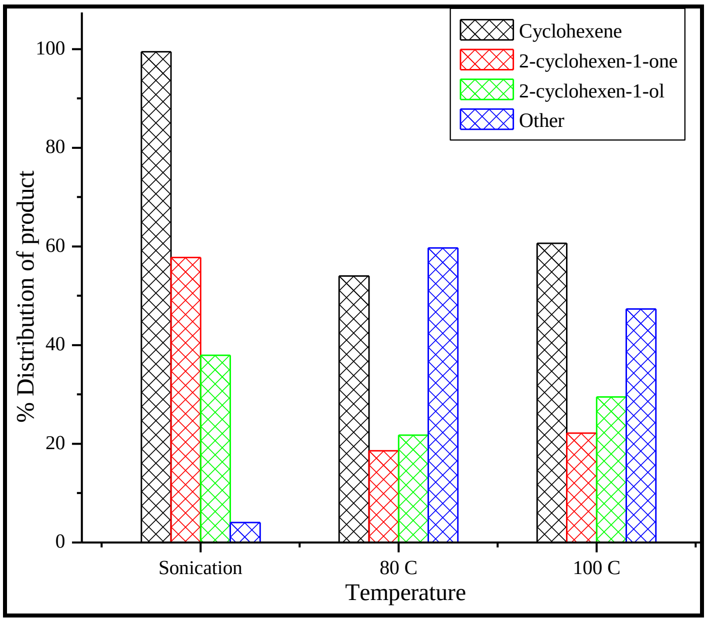
Figure 1: Effect of catalyst variation

Role of temperature

To find out the role of temperature on oxidation of cyclohexene was carried out at different temperatures such as 353, 373 K. While reaction was also carried out in ultrasound irradiation. As shown in figure 2, the elevation in temperature from 353-373 K, helped to increases the conversion of cyclohexene from 54 to 60 %. Furthermore, the data revealed that 353 and 373K temperature favored the formation of the by-products. But when the reaction mixture was irradiated in ultrasound gave maximum conversion of cyclohexene (99.47%) with increased selectivity of 2-cyclohexen-1-one (59.24 %). In ultrasonic reaction, selectivity of byproducts were decreased after 2 hrs of reaction time. Ultrasonic waves can activate the surface of catalyst and force impregnation of catalyst in organic reaction. The ultrasonic reaction gave the target products in higher yields within shorter reaction time compared with the other method. Hence, reaction has carried out under ultrasonic irradiation for further optimization of reaction parameters.

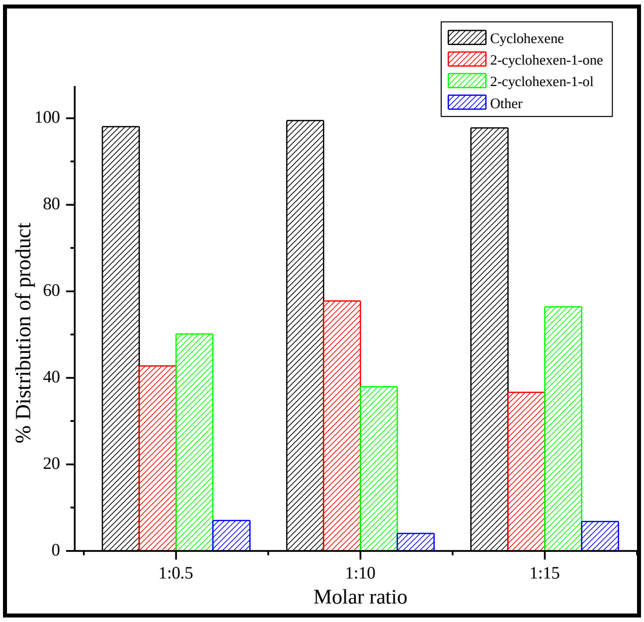
Amount of oxidant:

The effect of amount of H_2O_2 (30% H_2O_2) on the oxidation of cyclohexene was investigated and the results are presented in (fig 3). Lower amount of H_2O_2 gave relatively similar conversion of cyclohexene with change in selectivity of 2-cyclohexen-1-one and 2-cyclohexen-1-ol. At higher H_2O_2 amount i.e.10 mmol showed slight increase in conversion with higher selectivity for 2-cyclohexen-1-one. Further increase in concentration of H_2O_2 i.e. 15 mmol did not lead to a considerable increase of activity and selectivity in the oxidation reaction. It indicated that 10 mmol i.e. optimum amount of oxidant was required for the oxidation of cyclohexene. Interestingly, increase the amount of H_2O_2 in the mixture did not significantly vary the activity and selectivity of the catalyst under the reaction conditions. With 10 mmol H_2O_2 amount was selected as optimum in further oxidation of the cyclohexene.



Reaction condition: Cyclohexene: 30%H_2O 1:10, 15 wt.% CMS, 0.4gm, 2hr & sonication

Figure 2: Role of temperature

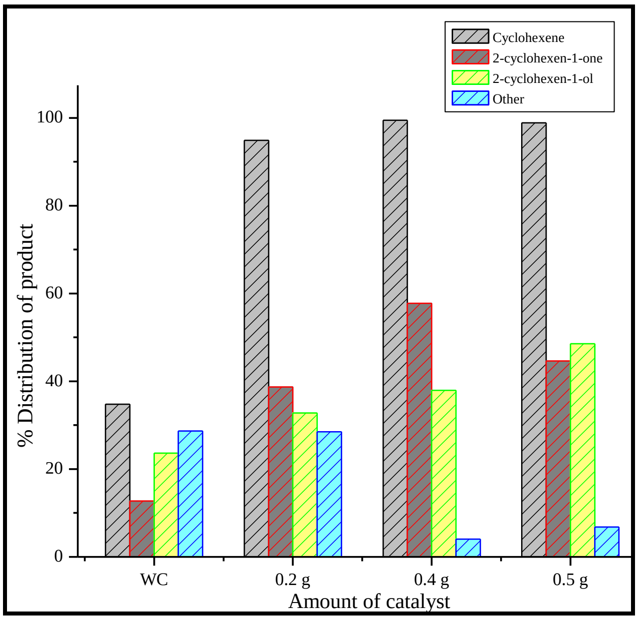


Reaction condition: 15wt.% CMS-0.4 gm, 2hr & sonication

Figure 3: Amount of oxidant

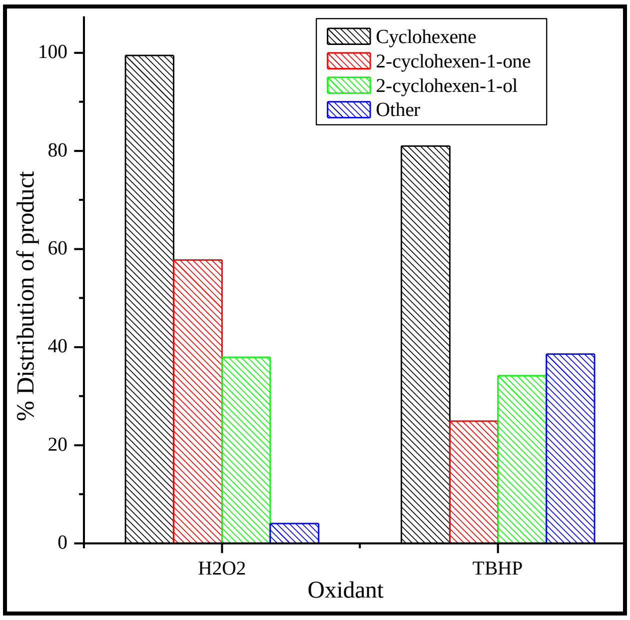
Amount of catalyst

Amount of catalyst was varied from 0.2 – 0.5g in the reaction and results showed in fig 4. A gradual increase in conversion was observed with the increase in catalyst amount. It was observed that the conversion rate reached to 99.47 % when the 0.4g of catalyst amount was tried. Further the increase of catalyst weight to 0.5 g caused an increased in the selectivity of 2-cyclohexen-1-ol, which was due to by suppressing 2-cyclohexen-1-one. At moderate conversions maximum selectivity of 2-cyclohexen-1-one formation observed. An optimum catalyst amount of 0.4 g was selected for further reactions.



Reaction condition: Molar ratio- Cyclohexene: 30%H_2O_2-1:10, 15wt.% CMS, 2hr & sonication

Figure 4: Amount of Catalyst



Reaction condition: Molar ratio- Cyclohexene:Oxidant-1:10 , 15wt.% CMS-0.4gm, 2hr & sonication

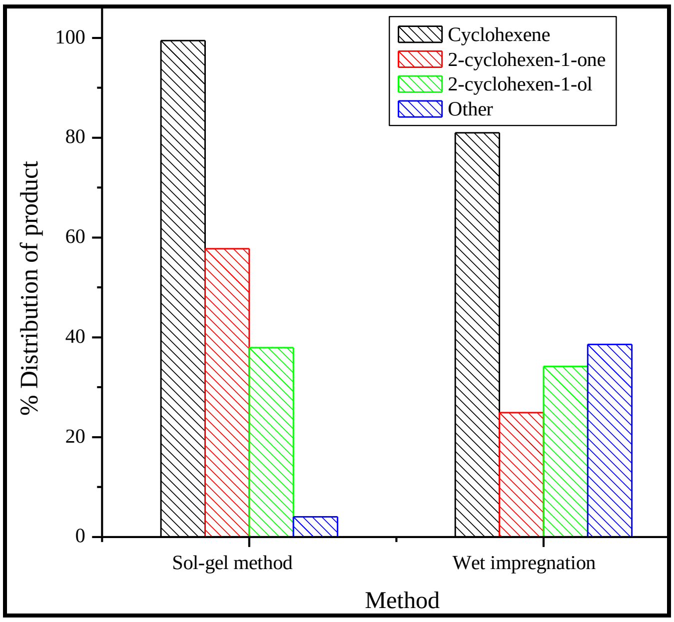
Figure 5: Influence of oxidant

Influence of oxidant

The effect of different oxidants such as H_2O_2 and TBHP on cyclohexene oxidation was carried out by choosing optimum reaction parameters. The data presented in fig 5 showed that use of hydrogen peroxide as an oxidant gave a higher conversion of cyclohexene as well as selectivity of 2-cyclohexen-1-one. By using TBHP as an oxidant in cyclohexene reaction showed lower conversion with increased other byproducts. Hydrogen peroxide was more applicable than other oxidant due to more effective, quite cheap, easy to handle and yield water as a byproduct. Hence, hydrogen peroxide was selective as an oxidant throughout for further the catalytic reaction.

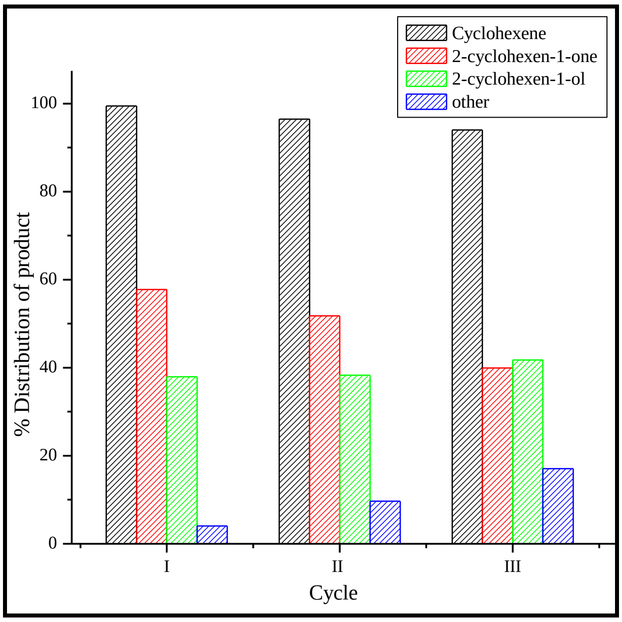
Effect of method of preparation of catalyst

Catalyst prepared by different method such as sol gel and wet impregnation was used in the reaction and results are presented in fig. Equimolar amounts of cyclohexene and 30% H_2O_2 were sonicated and the observed results are given (fig 6). Catalyst synthesized by sol-gel method gave maximum conversion with higher selectivity of 2-cyclohexen-1-one, but in case of impregnated catalyst showed slightly lower conversion with low selectivity of 2-cyclohexen-1-one. Best results obtained using catalyst prepared by sol gel method. Sol-gel method play an important in versatility, which allows control of the texture, composition, homogeneity and structural properties of the finished catalysts. Sol-gel method used for the preparation of catalyst showed 99.47% conversion of cyclohexene and selectivity of 2-cyclohexen-1-one was 59.24%. Hence, sol gel prepared catalyst was selective for oxidation of cyclohexene used for further analysis.



Reaction condition: Cyclohexene: Oxidant-1:10 , 15wt.% CMS-0.4gm, 2hr & sonication

Figure 6: Effect of method of preparation of catalysts



Reaction condition: Molar ratio- Cyclohexene:H_2O_2-1:10 , 15wt.% CMS-0.4gm, 2hr & sonication

Figure 7: Recyclability

Recyclability

Special tests were performed to assess the catalyst stability and activity after recycling, results are shown in (fig 7). After each operation cycle, the catalyst was separated, washed with water and then methanol, dried, calcined at 500^0C for 5h and used in the next run. The mixed oxide catalyst was found to be highly reusable, preserving up to 95% of its initial catalytic activity after four reuses. It was established that the catalytic activity with respect to 2-cyclohexen-1-one formation decreased significantly after each run due to using hydrogen peroxide although the conversion of cyclohexene was still attained. The formation of 2-cyclohexen-1-ol was faster after regeneration of the catalyst, which was attributed to the modification of the catalyst surface during the first run of the process. During second run, selectivity of 2-cyclohexen-1-ol and diol was increases but conversion of cyclohexene remains same. From the data it was clear that, recycled catalyst showed good stability.

CONCLUSION

Oxidation of cyclohexene was carried by using 15 wt. % CMS catalyst, with molar ratio 1:10 (Cyclohexene: H_2O_2) gave higher % conversion of cyclohexene (99.47%) with 59.24 % selectivity of 2-cyclohexen-1-one as a major product. This reaction was carried out in ultra sonicator as a green method. Reuse of the catalyst for four times with similar results and also proved that recycling does not affect the efficiency of the catalyst. Lewis acid sites of the catalysts were mainly responsible for the good catalytic performance in the oxidation reaction. The catalyst offered a very clean, green synthesis and ecofriendly process for the oxidation reaction to produce desired product with very high yield. CMS enabled a better accessibility of active sites to the substrate molecules which was reflected in the high conversions of cyclohexene and better selectivity to the 2-cyclohexen-1-one over these catalysts.

REFERENCES

[1] D.D. Davis, in: W. Gerhartz, S.Y. Yamamoto, T.F. Campbell, R. Pfefferkorn, J.F. Rounsaville (Eds.), 5th ed., Ullmann's Encyclopedia of Industrial Chemistry, vol. A1, VCH Publishers, Weinheim, 1985, pp. 269–278.

[2] S. Bhaduri, D. Mukesh, Homogeneous Catalysis: Mechanisms and Industrial Applications; Wiley-Interscience: New York, 2000.

[3] B. Cornils, W. A. Herrmann. Eds. Applied Homogeneous Catalysis with Organometallic Compounds, 2nd ed.; Wiley-VCH: Weinheim, 2002.

[4] E. Roduner, W. Kaim, B. Sarkar, V. B. Urlacher, J. Pleiss, R. Gläser, W. D. Einicke, G. A. Sprenger, U. Beifu, E. Klemm, C. Liebner, H. Hieronymus, S. F. Hsu, B. Plietker, S. Laschat, *ChemCatChem,* 2013; 5: 82.

[5] A. Sakthivel, P. Selvam, *J. Catal.,* 2002; 211: 134.

[6] L. Gómez-Hortigüela, F. Corà, C. R. A. Catlow, *ACS Catal.,* 2011; 1: 18.\

[7] D. G. Lee, M. van der Engh, in: W.S. Trahanovsky (Ed.), Oxidation in Organic Chemistry, Academic Press, New York 1973 p. 186

[8] R. A. Sheldon, J. Kochi, Metal-Catalyzed Oxidation of Organic Compounds, Academic Press, New York, 1981.

[9] W. Merk, G. Schreyer, W. Weigert, Ger. Offen. 2, 106, 307. ; W. Merk, G. Schreyer, W. Weigert, Chem. Abstr. 1972; 77: 151485.

[10] S. Wolfe, S. K. Hasan, J. R. Campbell, J. Chem. Soc., Chem. Commun., 1970; 1420-1421.

[11] H. J. Carlsen, T. Katsuki, V. S. Martin, K. B. Sharpless, J.Org. Chem., 1981; 46: 3936-3938.

[12] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, J.Org. Chem., 1996; 61: 8310-8311.

[13] T. J. Collins, Acc. Chem. Res., 2002; 35: 782-790.

[14] J. M. Bregeault, Dalton Trans., 2003; 3289.

[15] R. A. Sheldon, J. Dakka, Catal. Today., 1994; 19: 215.

[16] M. A. Camblor, A. Corma, J. Perez-Pariente, Zeolites, 1993; 13: 82-87.

[17] M. H. Zahedi-Niaki, M. P. Kapoor, S. Kaliaguine, J. Catal., 1998; 177: 231-239.

[18] T. Blasco, A. Corma, M. T. Navarro, J. P. Pariente, J. Catal., 1995; 156: 65-74.

[19] L. Y. Chen, G. K. Chuah, S. Jaenicke, Catal. Lett., 1998; 50: 107.

[20] G. A. Eimer, S. G. Casuscelli, C. M. Chanquia, V. E. Monica, E. Crivello, E. R. Herrero, Catalysis Today, 2008; 891: 133-135.

[21] R. Sever, R. Alcala, J. Dumesic, T. Root, Microporous and Mesoporous Materials, 2003; 66: 53-67.

[22] C.Y. Cheng, K. J. Lin, M. R. Prasad, S. J. Fu a, S.Y. Chang, S. G. Shyu, H. S. Sheu, C. H. Chen, C. H. Chuang, M. T. Lin, Catal. Commun.,2007; 8: 1060.

[23] A. Kumar, D. Srinivas, P. Ratnasamy, Chem. Commun., 2009; 6484-6486.

[24] R. Noyori, M. Aoki, K. Sato, Chem. Commun., 2003; 16: 1977-1986.