

Ruthenium Nanoparticles Immobilized on Nano-silica Functionalized with Thiol-Based Dendrimer: A Nanocomposite Material for Oxidation of Alcohols and Epoxidation of Alkenes

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Abstract

In this work, ruthenium nanoparticles were immobilized on thiol-based dendrimer functionalized nano-silica and its catalytic activity was investigated in the oxidation reactions. To do this, silica nanoparticles were functionalized with a thiol-based dendrimer, and this dendritic material was used as a host for immobilization of ruthenium nanoparticles as guest species. Different analytical tools such as FT–IR and UV–vis spectroscopies, CHNS, ICP and TGA analyses, and TEM and SEM microscopic techniques were used to characterize the prepared catalyst. The catalytic activity of this nanocomposite material as a heterogeneous catalyst was studied in the epoxidation of alkenes and oxidation of alcohols with *tert*-butyl hydroperoxide (*tert*-BuOOH) and the corresponding products were obtained in good to excellent yields. Moreover, this catalyst can be well-dispersed in the reaction medium, conveniently separated from the reaction mixture, and reused several times without significant loss of its activity.

Graphical Abstract

Ru_{np}-nSTDP provided a highly stable, active, reusable, and solid-phase catalyst for preparation of a series of epoxides and aldehydes.



Keywords Ruthenium nanoparticles · Thiolated dendrimer · Reusable catalyst · Nanocomposite · Oxidation reaction

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1 Introduction

Application of transition metal nanoparticles has received much attention in the field of catalysis [1]. But these nanoparticles should be stabilized by various methods such as using ionic liquids [2], polymers [3], low molecular weight [4] and macromolecular organic ligands [5]. Dendrimers are tree- like hyper branched macromolecular polymers in

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which their size depends on the generation [6]. One of the most useful applications of dendrimers is their ability in the stabilization of nanoparticles in solution by their internal functional groups that act as coordination sites for nanoparticles [7, 8].

Epoxidation of alkene is an important reaction in organic synthesis because epoxides as useful starting materials in the synthesis of fine chemicals [9]. For example, cyclohexene oxide is an important organic intermediate for production of pharmaceuticals, plant-protection agents, pesticides, and stabilizers for chlorinated hydrocarbons [10]. In this way, a wide variety of homogeneous catalysts have been reported for epoxidation of alkenes [11–17]. But catalysis under homogeneous conditions suffers from disadvantages such as difficulty in the catalyst recovery and reuse and also contamination of the reaction media with metal species. Application of heterogeneous catalysts instead of homogeneous ones can solve the above mentioned problems [18, 19]. For example nanosilica supported metal nanoparticles have been used as catalysts in organic reactions [20–23].

Another important reaction in organic synthesis is oxidation of alcohols to aldehydes or ketones [24, 25], or their complete oxidation to carboxylic acids [26–29]. Also, these reactions are of interest for the development of environmentally benign processes [30, 31], production of new materials [32, 33] and energy sources [34, 35].

Ruthenium catalysts have been used in many reactions such as *cis*-dihydroxylation and oxidative cleavage of alkenes [36], Heck-type olefination and Suzuki coupling reactions [37], conversion of nitriles to amides [38], hydrogenation of quinolone [39], oxidative Wittig coupling reactions [40], semihydrogenation of alkynes [41], transfer hydrogenation of carbonyl compounds [42] and oxidation reactions [43].

Recently, we reported the application of dendritic materials containing metals nanoparticles and metal complexes in organic synthesis [44–51]. By combination of the potential activity of ruthenium nanoparticles in the oxidation reactions [52–57] and also the ability of dendrimers in stabilizing the nanoparticles [58, 59], here we wish to report the preparation, characterization and investigation of catalytic activity of ruthenium nanoparticles supported on nano–silica functionalized with a thiol-based dendrimer in the alkene epoxidation and oxidation of alcohols with *tert*-BuOOH (Scheme 1).

2 Experimental Section

2.1 General Remarks

The chemicals used were purchased from Fluka and Merck chemical companies. FT-IR spectra were recorded on a



Scheme 1 Alkene epoxidation and alcohol oxidation with *tert*-BuOOH catalyzed by Ru_{np} -nSTDP

Jasco 6300D spectrophotometer. Diffuse reflectance UV-vis (DR UV-vis) spectra were obtained on a JASCO V-670 spectrophotometer. The SEM and TEM images were taken by a Hitachi S-400 field emission-scanning electron microscope (FE-SEM) and a Philips CM10 Transmission Electron Microscope operating at 100 kV, respectively. BET measurements were performed using Micromeritics TriStar II Plus. Thermogravimetric analysis was carried out with a TG 50 Mettler thermogravimetric analyzer, under nitrogen flow at a uniform heating rate of 20 °C min⁻¹ in the range of 30-900 °C. The Ru content of the catalyst was determined by a Jarrell-Ash 1100 ICP analysis. The X-ray photo-electron spectroscopy (XPS) measurements were performed using a Gamma data-scienta ESCA200 hemispherical analyzer equipped with an Al (K α = 1486.6 eV) X-ray source. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument equipped with a FID detector using a 2 m column packed with silicon DC-200 or Carbowax 20M. The GC yields were calculated by the "internal standard addition" method and in this manner; n-decane was used as internal standard. All products were isolated and characterized by ¹H NMR spectroscopy.

2.2 Preparation of Nano-silica Thiolated Dendritic Polymer Supported Ruthenium Nanoparticles (Ru_{np}-nSTDP)

Ruthenium(III) chloride (50 mg) was added to a suspension of nano-silica supported dendrimer (200 mg) in distilled water (100 ml). The suspension was rapidly turned black. The reaction mixture was stirred at room temperature for 12 h. At the end of reaction, the mixture was evaporated to dryness by a rotary evaporator. The obtained powder was suspended in a mixture of EtOH (50 ml) and water (10 ml). Then, NaBH₄ (90 mg) was added to the resulting slurry and the reaction mixture was stirred at room temperature for 12 h. After then, the solvent was evaporated and the obtained dark grey powder washed twice with water and ethanol and dried under air. The nano–silica thiol–based dendritic polymer (nSTDP) was prepared according to our recently reported procedure [51].

2.3 General Procedure for Epoxidation of Olefins with *tert*-BuOOH Catalyzed by Ru_{np}-nSTDP

The catalytic oxidation reactions of alkenes were carried out in a 25 ml flask equipped with a magnetic stirrer and a reflux condenser. In a typical run, the reaction vessel was charged with ruthenium catalyst (40 mg, 0.84 mol %), CH₃CN (5 ml), substrate (0.5 mmol) and *tert*-BuOOH (1 mmol). The reaction mixture was refluxed in an oil bath at 80 °C and its progress was monitored by GC. At the end of the reaction, the catalyst was removed by simple filtration and washed with the adequate amount of acetonitrile (5 ml) and H₂O (5 ml). Later on, the products were extracted with Et₂O and purified on a silica gel column (Et₂O/*n*-hexane: 4:1).

2.4 General Procedure for Oxidation of Alcohols with tert-BuOOH Catalyzed by Ru_{np}-nSTDP

Ru_{np}-nSTDP (40 mg, 0.84 mol %) were stirred in 5 mL of acetonitrile taken in a round bottomed flask equipped with a condenser and a stirring bar. The substrate (0.5 mmol), oxidant (1 mmol) was added to the stirring solution, and then the mixture was refluxed at 80 °C under atmospheric pressure of air. The reaction progress was monitored by GC. After completion of the reaction, the nanocatalyst was separated from the reaction mixture by simple centrifugation, washed with the adequate amount of acetonitrile (5 ml) and H₂O (5 ml). Later on, the products were extracted with Et₂O and purified on a silica gel column.

3 Results and Discussion

3.1 Synthesis and Characterization of Ru Nanoparticles Immobilized on Nano–Silica Thiol–Based Dendritic Polymer

Very fine metal particles have found numerous applications in catalysis. When very fine particles are desired, stabilizing agents must be used to prevent growth of primary particles by agglomeration. This stabilization can be provided by polymers or by surfactants such as thiols and amines with long alkyl chains. Supporting of metal nanoparticles with alkanethiol and more generally by an appropriate surfactant allowed in several cases the formation of self-assembled arrays [58]. Therefore, we decided to use a thiol–containing dendritic material for supporting and stabilizing of Ru nanoparticles. After preparation and characterization of nSTDP [51], the ruthenium nanoparticles were immobilized onto this dendritic polymer by reduction of ruthenium(III) chloride with sodium borohydride at room temperature (Scheme 2).

Ruthenium nanoparticles immobilized on nano-silica thiol-based dendritic polymer (Ru_{np}-nSTDP) was characterized by different analytical techniques.

The DR UV–vis spectrum of nSTDP and Ru_{np} –nSTDP are depicted in Fig. S1. The dendrimer shows one peak at 203 nm while nano ruthenium catalyst shows three peaks at 214, 262 and 397 nm. On the other hand, the solution of RuCl₃ has a peak at 494 nm. These observations imply that the Ru³⁺ has completely reduced to Ru⁰ [59].

The FT–IR spectroscopy was also used to characterize the nSTDP and Ru_{np} –nSTDP (Fig. 1). The FT–IR spectrum of the nSTDP showed a broad O–H stretching band at 3200–3400 cm⁻¹ and a strong Si–O–Si stretching band about 1000–1100 cm⁻¹. Also, the characteristic bands for C–H_{aliph} appear at 1450 and 2950 cm⁻¹. The appearance of bands at 1690–1710 cm⁻¹ (C=O) is a good indication for the presence of carbonyl groups on the nano-silica [51]. All these bands are also observed for Ru_{np} –nSTDP. The vibration of S–H bonds was not observed in the FT–IR spectra both materials. Therefore, it is difficult to judge about the presence of Ru nanoparticles in the catalyst texture, we preferred to anchor the Ru nanoparticles to thiol groups.

Further characterization of Ru_{np} -nSTDP was performed by thermogravimetric analysis (Fig. S2). The weight loss of nSTPD and catalyst as a function of temperature in the range of 30 to 900 °C showed that organic weight loss of nSTPD and the Ru_{np} -nSTDP were 74 and 70%, respectively. This indicates that the amount of organic material decreased upon attachment of nano ruthenium to nSTPD.

The size and surface morphology of nSTDP and Ru_{np} -nSTDP were studied by FE–SEM analysis (Fig. S3 A and B). As clear in both images, the particles are spherical and their sizes are in the range of 40–70 nm.

The energy dispersive X-ray (EDX) results obtained from SEM analysis for the nSTDP and clearly show the presence of constituent elements (Si, O, C and S) in the dendrimer texture (Fig. S3 C). Upon reaction of nSTDP with Ru nanoparticles, the peak correspond to Ru appears in EDX spectrum (Fig. S3 D).

Also, the elemental mapping of Ru_{np} -nSTDP shows the uniform and homogenous dispersion of C, Si, O, S and Ru elements in the catalyst texture (Fig. S4).

Further characterization of Ru_{np} -nSTDP catalyst was performed by TEM analysis (Fig. 2). The TEM images of Ru_{np} -nSTDP showed well-defined spherical Ru particles (dark spots) dispersed in nSTDP. The size of Ru nanoparticles was about 2.0±0.5 nm (Fig. 3), indicating that







Fig.1 FT–IR spectrum of: (A) nSTDP (dendrimer) and (B) Ru_{np} – nSTDP (nano catalyst)



Fig. 2 TEM images of Ru_{np}-nSTDP catalyst



Fig. 3 Particle size distribution results for Ru_{np}-nSTDP catalyst



Fig. 4 XPS spectrum of Ru_{np}-nSTDP catalyst

ruthenium nanoparticles did not aggregate upon complexation with nSTDP.

The ICP analysis was used to determine the ruthenium content of catalyst which showed a value of about 0.21 mmol Ru/g $(1.265 \times 10^{20} \text{ atom/g})$ of heterogeneous catalyst. From the TEM size distributions, one can obtain the average core diameter (*D*) of the nanoparticles. The total number of atoms per a Ru nanoparticle (N_{Ru}) can then be calculated using Eq. (1), in which *d* is the density of ruthenium (72 atoms nm⁻³) [44].

$$N_{Ru} = d\left(\frac{\pi}{6}\right)D^3\tag{1}$$

In this work, the average core diameter (D) is about 2 nm. Therefore, the value of N_{Ru} is 3×10^2 atoms in a hypothetical nanoparticle. By considering of the results of ICP analysis, the number of Ru nanoclusters is about 4.22×10^{17} per gram of catalyst.

In the XPS elemental survey scans of the surface of Ru_{np} -nSTDP the peaks corresponding to carbon and ruthenium are detected (Fig. 4). The RuNPs showed a Ru $3d_{5/2}$ peak at 280.8 eV which was attributed to metallic Ru [58]. The calibration was performed with the C1s peak (E = 284.5 eV).

Figure 5 shows the BE for Ru $3p_{3/2}$ at 461.6 eV and Ru $3p_{1/2}$ at 484.2 eV, which corresponds to the photoemission from metallic Ru [60].

 N_2 adsorption-desorption isotherm analysis (Fig. 6) provided information on the specific surface area and porosity of the prepared samples. The specific surface area values, the average pore diameter (according to BET method) and total pore volume were listed in Table 1. According to the BET isotherm, the active surface area of nSTDP and Ru_{np} -nSTDP was estimated to be 14.43 and 9.12 m²/g, respectively (Table 1). The very less amount adsorbed/desorbed N_2 and the absence of hysteresis



Fig. 5 XPS spectrum of Ru_{np}-nSTDP catalyst



Fig.6 $N_{\rm 2}$ adsorption–desorption isotherms of nSTDP and $Ru_{\rm np}\text{-}$ nSTDP

Table 1 BET results for nSTDP and Runp-nSTDP^a

Entry	Material	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)
1	nSTDP	14.43	0.050	13.8
2	Ru _{np} -nSTDP	9.12	0.035	10.24

^aCalculated by the BET method

suggests that the pores of nSTDP and Ru_{np} -nSTDP have been completely blocked [61].

3.2 Alkene Epoxidation with *tert*-BuOOH Catalysed by Ru_{np}-nSTDP

After preparation and characterization of the Ru nanocatalyst, its catalytic activity was investigated in the epoxidation of olefins with *tert*-BuOOH. To obtain the optimized reaction conditions, the ability of different oxidants such as, NaIO₄, *tert*-BuOOH and H₂O₂ was examined in the epoxidation of cyclooctene at 80 °C, and *tert*-BuOOH gave the best epoxide yield (Table 2, entries 1–3). Also, different amount of the catalyst were used in the model reaction, and the higher conversion was observed with 40 mg (0.84 mol%) of heterogeneous catalyst. Note that in the absence of catalyst only 5% of the corresponding epoxide was detected. Also, when nSTDP (without Ru nanoparticles) was used as catalyst, the result was as same as the reaction in the absence of catalyst (entries 7–11).

Different solvents, such as chloroform, ethanol, acetone, acetonitrile and methanol were examined for the oxidation of cyclooctene by *tert*-BuOOH. Among the studied solvents, acetonitrile was found to be the best one (entries 3, 12–15). The effect of reaction temperature was also investigated and the 80 °C was the optimum reaction temperature (entries 3-6).

Under the optimized reaction conditions, different alkenes were oxidized with *tert*-BuOOH and in the presence of the Ru_{nn} -nSTDP catalyst (Table 3).

Our experimental results showed that the Ru_{nn}-nSTDP/ TBHP catalytic system is able to epoxydize several alkenes to their corresponding epoxides in good to excellent yield (Table 3). Cyclooctene and Cyclohexene were converted to their corresponding epoxides in high yields and 100% selectivity (entries 1 and 2). Styrene was epoxidized in 80% yield. The by product in this system was benzaldehyde (5%) produced via ring opening reaction of the corresponding epoxide. Epoxidation of linear alkenes such as 1-heptene. 1-octene and 1-dodecene was also carried out and the corresponding epoxides obtained in good yields and high epoxide selectivity (entries 4-6). The location of the double bond is also known to have an influence on the rate of epoxidation. On the basis of inductive effects of alkyl groups on the double bond, a higher intrinsic activity is expected for an internal double bond. However, the differences in reactivities between the internal alkenes and the terminal alkenes tested is lower than would be expected purely on the basis of electronic effects, It is therefore assumed that steric factors also play a role. Also it is expected that more highly substituted C=C double bonds are more reactive [62].

Comparison of the catalytic activity of Ru_{np} -nSTDP with some of previously reported ruthenium based catalysts in the epoxidation of cyclooctene showed that Ru_{np} -nSTDP/*tert*-BuOOH catalytic system is more efficient than the others in terms of catalytic activities (higher TOFs values), reaction times or reusability (Table 4). This higher catalytic activity can be attributed to the dispersion of ruthenium nanoparticles on the nanosilica tiolated dendrimer which isolate the catalytic active.

The plausible mechanism is shown in Scheme 3. First, the Ru nanoparticles are oxidized upon reaction with *tert*-BuOOH (This confirmed by the XPS analysis of the recovered catalyst). This ruthenium oxide species produced the *tert*-BuOO[•] radicals (This also approved by addition of 2,6-di-*tert*-buthylphenol as radical scavenger which stopped the reaction). Reaction of these radicals with alkene gives

			1.			
Entry	Catalyst (mmol)	Oxidant	solvent	Yield $(\%)^{a}$	T (°C)	
1	0.0084	NaIO_4	CH ₃ CN/H ₂ O	54	80	
2	0.0084	H_2O_2	CH ₃ CN	73	80	
3	0.0084	tert-BuOOH	CH ₃ CN	93	80	
4	0.0084	tert-BuOOH	CH ₃ CN	73	60	
5	0.0084	tert-BuOOH	CH ₃ CN	64	40	
6	0.0084	tert-BuOOH	CH ₃ CN	55	RT	
7	0	tert-BuOOH	CH ₃ CN	5	80	
8	nSTDP	tert-BuOOH	CH ₃ CN	5	80	
6	0.0042	tert-BuOOH	CH ₃ CN	50	80	
10	0.0063	tert-BuOOH	CH ₃ CN	70	80	
11	0.0105	tert-BuOOH	CH ₃ CN	93	80	
12	0.0084	tert-BuOOH	CHCl ₃	44	80	
13	0.0084	tert-BuOOH	EtOH	78	80	
14	0.0084	tert-BuOOH	Acetone	75	80	
15	0.0084	tert-BuOOH	MeOH	80	80	
Reaction conditions ^a GC yield based on	: Cyclooctene (0.5 mmol), <i>tert</i> –BuC the starting cyclooctene	OH (1 mmol), catalyst, solvent	(5 ml)			

Table 2 Optimization of the reaction parameters in the epoxidation of cyclooctene by Ru_{np} -nSTDP after 4 h

Table 3 Epoxidation of alkenes with tert-BuOOH catalyzed by Ru_{np}—nSTDP



13.84
13.39
11.90
10.32
7.93 8.47

Reaction conditions: alkene (0.5 mmol), tert-BuOOH (1 mmol), catalyst (40 mg, 0.84 mol%), CH₃CN (5 ml)

^aGC yield based on starting alkene

^bYield in the parenthesis refers to isolated yield

^cThe by–product is benzaldehyde (5%)

Table 4	Comparison of the catal	vtic activity of Ru	-nSTDP with some of	previously re	eported sy	stems in the e	poxidation of c	vclooctene
Table I	comparison of the cuta	gue deurity of fun	noibi with some of	previously re	ported by	Sterns in the e	pomaution of c	, croocteric

		r					
Row	Catalyst amount (mmol)	Cyclooc- tene (mmol)	Oxidant	Time (h)	$TOF(h^{-1})$	Yield (%) after 4th run	References
Ru Salophen@Zeolite	0.01	0.5	NaIO ₄	5	10.25	32	[63]
[Ru(salophen)–PSI]	0.025	0.5	NaIO ₄	4	4.70	86	[64]
[Ru(salophen)–SiIm]	0.026	0.5	NaIO ₄	3	6.33	82	[65]
[Ru(salophen)–Amine–PS]	0.067	1	NaIO ₄	5	2.44-2.95	79	[<mark>66</mark>]
Achiral molybdenum(VI) dioxo complex supported on MCM-41	0.0087	8	tert-BuOOH	24	1.07	25 (3rd run)	[67]
Chiral molybdenum(VI) dioxo com- plex supported on MCM-41	0.0087	8	tert-BuOOH	24	1.14	22 (3rd run)	[63]
Ru-thiolated nano silica dendrimer	0.0084	0.5	tert-BuOOH	4	13.8	81	This work

the intermediate **I** which in the next step produces the epoxide and releases the catalyst for the next catalytic cycle.

3.3 Oxidation of Alcohols with *tert*-BuOOH Catalysed by Ru_{np}-nSTDP

The high catalytic activity of Ru_{np} -nSTDP/tert-BuOOH catalytic system in the epoxidation of alkenes encouraged us to investigate its catalytic activity in the oxidation of alcohols. In this manner, benzyl alcohol was used as

model substrate and the reaction conditions such as kind of oxidant (Table 5, entries 1–3), amounts of catalysts (entries 7–11), kind of solvent (entries 3, 12–15) and also the reaction temperature (entries 3–6) were optimized in this reaction (Table 5).

As can be seen from the results in Table 5, the optimized reaction conditions are substrate, oxidant and catalyst in a molar ratio of 10,000, 20,000 and 168, respectively in refluxing acetonitrile.



Scheme 3 Proposed mechanism for alkene epoxidation

Under the optimized reaction conditions, different benzylic alcohols were subjected to oxidation with Ru_{np}-nSTDP/tert-BuOOH catalytic system and the corresponding aldehydes were produced in high yields (Table 6). It is noteworthy that the nature of substituent on the phenyl ring has no obvious effect on the yield of the product. 1-Hexanol and cyclohexanol as linear and cyclic alcohols were successfully oxidized to their corresponding carbonyl compounds.

The proposed mechanism for oxidation of alcohols is as shown in Scheme 4. Since the oxidation of alcohols is an oxidation-reduction reaction, first, the Ru nanoparticles are oxidized to Ru oxide species with tert-BuOOH. Then, the alcohol is attached to the Ru oxide species via an addition step to produce the intermediate I which in turn releases H₂O and give the intermediate II. This intermediate is converted to final product and releases the Ru⁰ catalyst for the next catalytic cycle.

3.4 Catalyst Reusability

The main advantage of a heterogeneous catalyst is its recyclability and reusability. These parameters are of great importance from economic, environmental and industrial points of view. Therefore, the reusability of the Ru_{nn}-nSTDP was checked in the epoxidation of cyclooctene and also oxidation of benzyl alcohol with tert-BuOOH under the optimized reaction conditions. After each catalytic cycle, the catalyst was easily separated from the reaction mixture by centrifugation and used in the next run after washing with ethanol, H₂O and acetonitrile, and drying in an oven at 60 °C. The results, which are shown in Fig. 7, showed that the catalyst could be reused several times in both catalytic reactions without significant loss of its initial activity. The ruthenium content of the catalyst after fourth run was measured by ICP which showed a value of about 0.20 mmol/g (about 95% of the initial Ru content) for the catalyst used in the oxidation of benzyl alcohol and 0.198 mmol/g (about 94% of the initial Ru content) for the catalyst used in the epoxidation of cyclooctene. The filtrates after each run were used for determination of the amount of Ru leaching. The

Table 5 Optimization ofconditions in the oxidation of	Entry	Catalyst (mmol Ru)	Oxidant	Solvent	Yield (%) ^a	T (°C)
benzyl alcohol catalyzed by	1	0.0084	NaIO ₄	CH ₃ CN /H ₂ O	50	80
Ru _{np} –nSTDP	2	0.0084	H_2O_2	CH ₃ CN	65	80
	3	0.0084	tert-BuOOH	CH ₃ CN	90	80
	4	0.0084	tert-BuOOH	CH ₃ CN	48	RT
	5	0.0084	tert-BuOOH	CH ₃ CN	59	40
	6	0.0084	tert-BuOOH	CH ₃ CN	71	60
	7	0	tert-BuOOH	CH ₃ CN	6	80
	8	nSTDP	tert-BuOOH	CH ₃ CN	7	80
	9	0.0063	tert-BuOOH	CH ₃ CN	60	80
	10	0.0105	tert-BuOOH	CH ₃ CN	90	80
	11	0.0126	tert-BuOOH	CH ₃ CN	90	80
	12	0.0084	tert-BuOOH	CHCl ₃	48	80
	13	0.0084	tert-BuOOH	EtOH	80	80
	14	0.0084	tert-BuOOH	Acetone	75	80
	15	0.0084	tert-BuOOH	MeOH	81	80

Reaction conditions: benzyl alcohol (0.5 mmol), tert-BuOOH (1 mmol), catalyst, solvent (5 ml)

^aGC yield based on the starting benzyl alcohol

 Table 6
 Result of alcohol oxidation with tert-BuOOH catalyzed by Ru_{np}-nSTDP

Alcohol CH ₃ CN/ <i>tert</i> -BuOOH, 80 °C, 3 h						
Entry	Alcohol	Yield (%) ^{a,b}	TON	TOF (h ⁻¹)		
1	C ₆ H ₅ CH ₂ OH	90 (87)	53.57	17.85		
2	4-CH ₃ C ₆ H ₄ CH ₂ OH	92 (90)	54.76	18.25		
3	4-ClC ₆ H ₄ CH ₂ OH	91 (88)	54.17	18.05		
4	4-FC ₆ H ₄ CH ₂ OH	82 (80)	48.80	16.27		
5	4-BrC ₆ H ₄ CH ₂ OH	84 (81)	50.00	16.67		
6	4-NO ₂ C ₆ H ₄ CH ₂ OH	88 (86)	52.38	17.46		
7	3-CH ₃ OC ₆ H ₄ CH ₂ OH	89 (86)	52.98	17.66		
8	2-NO ₂ C ₆ H ₄ CH ₂ OH	89 (85)	52.98	17.66		
9	2,4-Cl ₂ C ₆ H ₃ CH ₂ OH	84 (81)	50.01	16.67		
10	1-Hexanol	60 (55)	35.71	11.90		
9	Cyclohexanol	68 (64)	40.48	13.49		

 Ru_{nn} -nSTDP (0.84 mol%)

Reaction conditions: alcohol (0.5 mmol), tert-BuOOH (1 mmol), catalyst (40 mg, 0.84 mol%), CH₃CN (5 ml)

^aGC yield based on starting alcohol

^bThe yields in the parenthesis refer to isolated product



Scheme 4 The proposed mechanism for oxidation of alcohols with *tert*-BuOOH

results, which are summarized in Table 7, showed that after second run, no Ru was leached in both catalytic reactions.

The hot filtration test was also carried out in the oxidation of benzyl alcohol. In this manner, the hot reaction mixture was centrifuged at about 50% conversion to remove the solid particles. The filtrates were stirred under the same conditions obtained in the presence of catalyst. The results showed that the reaction was completely stopped (Fig. 8).



Fig. 7 The results of nano Ru catalyst recovery in the Blue square oxidation of benzyl alcohol and orange square epoxidation of cyclooctene with *tert*-BuOOH

The possibility of the presence of induction period in the oxidation of benzyl alcohol was investigated. The reaction profiles (Fig. 8) showed no obvious induction period in this reaction.

The nature of recovered catalyst was studied by XPS spectroscopy (Fig. 9). Ru(IV) oxides have a typical Ru 3d binding energy at 282.2 eV [68, 69]. The peak at 286.1 eV might be attributed to ruthenium oxide [70]. The signals beyond C1s peak at 285 eV are attributable to the Ru $3d_{3/2}$ of higher oxidation species [58, 71]. TEM of reused catalyst is shown in Fig. 10. As can be seen the catalyst do not aggregate.

 Table 7
 Leaching of the Ru_{np}

 nSTDP catalyst in the recycling
 of epoxidation reaction of

 cyclooctene in 4 h and oxidation
 reaction of benzyl alcohol after

 3 h
 h

Ru leached (%) ^c						
Run	Epoxidation reaction	Oxida- tion reac- tion				
1	3	3				
2	3	3				
3	0	0				
4	0	0				

Reaction conditions: alkene (0.5 mmol), *tert*-BuOOH (1 mmol), Ru_{np} -nSTDP (40 mg, 0.84 mol %), CH₃CN (5 mL) at 80 °C

^bReaction conditions: alcohol (0.5 mmol), *tert*-BuOOH (1 mmol), Ru_{np} -nSTDP (40 mg, 0.84 mol %), CH₃CN (5 ml) at 80 °C

^cDetermined by ICP analysis



Fig. 8 The results of (A) time-yield and (B) hot filtration of benzyl alcohol oxidation

4 Conclusion

In summary, we present a new heterogeneous catalytic system containing ruthenium nanoparticles immobilized on nano-SiO₂ functionalized with thiolated dendrimer, and investigated its catalytic activity in alkene epoxidation reaction and oxidation of benzyl alcohol derivatives. Our experimental results showed that the proposed catalyst is able to oxidize several alkenes to their corresponding epoxides in good to excellent yield. Also, in the oxidation of benzyl alcohols, the corresponding aldehydes were produced in good to excellent yields. Moreover, this catalyst can be well-dispersed in the reaction medium,



Fig. 9 XPS spectrum of reused Ru_{np}-nSTDP catalyst



Fig. 10 TEM of reused Ru_{np}-nSTDP catalyst

conveniently separated from the reaction mixture, and reused several times without significant loss of their activity.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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