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Ruthenium Catalyst for Epoxidation Reaction

Raiedhah A. Alsaiari

Abstract

The role of ruthenium as a heterogeneous catalyst for epoxidation reaction has not been investigated extensively. Therefore, the purpose of this chapter is to provide overview of the epoxidation of alkene using ruthenium catalysts. The chapter is divided into two main sections. The first section is about epoxidation of alkene using supported ruthenium catalysts, while the second using ruthenium complexes (homogenous catalysts).

Keywords: ruthenium catalysts, epoxidation, alkene, homogeneous and heterogenous catalysis

1. Introduction

Synthetic organic chemistry relies on organic substrate oxidation not only in applications of large scale, but also in fine chemical production. Affording greater control over chemical process activity and selectivity whilst concomitantly ensuring sustainability is currently the pursued goal for catalyst design. Among the existing techniques of C=C bond functionalization, a major one is epoxidation [1].

Both laboratory syntheses and chemical production draw on epoxides as useful intermediate. Epoxide is one of the key intermediates in the manufacture of functionalized fine chemicals, pharmaceutics, agrochemical, and perfume industry as well as in natural product synthesis [2–4].

The most eloquent instance is Sharpless asymmetric epoxidation based on titanium tartrate complexes [5]. A significant aspect related to epoxidation catalysts; ruthenium complexes have enjoyed considerable advancement in recent times.

Another domain that has been developed substantially is heterogeneous epoxidation with ruthenium catalysis. In this context, catalysts have been devised through several effective processes, such as derivatization and immobilization, involving known homogeneous catalysts.

The role of ruthenium as a heterogeneous catalyst for epoxidation has not been investigated extensively. Herein, it will be provided an updated overview of developments in the epoxidation of alkene using ruthenium catalysts (**Figure 1**).
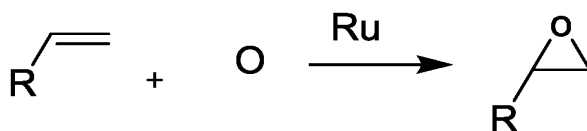

Figure 1.
Epoxidation of alkene using ruthenium catalysts.

This chapter is divided into two major sections. The first section focuses exclusively on using supported ruthenium catalysts to catalyze alkene epoxidation, while the second covers using ruthenium complexes for this reaction.

2. Supported ruthenium catalysts for epoxidation of alkenes

In 1998 [6], Mesoporous MCM-41 molecular sieves are used for the immobilization of a ruthenium complex of meso-tetrakis (2,6-dichlorophenyl)porphyrin (**Figure 2**), [Ru^{II}(TDCPP)(CO)(EtOH)]. The supported Ru catalyst can affect highly selective heterogeneous alkene epoxidations with the terminal oxidant of choice being 2,6-dichloropyridine N-oxide in the presence of CH_2Cl_2. Conversion of aromatic and aliphatic alkenes to their epoxides can be successfully undertaken, with satisfactory amounts and selectivity, while the epoxidation of cis-alkenes (e.g. cis-stilbene) can be undertaken in a stereospecific manner as shown in **Table 1**. The leaching and/or deactivation of the catalyst may be the reason why activity is lost.

Another study in 2002 observed that poly(ethylene glycol) (PEG) binds to ruthenium porphyrin through a covalent etheric bond. What characterizes these catalysts is that they are highly reactive and selective for epoxidation of alkenes with 2,6-dichloropyridine N-oxide as terminal oxidant [7].

Ethene was subjected to electrochemical epoxidation with 0.3 M chloride ion concentration by employing nanocrystalline RuO_2 and Co-doped RuO_2 deposited electrodes in aqueous acidic media [8]. The by-products of this reaction were oxirane and 2-chloroethanol. Epoxide formation was achieved based on a three-membered transition state involving the binding of ethylene to an oxygen on the surface of RuO_2. Furthermore, a single-step sol gel process (SSSG) facilitated the synthesis of RuO_2-loaded meso-porous assembled TiO_2 nanocrystals with high selectivity and recyclability for the purpose of liquid-phase cyclohexene epoxidation employing H_2O_2 [9]. In this context, it was observed that the temperature of calcination influenced both the catalytic activity and the catalyst selectivity. In the case of SSSG, the optimal calcination temperature was established to be 450 °C, which yielded maximal epoxide selectivity of up to 80%. The epoxide selectivity and conversion related to the calcined SSSG did not alter even on the third sequential run.
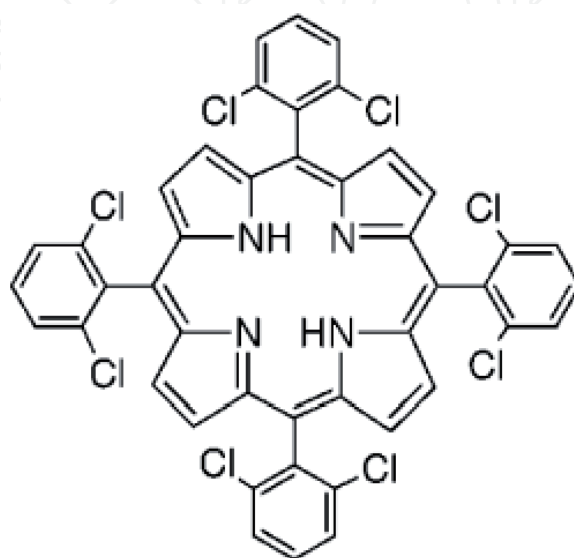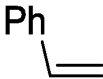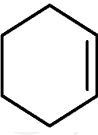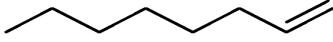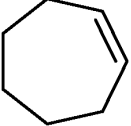

Figure 2.
Meso-Tetrakis(2,6-dichlorophenyl)porphyrin (TDCPP).

Entry	Alkene	Reaction time (h)	Conversion (%)	Epoxide yield (%)[a]	TOF/h^{-1}
1	Ph	24	98	91[b]	4550 (209)
2	Ph Ph	30	76	98	3819
3		18	84	61[c]	2628 (142)
4		24	80	92	3774 (158)
5		20	89	91	3762 (161)

Reaction conditions: alkene (1 mmol), Cl$_2$pyNO (1.1 mmol), 0.4 wt % Ru/M-41(m) (0.195 μmol of Ru), HCl (~0.3 mmol), CH$_2$Cl$_2$ (5 mL), 40 °C under an Ar atmosphere.
[a]Yields are based on the number of substrates consumed; products were identified and quantified by either GLC or 1H NMR.
[b]Trace amounts of benzaldehyde and phenylacetaldehyde were also detected.
[c]2-Cyclohexen-1-ol (14%) and 2-cyclohexen-1-one (11%) were formed. TOF were determined by monitoring the reactions using GC within the first 2 h of the reactions.

Table 1.
Epoxidations of different alkenes using a MCM-41-supported ruthenium porphyrin complexes [6].

In one synthetic approach that has been proposed, an amino acid L-valine was affixed to styrene-divinylbenzene co-polymer beads with 8% and 6% cross-linking. The formation of the metal complex on the support was achieved by applying a ruthenium (III) chloride solution to polymeric ligands that included bidentate N,O donor sites. The supported catalysts were employed to investigate the catalytic epoxidation of styrene, Norbornylene, cyclooctene and cyclohexene, with *tert*-butyl hydroperoxide as the terminal oxidant. In the case of Norbornylene and cis-cyclooctene, it was noted that epoxides formed selectively and with increase the reaction temperature from 28 °C to 45 °C there is an increase in the epoxide yield at similar levels of catalyst concentration. Meanwhile, the equivalent epoxide, benzaldehyde and acetophenone were derived for styrene. Although the catalyst could be reused, repeated recycling caused the metal to leach gradually from the support, with negative implications for its use [10].

One study investigated alkene epoxidation with ruthenium(III) salophen chloride [Ru(salophen)Cl] based on support of functionalized chloromethylated polystyrene (PS). 1,4-diaminobenzene, 4-aminophenol and 4-aminothiophenol were used for PS modification, while axial ligation facilitated the binding of [Ru(salophen)Cl] to the supports. Alkene epoxidation with sodium periodate (NaIO$_4$) as a best oxidant at ambient temperature was successfully performed with the employed catalysts, satisfactory activity being noted. It was possible to use the heterogeneous catalysts again in the reactions, and they were recycled repeatedly. They also observed that the benefits provided by these catalysts include the fact that they are uncomplicated to prepare and handle, the support is available on the market, and the supported catalysts can be readily recovered and reused [11].

Another study showed preparation of ruthenium-doped H-Montmorillonite (H-Mont) and Ti-pillared clay (PILC) was undertaken to investigate cyclohexene

oxidation, with the chosen source of oxygen being *tert*-butyl hydroperoxide (TBHP). Ru/Ti-PILC showed better effective catalytic activity than Ru/H-Mont. The use of 5% Ru/Ti-PILC as catalyst resulted in conversion of cyclohexene in proportion of 59%, selectivity of 87% and 13% respectively for 2-cyclohexene-1-one and 2-cyclohexene-1-ol at a temperature of 700 °C for six hours, without formation of epoxide. It was observed that the oxidation of cyclohexene was heterogeneous, and no leaching of ruthenium was observed [12, 13].

In our previous work, supported ruthenium catalysts (1%Ru/TiO_2) have been utilized for the epoxidation of 1-decene under solvent-free conditions. The reaction was continued for 24 h at 90 °C in atmospheric air with very small amount of *tetra*-butyl hydroperoxide (TBHP). 1% Ru/TiO_2 catalyst was prepared using two different preparation methods called sol-immobilization and wet-impregnation. For preparation of sol-immobilization, in brief, an appropriate quantity of $RuCl_3$.xH_2O was added to deionized water (800 mL) with continuous stirring. To protect and stabilize the Ru nanoparticles, a freshly prepared 1 wt.% solution of poly (vinyl alcohol) (m.w. = 10 000, 80% hydrolyzed) was added (PVA/Ru (by wt) = 0.65). After a further 15 min of stirring, a dark brown sol was generated by the addition of a freshly prepared solution of sodium borohydride (0.2 M, molar ratio $NaBH_4$/ Ru = 5). The sol was stirred for a further 30 min with dropwise addition of H_2SO_4 to adjust the acidity to pH = 2. The TiO_2 support (~1.98 g) was then added and the mixture stirred for 2 h prior to wash thoroughly with deionized water (2 L) and dried at 110 °C for 16 h. In the wet-impregnation method, catalyst (1 g) was prepared by dissolving an appropriate quantity of $RuCl_3$·xH_2O in deionized water and added an appropriate amount of TiO_2 support and allowed water to evaporate with continuous stirring at 80 °C. The obtained paste was dried for 16 h at 110 °C and grounded prior to calcination for 3 h in static air at 300 °C (heating rate = 20 °C/min).

For the preparation of 1 g of catalyst via the wet impregnation technique, a suitable amount of $RuCl_3$·xH_2O was dissolved in deionized water, after which a suitable quantity of TiO_2 support was added, and water evaporation was permitted with constant stirring at 80 °C. This process yielded a paste that was left to dry for 16 hours at 110 °C and was ground before being calcined for 180 minutes in static air at 300 °C, with a heating rate of 20 °C min^{-1}. The standard reaction of epoxidation involved addition of 0.1 g catalyst to 1-decene (53 mmol, 10 mL) in a glass flask with a round bottom and 50 cm_3 volume affixed with a reflux condenser. Following the addition of 0.01 mL *ter*-butyl hydroperoxide (TBHP) as the radical initiator, the reaction mixture was placed on a hotplate to heat to 90 °C with magnetic stirring. When the established reaction time ended, the mixture was allowed to reach ambient temperature and was subjected to filtration before being analyzed via gas chromatography (GC) [14].

1-Decene epoxidation under solvent free conditions was investigated based on 1%Ru/TiO_2. The reaction was performed for 24 hours at 90 °C in air with a catalytic quantity of TBHP. The initial step involved assessing the blank reaction with solely TBHP present, which revealed poor epoxidation reaction activity, with 2% conversion, and 10% selectivity to 1,2-epoxydecane (**Figure 3**). Subsequent assessment of TiO_2 displayed poor 1-decene conversion (4%) and epoxide selectivity (16%) as well. However, when 1% Ru/TiO_2 synthesized via sol-immobilization was used, the epoxide yield improved substantially. This was reflected in the increase in 1-decen conversion from 4 to 16% and in the increase in epoxide selectivity from 16 to 37% (**Figure 3**) [14].

High epoxide selectivity continues to pose difficulties in the context of the epoxidation reaction. This has led to the identification and quantification of several additional by-products, which have been comprehensively detailed in earlier studies
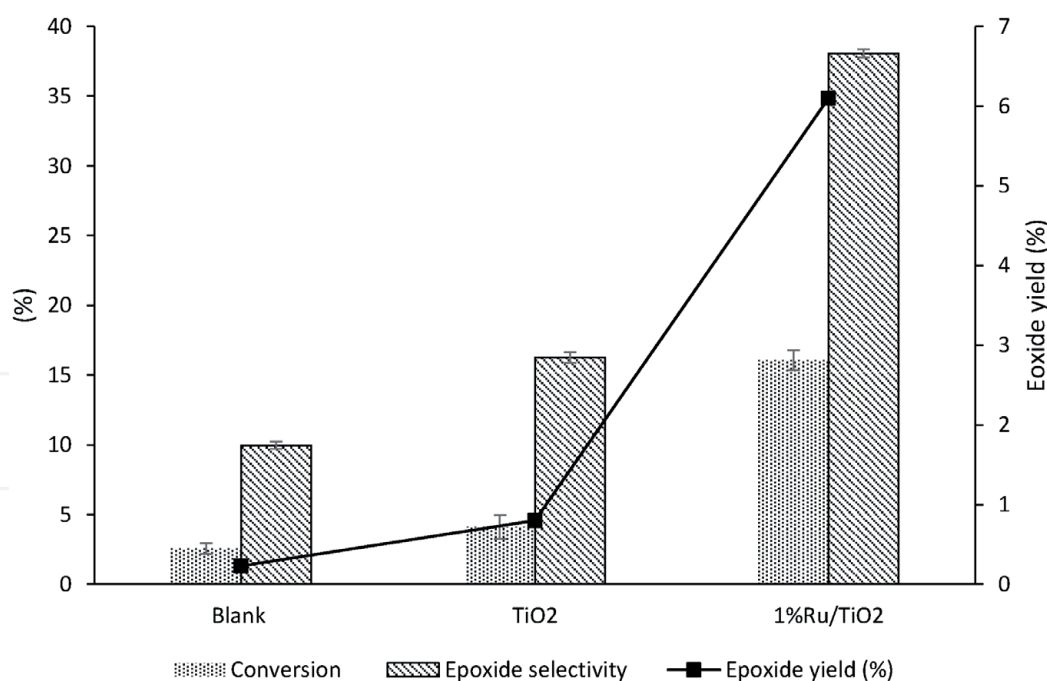
Figure 3.
Effect of TiO$_2$ and 1% Ru/TiO$_2$ on 1-decene epoxidation. Reaction conditions: Catalyst (0.1 g), 1-decene (53 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 90 °C, atmospheric pressure air, reaction time 24 h, rate of stirring 900 rpm. Error bars indicate range of data based on three repeat experiments.

[15, 16]. When the reaction runs for 24 hours, it results in the formation of substantial amounts of allylic products. Therefore, since the formation of certain products may accompany the oxidation of other products, it is useful to examine the product profile as the reaction unfolds. Time online studies were undertaken for 96 hours to gain insight into the reaction profile of 1-decene epoxidation with 1% Ru/TiO$_2$ catalyst. The increase in the reaction time from 4 to 96 hours determined an equivalent increase in 1-decene conversion from 1 to 35%, without an interval of induction (**Figure 4**). This means that the lengthier the reaction run, the higher the 1-decene conversion is likely to be. Furthermore, at the start of the reaction, epoxide selectivity was poor, with the main products being allylic compounds. However, as the reaction time increased up to 48 hours, so did the epoxide selectivity. On the other hand, epoxide selectivity gradually declined to 18% at 96 hours when the reaction time exceeded 48 hours, which is usually explained in terms of the ring opening reaction that occurs between epoxide and water as a by-product of condensation reactions or the breakdown of hydroperoxyl intermediate to the allylic ketone and water [16]. After formation of water, epoxide is immediately hydrolyzed to diol. Earlier studies also found that increase in reaction time improved alkene conversion and epoxide selectivity in the case of the terminal alkenes 1-decene, 1-hexene, and 1-octene. Additionally, it was observed that cracking of heptanoic, octanoic, and nonanoic acids was accompanied by enhanced selectivity as well [16].

The technique of synthesis is a major determinant of catalytic activity [17]. By contrast to the wet-impregnation technique, preparation of 1% Ru/TiO$_2$ catalyst via sol-immobilization displays greater activity for 1-decene epoxidation (**Figure 5**). More specifically, 1% Ru/TiO$_2$ is associated with 15% conversion and 37% epoxide selectivity when prepared via sol-immobilization and 10% conversion and 29% epoxide selectivity when prepared via wet impregnation.

The 1% Ru/TiO$_2$ catalyst synthesized via sol-immobilization was employed in excess amount to conduct the above reaction and thus evaluate reusability [14]. The procedures that followed reaction termination included catalyst filtration, washing with acetone, and 16-hour oven drying at 110 °C. Subsequently, the amount
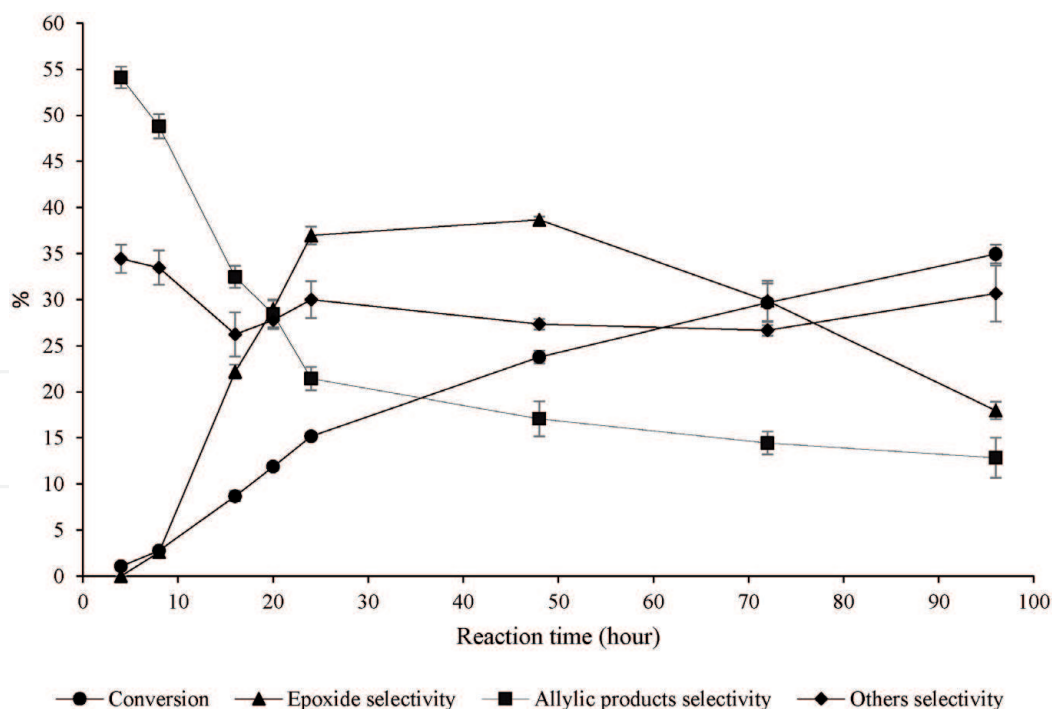
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Figure 4.
Effect of reaction time on conversion and selectivity. Reaction conditions: 1% Ru/TiO$_2$ (0.1 g), 1-decene (53 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 90 °C, atmospheric pressure air, rate of stirring 900 rpm. Allylic products = $\sum$ (1-decen-3-one, 1-decen-3-ol, 2-decenal, 2-decen-1-ol). Others = $\sum$ (C$_7$ + C$_8$ + C$_9$ acids, C$_8$ + C$_9$ aldehyde, C$_7$ + C$_8$ alcohols, 3-nonen-1-ol, 3-nonanone, cyclododecane, 2-decenoic acid). Error bars indicate range of data based on three repeat experiments.
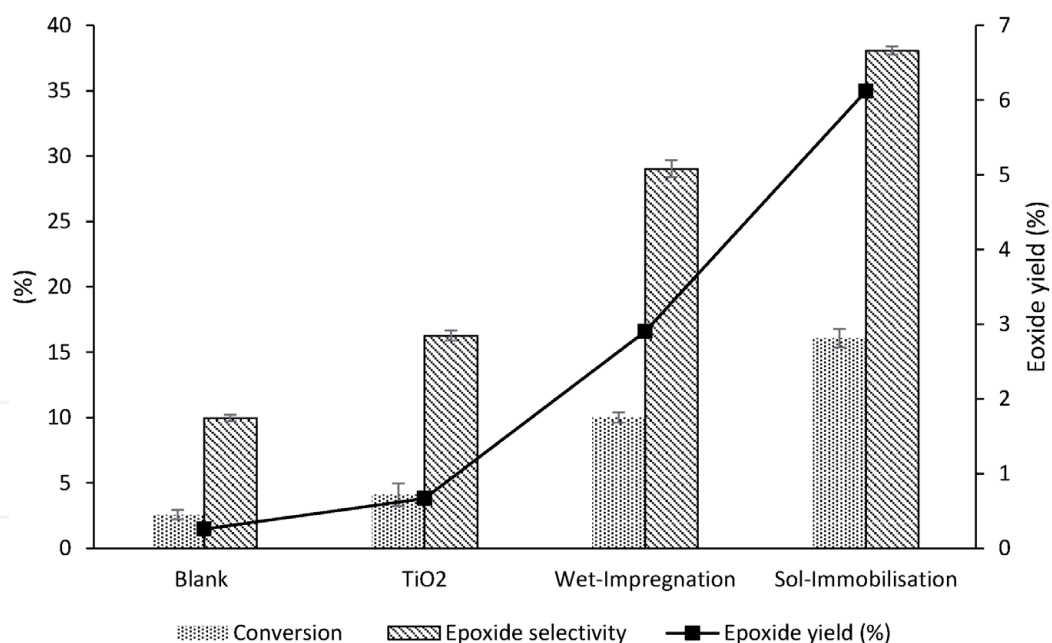

Figure 5.
Effect of the catalyst preparation method on 1-decene oxidation [14]. Reaction conditions: 1% Ru/TiO$_2$ (0.1 g), 1-decene (53 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 90 °C, atmospheric pressure air, rate of stirring 900 rpm. Error bars indicate range of data based on three repeat experiments.

of catalyst necessary for regular reaction was extracted to be used again. **Table 2** provides the activity data related to both the fresh and reused catalysts. Thus, by contrast to the fresh catalyst, which allowed 15% conversion of 1-decene and 37% epoxide selectivity, the reused catalyst subjected to drying with no previous washing showed suboptimal activity, so reuse was unsuccessful. One reason for this could be the fact that the adsorbed reaction products that were present caused the catalyst

Washing conditions	Conversion (%)	Epoxide selectivity (%)
Fresh catalyst	15	37
Reused without washing, dried static air at 110 °C for 16 h	7	17
Reused and washed with acetone (200 mL), dried static air at 110 °C for 16 h	10	24

Reaction conditions: 1% Ru/TiO$_2$ (0.1 g), 1-decene (53 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 90 °C, atmospheric pressure air, reaction time 24 h, rate of stirring 900 rpm.

Table 2.
Catalyst reusability study for epoxidation of 1-decene: 1% Ru/TiO$_2$.

to deactivate. On the other hand, better conversion (10%) and epoxide selectivity (24%) were exhibited by the catalyst washed with acetone before being reused, but even so, the activity was still poorer compared to that of fresh catalyst, most likely owing to the fact that carbon inhibited active sites. Active component leaching into the solution is major problem of heterogeneous catalysts, particularly in the liquid phase. However, ICP analysis suggested that ruthenium did not leach.

3. Ruthenium complexes for epoxidation of alkene

Being a transition metal, ruthenium displays several oxidation states that can be readily interchanged. Consequently, ruthenium facilitates the exchange or replacement of ligands in the complexed state, thus mediating access for metal-oxo species. The latter represent the main olefin epoxidation intermediate and are highly useful catalysts because they act as oxygen donor to alkenes. A variety of ruthenium-catalyzed epoxidation catalysts are supplied by homogeneous ruthenium complexes with ligands like porphyrin [18], polypyridyl [19], Schiff base [20], oxazoline [21], and pyrazolyl [22].

In 1984, Balavoine and colleagues suggested that RuCl$_3$, 2,2′-bipyridyl and sodium periodate could be employed in a two-phase reaction medium for alkene epoxidation [23]. Although the mechanism remained unclear, it was possible that a Ru(IV)-0x0 complex, potentially [Ru″'(bipy)&l(O)]', represented the active species. In 1985, Eskanazi and colleagues demonstrated that it was possible to control the rate and stereoselectivity of alkene oxidation by substituting the 2,2′-bipyridyl with different ligands [24].

Fackler and colleagues applied the method of Sonogashira coupling with a bromo-substituted porphyrin and terminal alkyne to create a ruthenium porphyrin epoxidation catalyst of high enantioselectivity and regioselectivity. This catalyst achieved enantioface-selective oxo transfer to alkene functionalized quinolones, pyridones, and amides via non-covalent hydrogen bond interactions. [25–26]

In 1998 [27], ruthenium complexes that included pyridine and picoline ligands were used to subject cyclohexene and styrene to catalytic oxidation. Alteration of the oxidant character led to marked variability. Cyclohexene oxidation yielded 2-cyclohexen-l-ol and 2-cyclohexenone when the oxidizing agent was cumene-hydroperoxide (CHP), and 2-cyclohexenone when the oxidizing agent was N-methylmorpholine-N-oxide (NMO). Contrary to expectations, it was not epoxide but benzaldehyde that resulted from the oxidation of styrene. Hydrogen bond interactions could facilitate the engagement of the diaxial-dioxoruthenium species displaying catalytic activity with vinyl or alkenyl fragments (**Figure 6**). In this way, oxygen can be supplied to a specific alkene prochiral face [28].
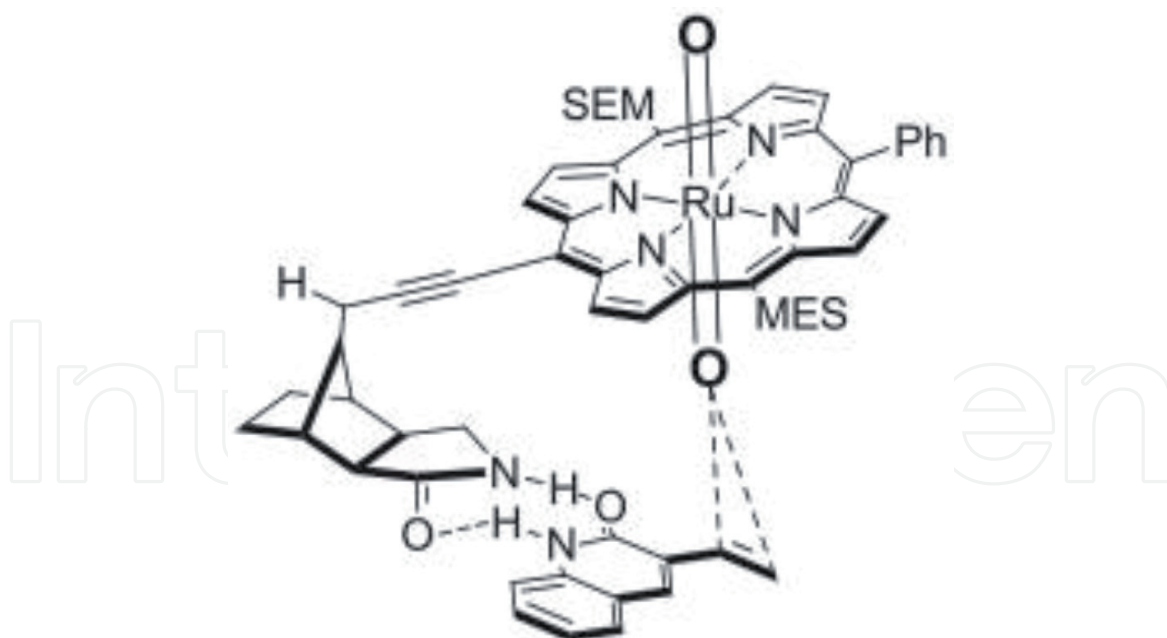
Figure 6.
Dioxo ruthenium-substrate interaction visualized based on semi empirical calculation [28].

Stoichiometric quantities of Cl_2pyNO were used as oxidant to perform the epoxidations in benzene. Epoxidation of n-hydro-3-vinylquinolones was achieved with high enantioselectivity, which was reduced for N-methylated quinolones as one of the two hydrogen bond interactions was lost. Meanwhile, 3,7-divinylquinolone exhibited high regioselectivity, with epoxidation of the vinyl group since it was readily accessible to ruthenium oxocentre. Trans-epoxides with enantioselectivity higher than 90% were obtained by subjecting the 3-alkenyl quinolones to stereospecific and enantioselective epoxidation.

Another study by Man and his group [29] was found that olefin asymmetric epoxidation with ruthenium as catalyst was significantly improved when $PhI(OAc)_2$ was present. The increase in the reaction rate when water was added was two orders of magnitude. It was possible to achieve reactions of aliphatic as well as aromatic olefins, with enantioselectivities being as high as 71% ee.

A novel pentadentatepolypyridine (L_5pyr) ruthenium complex $[Ru(L_5pyr)(CH_3CN)]_2P$ was proposed by Hamelin and colleagues. When iodosyl benzene was employed as oxidant, this complex was observed to generate satisfactory amounts of epoxide for cyclooctene and trans-b-methyl styrene. The preparation of the complex involved use of $RuCl_2 (dmso)_2$ to reflux L_5pyr and subsequent replacement with acetonitrile. Enhanced catalytic activity of $[Ru(L_5pyr)(CH_3CN)]_2þ$ depends greatly on the pentadentate ligand with electron abundance. This is reflected by the fact that epoxidation with lower dentate pyridine analogues $[Ru(bpy)_2(CH_3CN)_2]_2þ$ produce suboptimal yields and turnover frequencies [30].

Two $Ru(^{II})$-aqua complex catalysts underpinned by oxazoline ligands viz. $[Ru^{II}(iPr-box-C)(tpm)OH_2](PF_6)_2$ and $[Ru^{II}(iPr-box-O)(tpm)OH_2](PF_6)$ were developed in recent times. The preparation of the complexes involved derivation from $[Ru^{III}Cl_3(tpm)]$ by base catalyzed oxazoline ligand exchange, with the generated chloro complex being subsequently hydrolyze with silver acting as catalyst. $PhI(OAc)_2$ was employed as oxidant to analyze the potential of the two complexes as epoxidation catalysts for trans-stilbene. Results showed that catalyst 1 was associated with 85% epoxide selectivity and catalyst 2 was associated with 81% epoxide selectivity, while the conversion was nearly identical in both cases. Furthermore, catalyst 1 was regioselective for the terminal alkene segment of 4-vinylcyclohexene [31] (**Figure** 7).
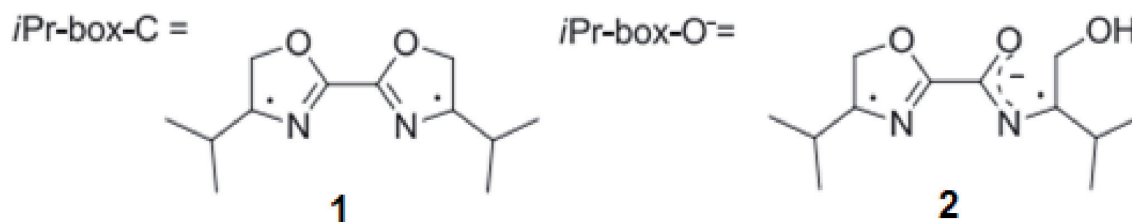
Figure 7.
Oxazoline ligands [31].

In another study, a range of olefins were subjected to asymmetric epoxidation with ruthenium as catalyst and TBHP as oxidant. Under catalysis by ruthenium(pyridinebisoxazoline)-(pyridinedicarboxylate) complexes, aromatic and aliphatic olefins produced the equivalent epoxides at ambient temperature in moderate-to-high yields and enantioselectivity as high as 65% ee. The reaction yield and chemoselectivity were markedly enhanced by adding the stoichiometric oxidant in a gradual way [32].

In a similar study [33], olefins were subjected to asymmetric epoxidation with general ruthenium as catalyst and hydrogen peroxide as oxidant. Various aromatic olefins exhibited enantioselectivity as high as 84%. The reaction was successful especially because pyboxazines, a novel group of ligands, were added. It was anticipated that the catalytic behavior of common pybox derivatives harmonized well with such ligands. Furthermore, differences in catalyst structure were diminished by employing two distinct ligands, facilitating refinement of catalytic attributes.

One study undertook the synthesis of bis-facial dinuclear ruthenium complex that included a hexadentate pyrazolate-bridging ligand (Hbimp) and bpy as auxiliary ligands [34]. Additionally, the ability of water and alkene oxidation of this complex was assessed. Various alkenes were successfully subjected to epoxidation under catalysis by the *in situ*-produced bis-aqua complex, $\{[Ru^{II}(bpy)(H_2O)]2(\mu\text{-bimp})\}^{3+}$.

The difficulty of ruthenium complex heterogenization stems from the fact that it is necessary to preserve the ligand properties (e.g. lability, enantiopurity, relative orientation) that greatly influence epoxidation reactivity, enantioselectivity, regioselectivity, and chemoselectivity. One possible approach is to anchor the catalyst to a polymer, for which one of the ligands must include a reactive functional group or polymerizable moiety. An additional viable option is to immobilize catalysts in channels of materials of high porosity (e.g. zeolites, molecular sieves), with shape selectivity being afforded by characteristic pore sizes.

To conclude, It was shown that the chemical nature of the solvent, oxidant, type of catalysts and type of the ligand have a significant effect on the catalytic properties and stability of the active species.

Acknowledgements

Conflict of interest

The author declares no conflict of interest.

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References

[1] Ansmann A., Kawa R. and Neuss M., US Patent 7,083,780 B2, Aug. 1, 2006.

[2] Everett, J. L.; Roberts, J. J.; Ross, W. C. J. J. Chem. Soc. 1953, 2386.

[3] Levene, P. A.; Walti, A. J. Biol. Chem. 1931, 94 (1931) 367.

[4] Beracierta, A. P.; Whiting, D. A. J. Chem. Soc., Perkin Trans. 1(1978) 1257.

[5] Katsuki, T.; Sharpless, K. B. J. Am. Chem. Soc. 1980, 102 (1980) 5974.

[6] Chun-Jing L., Wing-Yiu Y., Shou-Gui L. and Chi-Ming C., J. Org. Chem. 63 (1998) 7364.

[7] Jun-Long Z. and Chi-Ming C., Org. LETTERS 4 (2002) 1911.

[8] Jirkovsky, J. S.; Busch, M.; Ahlberg, E.; Panas, I.; Krtil, P. J. Am. Chem. Soc. 2011,133 (2011) 5882.

[9] Woragamon, K.; Jongpatiwut, S.; Sreethawong, T. Catal. Lett. 2010, 136 (2010) 249.

[10] Vaibhav B. V., Gopal L. T., Marayil R. and Rama H.S., REACT. FUNCT. POLYM. 56 (2003) 1.

[11] Moghadama M., Mirkhania V., Tangestaninejada S., Mohammadpoor-Baltorka I., Kargarb H., Sheikhshoaeic I. and Hatefid M., J. Iran.Chem. Soc. 8 (2011) 1019.

[12] Dali A., Rekkab-Hammoumraoui I., Choukchou-Braham A. and Bachir R., RSC Advances 5 (2015) 29167.

[13] Ahmed D., Rekkab-Hammoumraoui I., Sanaa E. K., Souheyla B. and Abderrahim C. B., Bull. Chem. React. Eng. Catal. 14 (2019) 614.

[14] Alsaiari R., Asian J. Chem. 32 (2020) 771.

[15] Engel R.V., Alsaiari R., Nowicka E., Pattisson S., Miedziak P.J., Kondrat S.A., Morgan D.J. and Hutchings G.J., Top. Catal., 61 (2018) 509.

[16] Gupta U.N., Dummer N.F., Pattisson S., Jenkins R. L., Knight D.W., D. Bethell and G.J. Hutchings, Catal. Lett., 145 (2015) 689.

[17] Miedziak P., Sankar M., Dimitratos N., Lopez-Sanchez J.A., Carley A. F., Knight D.W., Taylor S.H., Kiely C.J. and Hutchings G.J., Catal. Today, 164 (2011) 315.

[18] Lai, T. S.; Zhang, R.; Cheung, K. K.; Kwong, H. L.; Che, C. M. Chem. Commun. 1998,1583.

[19] Gallagher, L. A.; Meyer, T. J. J. Am. Chem. Soc., 123 (2001) 5308.

[20] Nakata, K.; Takeda, T.; Mihara, J.; Hamada, T.; Irie, R.; Katsuki, T. Chem.d Eur. J., 7 (2001) 3776.

[21] Nishiyama, H.; Shimada, T.; Itoh, H.; Sugiyama, H.; Motoyama, Y. Chem. Commun. 1997, 1863.

[22] Zhang, R.; Yu, W. Y.; Lai, T. S.; Che, C. M. Chem. Commun. 1999, 409.

[23] Eskerazi C., Meunier F. and Riviere H., Tetrahedron L&t. 25 (1984) 3187.

[24] Eskanazi C., Balavoine G., Meunier F. and Riviere H., Chem. Commun. 1985, 1111.

[25] Fackler, P.; Berthold, C.; Voss, F.; Bach, T. J. Am. Chem. Soc., 13, (2010) 15911.

[26] Fackler, P.; Huber, S. M.; Bach, T. J. Am. Chem. Soc.,134 (2012) 12869.

[27] Kanmani A. S. and Vancheesan S.,
Stud Surf Sci Catal. 113 (1998) 285.

[28] J. Am. Chem. Soc. 132 (2010) 15911.

[29] Man Kin T.,
Santosh B., Markus K., Christian D.
and Matthias B., Tetrahedron L&t. 44
(2003) 7479.

[30] Hamelin, O.; Menage, S.; Charnay,
F.; Chavarot, M.; Pierre, J. L.; Pecau,
J.; Fontecave, M. Inorg. Chem. 47
(2008) 6413.

[31] Serrano, I.; Lopez, M. I.; Ferrer,
I.; Poater, A.; Parella, T.; Fontrodona,
X.; Sola, M.;Llobet, A.; Rodriguez,
M.; Romero, I. Inorg. Chem., 50
(2011) 6044.

[32] Bhor S., Tse M. K., Klawonn M.,
Döbler C., Mägerlei W. and Beller M.,
ADV. SYNTH. CATAL. 346 (2004) 263.

[33] Tse M. K., Döbler C., Bhor S.,
Klawonn M., Mägerlein W., Hugl H.
and Beller M., Angew. Chem. Int. Ed. 43
(2004) 5255.

[34] Aguiló J., Francàs L., Bofill R.,
Gil-Sepulcre M., García-Antón J.,
Poater A. and Sala X., J. Inorg. Chem. 54
(2015) 6782.