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SCIENTIFIC PAPER

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OXIDATION OF CYCLOALKENE USING SUPPORTED RUTHENIUM CATALYSTS UNDER SOLVENT-FREE CONDITIONS

Article Highlights

- The reaction completed under solvent-free conditions, without any oxidant, only using air as primary oxidant
- No leaching of the supported ruthenium catalyst in the reaction solution
- Increase in the cyclooctene conversion and epoxide selectivity compared to other studies under these green conditions

Abstract

The present paper employs supported ruthenium nanoparticles alongside catalytic quantities of the radical initiator, which are proven to be capable of cyclooctene oxidation with green conditions, in the absence of solvent, with air as the main oxidant and without sacrificial reductant. The paper examines the effects of a range of radical initiators and how the products are distributed over time. Furthermore, the paper addresses the reaction pathways to the epoxides and allylic alcohol, the latter being the primary by-product, whilst also analysing the impact of the technique of synthesis, reaction time, and various supports. Catalyst activity can be markedly improved by adopting a sol-immobilisation technique to synthesise the catalysts, with retention of selectivity to the epoxide.

Keywords: cyclooctene oxidation, epoxide, ruthenium catalyst, sol-immobilisation.

A major mechanism underpinning commercial applications is selective oxidation, which is particularly important for preparing chemical intermediates in the context of production of functionalized fine chemicals and pharmaceutical agents. This makes synthesis of oxygen-containing compounds via hydrocarbon oxidation an essential industrial reaction [1,2]. Epoxidation of alkenes used to be achieved by adding stoichiometric quantities of peroxides like peracids, *tert*-butyl hydroperoxide (TBHP) or hydrogen peroxide. However, such peroxides present the disadvantages of being costly and dangerous [3-5]. Together with the specifications of green chemistry and atom efficiency, such considerations suggest that molecular oxygen is a more appropriate oxidant (Figure 1). Therefore, it is optimal to undertake epoxidation reactions based on an active catalytic system demonstrating selectivity and employing molecular oxygen or air. Nevertheless, epoxide formation through electrophilic addition of oxygen to alkenes is difficult, as shown by research with various heterogeneous catalysts [6]. The source of the difficulty is the occurrence of labile allylic H atoms, which induce the yield of allylic products rather than epoxides because they are readily abstracted [7,8]. A silver catalyst is employed for ethene epoxidation with molecular oxygen in industrial settings, whereas hydrogen peroxide is the preferred catalyst for the epoxidation of higher alkenes [9,10]

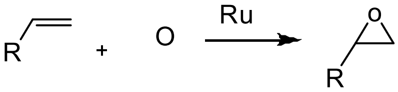

Figure 1. Epoxidation of alkene using ruthenium catalysts.

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There are few studies which evaluate the capacity of ruthenium (Ru) to act as a heterogeneous catalyst for epoxidation reactions. Mesoporous MCM-41 sieves were utilised in 1998 [11] for the immobilisation of meso-tetrakis, *i.e.*, (2,6-dichlorophenyl)porphyrin, [RuII(TDCPP)(CO)(EtOH)], which is a Ru compound. Heterogeneous alkene epoxidations were influenced by the supported Ru catalyst; the ideal terminal oxidant was 2,6-dichloropyridine N-oxide alongside CH_2Cl_2. Four years later, researchers determined that polyethylene glycol is able to employ a covalent etheric bond to attach to Ru porphyrin. Specific properties of these catalysts include their extreme reactivity and the fact that they can target alkene epoxidation where the terminal oxidant is 2,6-dichloropyridine N-oxide [12].

Additional research explored the utility of catalysts comprising Ru-loaded H-montmorillonite (H--Mont) and Ti-pillared clay (PILC) for cyclohexene oxidation; the oxygen source selected was tert-butyl hydroperoxide (TBHP). In comparison to Ru/H-Mont, Ru-Ti-PILC demonstrated more efficacious catalytic operation. 5% of the latter led to a cyclohexene transformation of 59%; the differentiation for 2 cyclohexene-1-one was 87%, and for 2-cyclohexene-1-ol, 13%. The reaction was performed for 6 h at 70 °C; no epoxide was generated [13]. Earlier research from this laboratory has deployed supported Ru catalysts (1% Ru/TiO_2) for 1-decene epoxidation in a solvent-free setting. The process of sol-immobilisation was utilised to form the 1% Ru/TiO_2 catalyst; this induced heightened activity for the epoxidation of 1-decene [14].

The present work builds on previous research [14] to investigate cyclooctene epoxidation with supported ruthenium catalysts, as well as to determine whether such catalysts are reusable, which is an important requirement for green chemistry.

MATERIALS AND METHODS

The chemicals employed in the present work were acquired from commercial suppliers and used without additional purification. Metal catalyst loading on the support is specified as metal percentage by support weight and the catalyst was prepared via the wet-impregnation technique as well as the sol-immobilisation technique.

For the synthesis of 1 g of catalyst through the wet-impregnation technique, a suitable amount of $RuCl_3{\cdot}xH_2O$ was dissolved in deionised water, the required support (TiO_2, SiO_2, graphite) was added in an adequate quantity, and water evaporation was permitted, with the mixture being stirred continuously at a temperature of 80 °C. This process yielded a paste that was allowed to dry for 16 h at 110 °C before being ground and calcined for 180 min in static air at a temperature of 300 °C, with a heating rate of 20 °C min^{-1}. The sol-immobilisation preparation methods were explained in a previous work [14].

The standard reaction of epoxidation was carried out in a magnetically stirred, 50 cm^3 round-bottomed glass flask equipped with a reflux condenser. 0.1 g of catalyst was added to cyclooctene (75.7 mmol, 10 mL) and catalytic amount (0.01 mL) of TBHP as the radical initiator (not oxidant) and molecular oxygen from air is the primary oxidant for this reaction. The reaction mixture was subjected to heating to required reaction temperature on a hotplate. After the required reaction time, the mixture of the reaction products and un-reacted cyclooctene was cooled down to room temperature, filtered and then examined using a Varian star 3400 CX GP system with a CP wax 52 capillary column (25 m, 0.35 mm ID, 0.2 μm) coupled with an FID detector.

The analysis of XRD was completed using a PANalytical X'pert pro diffractometer using a CuKα X-ray source. Scans were started from 10 to 80° 2θ at 40 kV. The analysis of surface area were done using a Micromeritics Gemini 2360 Analyser. Samples for measuring the surface area were prepared by degassing for approx. 50 min at 120 °C in presence of He. Then the sample was placed in a sample vessel connected to a gas inlet (liquid N_2 at −196 °C). The leaching of active catalyst was checked using inductively coupled plasma mass spectrometry (ICP-MS). It was performed on an Agilent 7900 ICP-MS equipped with a MicroMist nebuliser. Analysed ruthenium quantification was carried out by comparison with a calibration curve. Infrared spectra were obtained using FT/IR--660Plus Fourier-transform infrared spectrometer (JASCO). The instrument used for TEM analysis was a JEOL 2000FX TEM operating at 200 kV.

RESULTS AND DISCUSSION

Catalyst characterization

Ru integration into the support pores may be reflected by the fact that the 1% Ru/TiO_2 catalyst had a smaller surface area than the undoped supports as shown in Table 1. Likewise, the reused 1% Ru/TiO_2 exhibited a minor reduction in surface area from 46 to 42 m^2 g^{-1}, which could be due to adsorption of certain products and the rest of the substrate on the surface. The analysis was performed twice, with error not exceeding 1 m^2 g^{-1}.

Table 1. Analysis of nitrogen physisorption of the surface area by employing the BET method of TiO_2 and 1% Ru/TiO_2

Catalyst	Surface area (m^2 g^{-1})
TiO_2	53
1% Ru/TiO_2	46
Reused 1% Ru/TiO_2	42

No observation was made of the typical XRD reflections of the ruthenium ion. This suggests that Ru was dispersed uniformly in the TiO_2 support. For the fresh and reused 1% Ru/TiO_2, Figure 1 indicates that the XRD reflections did not exhibit sufficient noticeable differences.

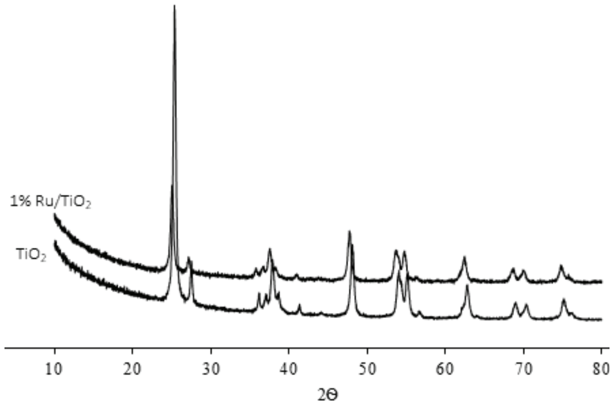

Figure 2. X-ray diffraction patterns for TiO_2 and fresh and 1% Ru/TiO_2.

Influence of radical initiators on cyclooctene epoxidation

The conditions under which no reaction takes place when the catalyst is not present must be identified. In the present case, no reaction occurred within the examined range of temperatures when neither a peroxy initiator nor a catalyst were present. The oxidation of cyclooctene did not begin at temperatures under 100 °C. However, once the temperature of 100 °C was reached, the reaction started spontaneously, attaining a conversion of 0.8 and 60% epoxide selectivity. Hence, temperatures exceeding 100 °C were avoided for this reaction for the purpose of avoiding autoxidation.

To make the epoxide more selective, it is essential for a radical initiator to be present in alkene oxidation [14]. Furthermore, cyclooctene can be more easily oxidised at reduced temperature when small quantities of radical initiators are used as TBHP. In this reaction, molecular oxygen from air is the primary oxidant and very small amount of radical initiator will be consumed in the early stage of the reaction and further propagate the reaction under mild green conditions. To gain insight into the function played by the catalyst, the radical reactions occurring when the catalyst is not present must be identified. *tert*-Butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP) and azobisisobutyronitrile (AIBN) were the three distinct radical initiators employed for cyclooctene oxidation in this work. TBHP and CHP are classified as hydroperoxide radical initiators, while AIBN is an azo radical initiator, Table 2 presents the obtained results.

Table 2. Effect of temperature on cyclooctene epoxidation using different radical initiators; reaction conditions: cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), AIBN (0.036 mmol, 6 mg), CHP (0.028 mmol, 0.01 mL), atmospheric pressure air, reaction time 24 h, rate of stirring 800 rpm.

Initiator	t = 60 °C		t = 70 °C		t = 80 °C	
	Conv. (%)	Sel. (%)[a]	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
-	0	0	0	0	0	0
AIBN	1.3	64	2.2	71	5	80
CHP	0.7	60	1.5	68	3	78
TBHP	0.4	58	0.9	63.2	2	72

[a] Selectivity for epoxide

At reduced temperatures, TBHP displayed minimal activity, whereas AIBN and CHP demonstrated greater activity. At a temperature of 80 °C, epoxide selectivity was improved by AIBN from 64 to 80%, by CHP from 60 to 78%, and by TBHP from 58 to 72%. Furthermore, cis-cyclo-oct-2-enol and cis-cyclooct-2--enone formed with 2:1 mole ratio represented the primary reaction by-products in the case of all three radical initiators. Out of the used initiators, the highest activity and selectivity toward epoxide was demonstrated by AIBN, regardless of temperature. At 80 °C, TBHP was associated with the lowest level of activity when comparatively examined against other radical initiators without the ruthenium catalyst. For this reason, additional experiments were undertaken with supported ruthenium catalysts using the same initiator.

Ruthenium-catalysed reactions

Cyclooctene epoxidation in conditions without solvent was investigated with 1% Ru/TiO_2 as catalyst, which was synthesised via the sol-immobilisation technique. The process began with testing of the TiO_2 support, which displayed cyclooctene conversion and epoxide selectivity in proportion of 2.5% and 74%, respectively; cyclooctene conversion is not markedly affected by the addition. Heightened cyclooctene conversion can be attained when ruthenium supported on TiO_2 is added; conversion increased to 8.3%, while selectivity increased to 87% when 1% Ru/TiO_2 catalyst was added, as shown in Table 3.

Table 3. Oxidation of cyclooctene using supported ruthenium catalyst; reaction conditions: 0.1 g catalyst, cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 80 °C, 24 h, 800 rpm

Catalyst	Conversion (%)	Selectivity (%)		
		Epoxide	Cy-one	Cy-ol
Blank	2	72	8	10
TiO_2	2.5	74	9	11
1% Ru/TiO_2	8.3	87	5	7

O-H homolysis in TBHP may be mediated by the ruthenium surface when Ru catalyst is present. The outcome of this homolysis is Me3COO$^{\bullet}$, which displays high activity in relation to hydrogen abstraction from the allylic position in hydrocarbons at moderate temperatures [15]. This can serve to elucidate why the addition of ruthenium supported on TiO_2 triggers such a sharp rise in activity.

Effect of the support

The characteristics of the support frequently influence catalyst activity. A marked support effect on conversion as well as selectivity has been demonstrated by earlier work on oxidation reaction [16]. Synthesis of several supported ruthenium catalysts on various oxide supports and graphite was undertaken, followed by testing of those catalysts in relation to cyclooctene oxidation. A reduction in the surface area of the 1% Ru/support catalysts was observed compared with the undoped supports, which may indicate the incorporation of Ru in the support pores. Testing was first conducted on the undoped supports (Table 4), but conversion was not observed to be enhanced considerably by comparison to the blank test. Although cyclooctene conversion was markedly improved when ruthenium was added to the support in every case as shown in Table 4, TiO_2 was overall the support with the highest activity when incorporate with Ru catalyst where 8.3% conversion and 87% epoxide selectivity were observed.

It is possible for TiO_2 and other reducible supports to diffuse onto Ru, which leads to a substantial impact in terms of the catalytic activity. This is referred to as the strong metal support interaction (SMSI) [17]. Additionally, it has been established in the literature that TiO_2 is a suitable material for oxidation reactions and interacts favourably with the metal when employed as a support [18,19]. Hence, TiO_2 was included in further experiments.

Table 4. The oxidation of cyclooctene using different supports; reaction conditions: 0.1 g catalyst, cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 80 °C, 24 hours, 800 rpm

Catalyst	BET	Conversion (%)	Selectivity (%)		
			Epoxide	Cy-one	Cy-ol
Blank	-	2	72	8	10
Graphite (G)	11	2	75	9	12
1% Ru/G	8	5	82	12	11
SiO_2	125	3	74	13	11
1% Ru/SiO_2	119	6	84	9	8
TiO_2	53	2.5	74	9	11
1% Ru/TiO_2	46	8.3	87	5	7

Effect of reaction time

The enhanced 1% Ru/TiO_2 catalyst prepared via sol-immobilisation was employed under ideal conditions to determine how the reaction time influenced the oxidation of cyclooctene. In keeping with expectations, both conversion and epoxide selectivity increased as the reaction time increased, as indicated by the results in Figures 3 and 4.

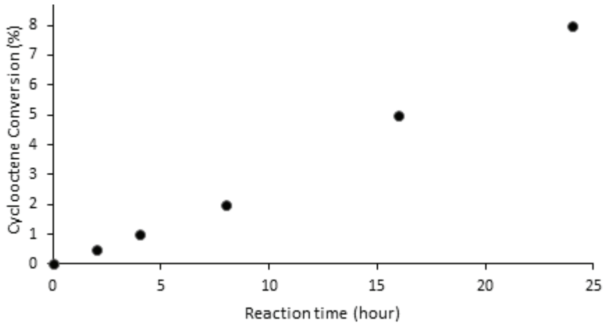

Figure 3. Effect of reaction time for the conversion of cyclooctene. Reaction conditions: 0.1g catalyst, cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 80 °C, 800 rpm.

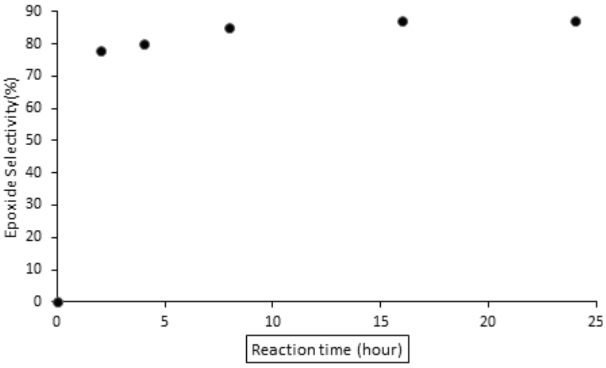

Figure 4. Effect of the reaction time for epoxide selectivity. Reaction conditions: 0.1 g catalyst, cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 80 °C, 800 rpm.

The effect of preparation method

The technique of synthesis is a major determinant of catalyst activity (Table 5). Both sol-immobilisation and wet-impregnation were used for synthesis of 1% Ru/TiO_2 catalyst, with more intense activity for cyclooctene epoxidation and epoxide selectivity being exhibited by the catalyst prepared via the former technique (8.3% and 87%, respectively) than via the latter technique (4.5% and 85%, respectively).

Table 5. The effect of preparation method on epoxidation of cyclooctene; reaction conditions: 0.1 g catalyst, cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 80 °C, 24 hours, 800 rpm

Preparation method	Conversion (%)	Selectivity (%)		
		Epoxide	Cy-one	Cy-ol
Sol-immobilization	8.3	87	5	7
Wet-impregnation	4.5	85	5.4	9.3

The catalyst exhibiting the greatest activity was the one synthesised via sol-immobilisation, namely, 1% Ru/TiO_2. This was subjected to TEM analysis and the outcomes of that analysis are illustrated in Figure 4 alongside the particle size distribution (PSD). According to the latter, 1% Ru/TiO_2 consisted of minute particles, the majority of which were no more than 3-4 nm, while the diameter of the distribution range was also small (1-7 nm), as shown in Figure 5. The smaller size of the particles enabled improved Ru dispersion, which could be why this catalyst displayed enhanced activity.

In contrast to the previous method, most of the particle size of 1% Ru/TiO_2 catalyst prepared by wet-impregnation method was in the range 7-12 nm as shown in Figure 6, which may decrease Ru dispersion, which could be why this catalyst displayed lower activity.

Reusability and stability of ruthenium catalysts

The 1% Ru/TiO_2 catalyst synthesised via sol-immobilisation was employed in excessive amount to conduct the above reaction so as to assess whether the catalyst could be reused. Once the reaction was completed, the catalyst was subjected to filtration, washing with acetone, and oven drying at 110 °C for

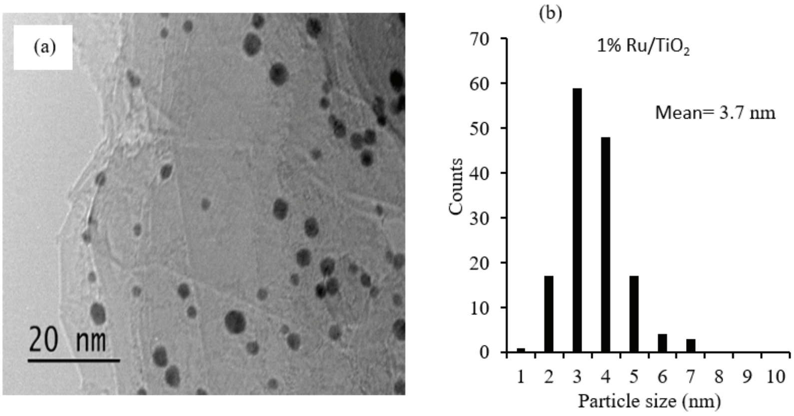

Figure 5. a) Transmission electron microscopy (TEM) and b) particle size distribution (PSD) for 1% Ru/TiO_2 prepared by sol-immobilisation method. Counts: number of occurrences of particles of indicated diameter within the sample assessed.

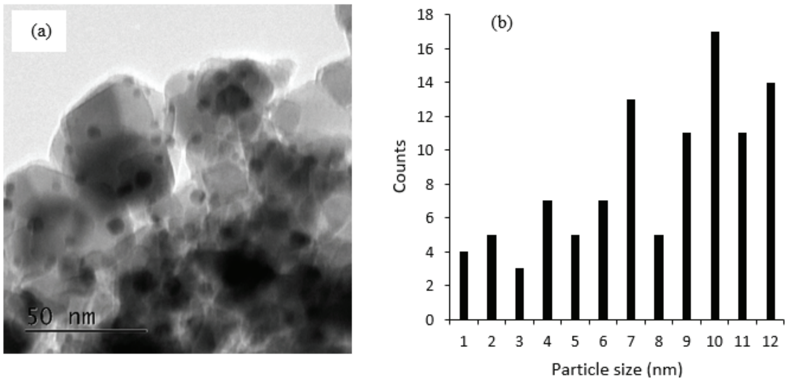

Figure 6. a) Transmission electron microscopy (TEM) and b) particle size distribution (PSD) for 1% Ru/TiO_2 prepared by wet-impregnation method. Counts: number of occurrences of particles of indicated diameter within the sample assessed.

16 h. Subsequently, the catalyst amount necessary for a regular reaction was extracted for use again. Table 5 provides the data related to the activity of the catalyst in both fresh and reused state. The use of the fresh catalyst allowed cyclooctene conversion and epoxide selectivity of 8.3 and 87%, respectively. By contrast, the reused catalyst showed reduced activity and failed to permit successful reuse when it was dried without having been washed beforehand. Such inferior performance may have been caused by the fact that the present adsorbed reaction products deactivated the catalyst. Thus, by comparison to the unwashed catalyst, the reused catalyst subjected to pre-washing in acetone showed higher activity, with conversion and epoxide selectivity of 5.5 and 80%, respectively. However, by contrast to the fresh catalyst, the catalyst washed before reuse performed poorly. This is most likely the result of active site inhibition by carbon. Furthermore, it can be seen that the yield of the recovery catalyst after wash with acetone is higher than that without the washing step (Table 6).

Table 6. Catalyst reusability study for oxidation of cyclooctene: 1% Ru/TiO_2; reaction conditions: 1% Ru/TiO_2 (0.1 g), cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL)

Washing conditions	Conversion (%)	Epoxide selectivity (%)	Yield (%)
Fresh catalyst	8.3	87	7.22
Reused without washing, dried static air at 110 °C for 16 h	3	76	2.28
Reused and washed with acetone (1 L), dried static air at 110 °C for 16 h	5.5	80	4.4

Extra species were revealed to be present when the reused catalyst was subjected to FTIR analysis. As shown in Figure 7, a C-H stretch may be reflected by the robust stretching in the area of 2900-2970 cm^{-1}, which may suggest that products were adsorbed on the used catalyst surface. There was a decrease in the dimensions of the FTIR defining bands upon washing the catalyst with acetone. This implied the elimination of a portion of the adsorbed products and minor recovery of catalytic activity.

Furthermore, as shown in Figure 8, there is increase in the particle size of the used 1% Ru/TiO_2 prepared by sol-immobilisation method which may also be a reason for the low activity of the reused catalyst.

Active component leaching in the solution is a fundamental difficulty associated with heterogeneous catalysts, especially in the liquid phase. In our previous study [16], supported cobalt catalysts have been used for epoxidation of alkene under the same reaction conditions reported in this work. The ICP AES analysis for this previous work showed that the materials were indeed leaching active components into the reaction mixture. ICP analysis showed cobalt leaching on the level of 45 ppm in the reaction effluent, corresponding to approximately 23% of the metal present in the supported cobalt catalyst. However, in this work, ruthenium leaching was not identified by ICP analysis.

The characteristics of active species in the reaction may be determined by conducting hot filtration experiments. A comparison between regular cyclooctene epoxidation at 8 and 24 h and a hot filtration reaction with filtration of the catalyst after a reaction time of 8 h and subsequent reaction running

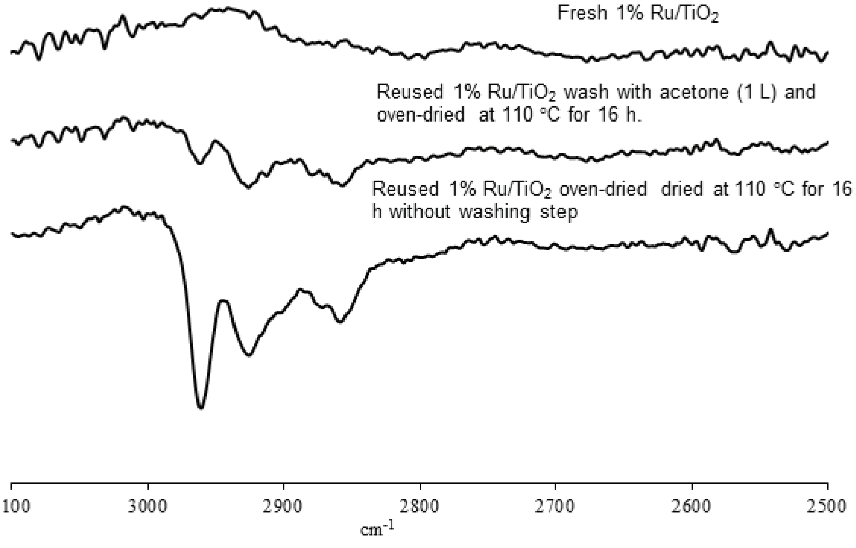

Figure 7. Fourier-transform infrared spectroscopy (FTIR) for the fresh and the reused 1% Ru/TiO_2 catalysts.

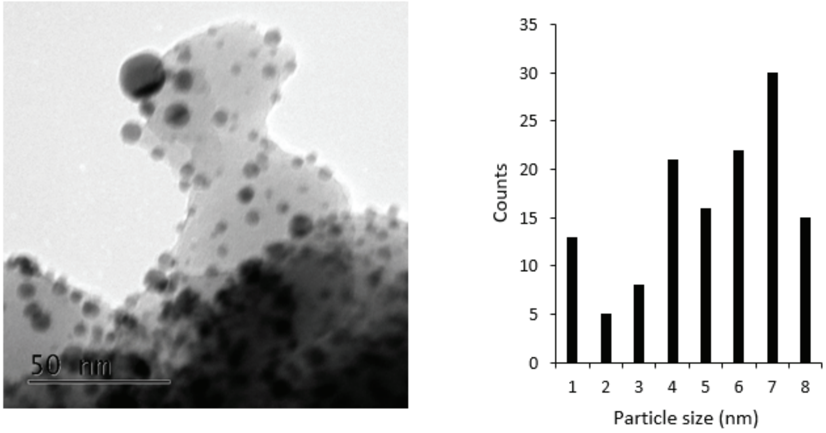

Figure 8. a) Transmission electron microscopy (TEM) and b) particle size distribution (PSD) for used 1% Ru/TiO$_2$ prepared by sol-immobilisation method. Counts: number of occurrences of particles of indicated diameter within the sample assessed.

for an additional 16 h is provided in Table 7. It can thus be observed that, even though the reaction continued after the catalyst was eliminated, the conversion of cyclooctene and epoxide selectivity both decreased markedly from 8.3 to 3% and from 87 to 84%, respectively. Based on this, it can be deduced that the primary catalytic pathway is heterogeneous in nature and homogeneous catalysis is not involved.

Table 7. Heterogeneous versus homogeneous ruthenium catalysis; reaction conditions: 1% Ru/TiO$_2$ (0.1 g), cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), 80 °C, atmospheric pressure air, rate of stirring 800 rpm

Reaction time (h)	Conversion (%)	Epoxide selectivity (%)
8	2	84
24	8.3	87
HF[a]	3	85

[a] *Hot filtration, the catalyst was filtered off after 8 h reaction time and then the reaction was run for another 16 h*

Cyclooctene oxidation did not take place when TBHP was absent, even with 1% Ru/TiO$_2$ catalysis. Consequently, just 0.3% conversion was achieved, whilst epoxide production was nil. Meanwhile, there was low conversion and epoxide selectivity when catalytic amount of TBHP was present. By contrast, the catalytic activity in cyclooctene oxidation increased considerably in the presence of both TBHP and 1% Ru/TiO$_2$. The function played by a small TBHP quantity for oxygen activation with 1% Ru/TiO$_2$ present was determined by employing the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT). This scavenger interacted with radicals and prevented the radical mechanism from propagating, as shown in Table 8. This implies that the reaction was underpinned by radical chemistry. Hence, it appears that free-radical species support the activation of oxygen from the air. The participation of oxygen in the reaction was also revealed by an additional diagnostic experiment, whereby the reaction was performed under N$_2$ atmosphere rather than air. The involvement of molecular oxygen from the air in the oxidation pathway was reflected by the non-detection of epoxide as shown in Table 8. Earlier empirical work employing oxygen from the air as the main oxidant generated comparable findings.

Table 8. Effect of radical scavenger on epoxidation of cyclooctene; reaction conditions: 1% Ru/TiO$_2$ (0.1 g), cyclooctene (75.7 mmol, 10 mL), TBHP (0.064 mmol, 0.01 mL), BHT (0.036 mmol, 7.93 mg), 80 °C, atmospheric pressure air, reaction time 24 h, rate of stirring 800 rpm

Catalyst	Radical initiator	Radical scavenger	Conversion (%)	Epoxide selectivity (%)
1% Ru/TiO$_2$	-	-	0.3	0
-	TBHP	-	2	72
1% Ru/TiO$_2$	TBHP	-	8.3	87
1% Ru/TiO$_2$	TBHP	BHT-	Trace	0
1% Ru/TiO$_2$ under N$_2$	TBHP		0.5	0

Oxidation of different cycloalkenes using supported ruthenium catalyst

Oxidation of cycloalkenes with larger ring size requires the use of higher temperatures, which would make the exact comparison of the reactivity of the cycloalkenes difficult. From Table 9 it can be suggested that cycloalkene with smaller ring size such as cyclopentene at 30 °C was more reactive (8% conversion) toward oxidation compared to cyclohexene at 40 °C (6% conversion). Slightly higher conversion was observed with cyclohexene at 60 °C (11%) compared to cycloheptene (9%) at the same temperature with low epoxide selectivity. Higher temperature was required for oxidation of larger ring sizes such as cyclooctene and cyclododecene. However, the epoxide selectivity was relatively low for the smaller ring sizes as shown in Table 9 and the selectivity to cyclooctane oxide and cyclododecane oxide significantly increased (86 and 64%, respectively).

Table 9. 1% Ru/TiO$_2$ for oxidation of cycloalkenes; reaction conditions: 1% Ru/TiO$_2$ (0.1 g), cycloalkene (10 mL), TBHP (0.064 mmol, 0.01 mL), atmospheric pressure air, reaction time 24 h, rate of stirring 800 rpm

Cycloalkene	Reaction *t* (°C)	Conversion (%)	Selectivity (%)		
			Epoxide	Cy-one	Cy-ol
Cyclopentene	20	2	18	45	21
	30	8	11	45	33
Cyclohexene	40	6	7	54	30
	50	8	6	50	36
	60	11	8	55	33
Cycloheptene	60	9	16	45	37
	70	11	20	48	33
Cyclooctene	70	5	77	11	9
	80	8.3	87	5	7
Cyclododecene	120	12	64	22	11

CONCLUSION

The results indicated that, when oxygen from air was used as the primary oxidant under the temperature condition of 80 °C, the supported Ru catalysts were active in the solvent-free epoxidation of cyclooctene. Within the selected conditions, high conversion in cyclooctene epoxidation and epoxide selectivity were achieved by using catalytic amount of TBHP as radical initiator alongside supported ruthenium catalysts. A hot filtration experiment underlined the heterogeneous nature of the supported ruthenium catalyst.

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NAUČNI RAD

OKSIDACIJA CIKLOALKENA RUTENIJUMSKIM KATALIZATORIMA NANETIM NA NOSAČE U USLOVIMA BEZ RASTVARAČA

Ovaj rad koristi nanočestice rutenijuma nanetim na nosače i katalitičke količine inicijatora radikala, za koje je dokazano da mogu da oksiduju ciklookten u zelenim uslovima, u odsustvu rastvarača, sa vazduhom kao glavnim oksidacionim agensom i bez štetnog redukcionog agensa. U radu se istražuju efekti niza inicijatora radikala i raspodela proizvoda tokom vremena. Nadalje, rad se bavi reakcionim putevima do epoksida i alil alkohola, koji je primarni nusproizvod; takođe, analizira se uticaj tehnike sinteze, vremena reakcije i raznih nosača. Aktivnost katalizatora može da se značajno poboljša primenom tehnike sol-imobilizacije za sintezu katalizatora, uz zadržavanje selektivnosti u odnosu na epoksid.

Ključne reči: oksidacija ciklooktena, epoksid, rutenijumski katalizator, sol-imobilizacija.