Highly Selective Cycloalkane Oxidation in Water with Ruthenium Nanoparticles

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Ruthenium(0) nanospecies, with small sizes of approximately 1.75 nm, proved to be active, selective, and retrievable nanocatalysts for the oxidation of various cycloalkanes in neat water, using tert-butylhydroperoxide as an oxidant and at room temperature. Relevant conversions and selectivities (up to 97%) were achieved towards the major formation of the ketone product, which constitutes a high-value-added intermediate for polymer or fine chemistry. The lifetime of the catalyst has been checked over several runs, with no significant loss of activity and selectivity. Kinetic and mechanistic investigations proved that radical species are involved in the oxidation process. A literature comparison showed the relevance and the usefulness of the present ruthenium nanocatalytic system in a benign reaction context.

Introduction

The selective oxidation of saturated hydrocarbons constitutes an outstanding value-creating synthetic strategy, ranging from the production of fine chemicals to the replacement of current petrochemical feedstocks by less expensive and more readily available alkanes.[1–3] The ensued oxygenated molecules could be used as building blocks in various branches of the chemical industry, ranging from polymer synthesis to medicinal chemistry.[4] In particular, cyclohexane oxidation remains a large-scaled industrial process, producing approximately 10^6 ton per year of cyclohexanone and cyclohexanol, also known as K-A oil,[5] which are mostly used in the manufacture of nylon-6 and nylon-6,6.[6] However, this process is among the least efficient industrial chemical processes, owing to the difficulty in controlling the selectivity toward the target products.[7] In the present cobalt-catalyzed industrial process, a very low conversion of less than 5% is preferentially required to achieve a 80% selectivity to K-A oil and to avoid the deep oxidation into over-oxidized by-products.[8,9] Therefore, in recent years, many research efforts have been devoted towards the search of alternative and more environment-friendly methodologies to achieve a high conversion in cyclohexane oxidation, while maintaining selectivity and reducing energy consumption.[10–13]

In that context, nanoheterogeneous catalysis could constitute a pertinent approach in the quest towards more sustainable processes for these oxidation transformations. In fact, nanometer-sized particles have been intensively pursued as potentially advanced catalysts owing to their outstanding intrinsic properties.[14–16] Besides their potential recovery potentialities, they could provide relevant catalytic activities owing to a high number of surface-exposed metal atoms and enhanced selectivities owing to a good shape control during the synthesis.[17–19] As a consequence, metallic nanospecies have found great applications in various catalytic reactions, such as hydrogenation, carbon–carbon coupling or oxidation reactions.[20,21] Over the last decade, fewer nanocatalysts,[22–25] such as Fe and/or Co nanostructured catalysts, supported gold nanoparticles or Au–Pd alloys, have been reported for the selective cyclohexane oxidation, but still suffer from low conversions and/or recyclability owing to metal leaching.

Herein, we report the use of ruthenium(0) nanospecies as catalysts in the liquid-phase oxidation of various cycloalkanes into the high-value-added ketone/alcohol products under mild conditions, in neat water as a suitable industrial green solvent (Scheme 1).[26] The tert-butylhydroperoxide (t-BHP) has been
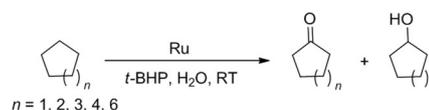
Scheme 1. Ru-catalyzed oxidation of various cycloalkanes in neat water.

chosen as an oxidant because it has emerged as a suitable oxidant for cyclohexane oxidation, possessing higher solubility than H_2O_2 or molecular oxygen.[27] After optimization of the reaction conditions, kinetic and mechanistic investigations have been performed.

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Results and Discussion

Aqueous suspensions of ruthenium colloids were obtained from ruthenium(III) trichloride hydrate in neat water. The TEM analyses showed the presence of well-dispersed metallic particles with a mean diameter of 1.75 nm and 77% of the nanoobjects between 1.50 nm and 1.75 nm (Figure 1 a,b). The ruthenium colloids have been further identified by high-resolution (HR) TEM experiments (Figure 1 c). The analyses of the fast Fourier transformation of the HRTEM picture mainly revealed the interplanar distances of 0.234, 0.214, and 0.206 nm corresponding to the (1 0 0), (0 0 2), and (1 0 1) planes lattice of ruthenium, respectively. The reduction of the Ru^{3+} species into Ru^0 colloids was checked by UV/Vis spectroscopic analyses, with the displacement of the original peak (398 nm) into blue shifts, as recently reported by Chakraborty et al.[28] This reduction could be assigned to a redox process with water, as reported with rhodium and ruthenium species in high oxidation states.[29]

The Ru^0 colloidal system was evaluated in the cyclohexane oxidation at room temperature (Scheme 2), in the presence of tBHP as oxidant, in a pure biphasic media (water/substrate). The conversion and the selectivity were determined by GC analyses. In this study, we focused on the target products, cyclohexanone 2 and cyclohexanol 3, considering the selectivity towards One/Ol only (cyclohexanone and cyclohexanol). However, other products could potentially be formed, in particular the (tert-butylperoxy)cyclohexane 4, as previously reported in the literature and from our previous works.[30–32] As a reference experiment, no oxidation products were demonstrated in the absence of ruthenium species under typical reaction conditions, proving an expected catalyzed oxidation reaction.

In a first set of experiments, the oxidant ratio was optimized, as well as the addition technique, to achieve relevant conversions and to limit the formation of coproducts (Table 1).

Table 1. Influence of the oxidant ratio and addition on the cyclohexane oxidation.

Entry	Oxidant ratio	Total reaction time [h]	Conv.[c] [%]	Select.[d] [%] 2	3	4	2/3 ratio
1[a]	1.0	4	35	21	5	9	4.2
2[a]	1.5	4	46	30	7	9	4.3
3[a]	3.0	4	71	40	6	25	6.7
4[b]	1×3.0	1.5	68	33	8	27	4.1
5[b]	2×1.5	3	73	43	5	25	8.6
6[b]	3×1.0	4.5	85	56	6	23	9.3
7[b]	6×0.5	9	97	90	–	7	∞

[a] Reaction conditions: cyclohexane (2.23 mmol, 1 equiv.), t-BHP (n× 2.23 mmol, n equiv.), substrate/metal = 125, 3 mL H_2O, 20 °C, 4 h. [b] Reaction conditions: cyclohexane (2.23 mmol, 1 equiv.), t-BHP (6.9 mmol, 3 equiv.), substrate/metal = 125, 3 mL H_2O, 20 °C, 1.5 h per t-BHP addition plus 1.5 h after last t-BHP addition. [c] Conversion = % 2 + % 3 + % 4. [d] Determined by GC analyses.

First, whatever the conditions were, the desired products, cyclohexanone 2 and cyclohexanol 3, were formed, and (tert-butylperoxy)cyclohexane 4 was also identified as a coproduct. Moreover, no reaction occurred without any colloidal ruthenium species, thus clearly showing their catalytic role during the oxidation reaction. In a same manner, in the absence of t-BHP, no oxidation products were observed. The increase in the t-BHP amount, from 1.0 to 3.0 equivalents (Table 1, entries 1 to 3), leads to an improvement of the cyclohexane conversion (up to 71%), but also to a higher amount of coproduct 4. Secondly, to limit its formation, the addition of small quantities of oxidant at regular intervals (1.5 h) was investigated, based on a global amount of 3 equivalents of t-BHP (entries 4 to 7). This study shows that the addition of 6×0.5 equivalents of t-BHP in 9 h leads to a quasi-complete conversion (97%), checked by a good mass balance control, with a high selectivity (90%) towards cyclohexanone (entry 7). It is noteworthy that an increase of the temperature from 20 °C (entry 2) to 75 °C leads to a lower conversion (17%) and selectivity (13%) towards the ketone, probably owing to a more rapid decomposition of the oxidant at higher temperatures.

The durability of the Ru^0 colloidal system was investigated through successive cyclohexane oxidation runs. The results are gathered in Figure 2. Throughout four consecutive runs, con-

Scheme 2. The model cyclohexane oxidation.

Figure 1. a) Transmission electron micrograph (scale bar = 20 nm), b) size distribution histogram of ruthenium colloids, and c) high-resolution transmission electron micrograph (scale bar = 2 nm).
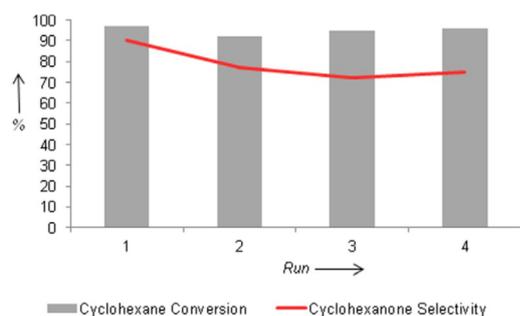
Figure 2. Conversion (columns) and cyclohexanone selectivity (line) as a function of the recycle runs with Ru colloids. Reaction conditions: substrate (2.23 mmol), t-BHP (6×0.5 equiv., 1.5 h per addition), substrate/metal = 125, 3 mL H_2O, 20 °C, 9 h.

versions remained high (>90%) whereas the selectivity towards cyclohexanone slightly decreased and reached an plateau at approximately 75%. TEM imaging after the fourth run revealed that the particle size remains unchanged (1.75 nm), with 57% of the nanoobjects between 1.25 nm and 1.75 nm (Figure 3).
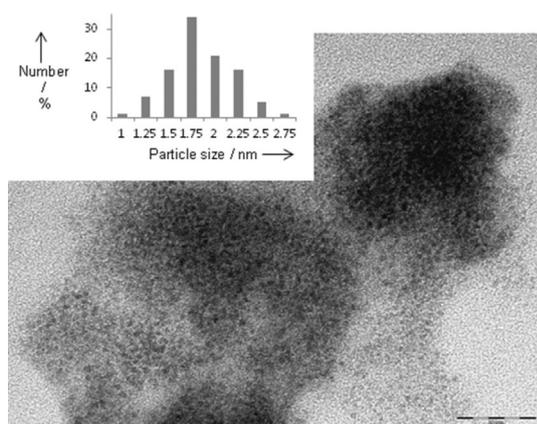
Figure 3. Transmission electron micrograph (scale bar = 20 nm) and the size distribution histogram of Ru^0 colloidal system after the fourth catalytic run.

The scope of the oxidation reaction using the Ru^0 colloidal suspension was extended to other cyclic alkanes possessing 5 to 10 carbon atoms, at room temperature and in neat water (Table 2). Encouraging results in terms of activity and selectivity were obtained for these various substrates. All the substrates studied afforded the corresponding ketones as major product with negligible or no formation of the respective alcohol. However, increasing the size of the ring leads to lower conversions, as also reported in the literature with some catalysts.[23,33] No significant increase in conversion was observed after longer reaction times (Table 2, entries 4 and 7). This result could not be attributed to the higher lipophilicity of the substrate, because adding a mass-transfer agent, such as an ammonium surfactant[34] or a randomly methylated β-cyclodextrin[35] (entries 5, 6), did not increase the conversion. Moreover, for cyclopentane (entry 1), a conversion of 45% was achieved in 24 h of reaction

Table 2. Investigation on various cycloalkanes using optimized reaction conditions.[a]

Entry	Cycloalkane	Conv.[b] [%]	Selectivity[c] [%]		
			Ketone	Alcohol	Alkane[d]
1	cyclopentane[e]	45	37	8	–
2	cyclohexane	97	90	0	7
3	cycloheptane	72	72	–	–
4	cyclooctane[f]	47	47	–	–
5	cyclooctane[g]	46	46	–	–
6	cyclooctane[h]	34	34	–	–
7	cyclodecane[i]	35	35	–	–

[a] Reaction conditions: cycloalkane (2.23 mmol, 1 equiv.), t-BHP (6× 0.5 equiv.), substrate/metal = 125, 3 mL H_2O, 20 °C, 1.5 h per t-BHP addition, total reaction time = 9 h. [b] Conversion = % ketone + % alcohol + % ($tert$-butylperoxy)alkane. [c] Determined by GC Analyses. [d] ($tert$-Butylperoxy)alkane. [e] After 24 h of reaction time. [f] 57% conversion in 24 h [g] In the presence of HEA16Cl (ammonium surfactant). [h] In the presence of a randomly methylated β-cyclodextrin. [i] 35% conversion in 24 h.

time, into the cyclopentanone, an important fine chemical intermediate and mainly used for the production of jasmon. Though the conversion is medium, the Ru^0 colloidal suspension developed in this work seems pertinent, considering the very recent work reported for this substrate.[36]

The reaction kinetic profile (Figure 4) in optimized conditions (6×0.5 equiv. t-BHP, 9 h) showed that the cyclohexanol amount remains limited all over the reaction. The alcohol is a potential intermediate in the reaction, because the cyclohexanol oxidation in similar conditions leads to the formation of the corresponding ketone in 4 h. Moreover, the reaction profile clearly showed an initiation period of 3 h, in which the conversion remains inferior to 10%.

The presence of such an induction time has already been reported in the literature for liquid-phase cyclohexane oxidation.[22,37] This phenomenon could be attributed to an insufficient amount of oxidant at an early stage or to the fact that cyclohexanone (the reaction product) could catalyze the initiation of the autoxidation process.[38] To check these hypotheses,
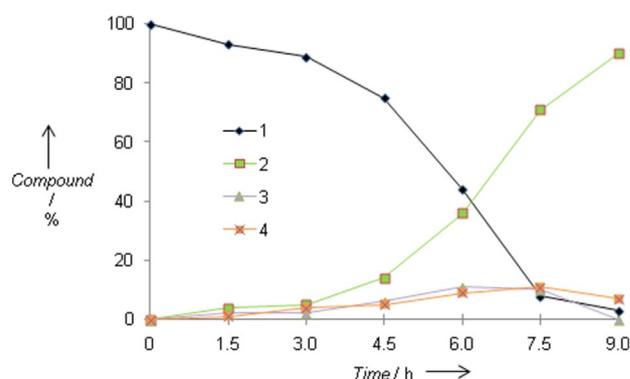
Figure 4. Cyclohexane conversion and product selectivity as a function of time (1 = cyclohexane, 2 = cyclohexanone; **3** = cyclohexanol; **4** = ($tert$-butylperoxy)cyclohexane. Reaction conditions: substrate (2.23 mmol, 1 equiv.), t-BHP (6×0.5 equiv., 1.5 h per addition), substrate/metal = 125, 3 mL H_2O, 20 °C, 9 h.
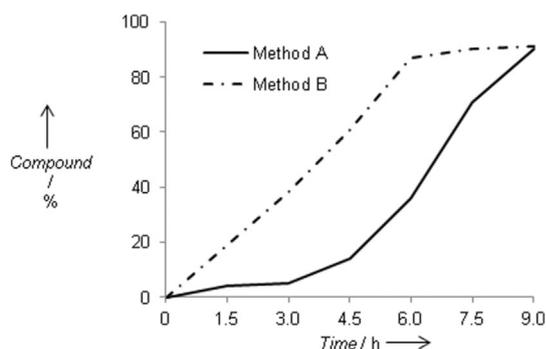
Figure 5. Influence of the oxidant ratio (method A: $0.5 + 5 \times 0.5$ equiv., method B: $1 + 4 \times 0.5$ equiv.).

Scheme 3. Proposed radical mechanism for cyclohexane oxidation with *t*-BHP.

two complementary experiments were performed. In a first experiment, the addition of a higher amount of oxidant at the beginning of the reaction (1 equiv. instead of 0.5, method B vs. method A) leads to an increase in the conversion at the earlier stage with a quite linear conversion (Figure 5).

In a second set of experiments, cyclohexanone (0.1 and 0.5 equiv.) was added to the early stage of the reaction, thus increasing the reaction rate with a linear conversion and no induction time (Figure 6). We demonstrated that the starting amount of *t*-BHP in the reaction mixture was the predominant parameter to control the kinetics of the catalyzed oxidation reaction.

Figure 6. Influence of the addition of cyclohexanone (0.1 and 0.5 equiv.).

In most cases, the reaction pathway for cyclohexane oxidation has been described, in the literature, through a radical mechanism.[39,40] To check the general type of mechanism involved in the catalytic oxidation of cyclohexane with ruthenium(0) colloids, the reaction was performed in the presence of radical traps such as the butylated hydroxytoluene or hydroquinone, which yielded no cyclohexanone product ($<1\%$). This result strongly indicates that the oxidation reaction preponderantly goes through a radical mechanism. Accordingly, a potential radical mechanism of the Ru^0 colloids-catalyzed oxidation of cyclohexane is proposed in Scheme 3. In the initial period of the reaction, the ruthenium active nanospecies catalyze the homolytic decomposition of *t*-BHP, generating the rad-

ical species, the *tert*-butoxyl (*t*BuO$^\bullet$) and *tert*-butylperoxyl (*t*BuOO$^\bullet$) radicals, as already reported in the literature.[27,41] *t*BuO$^\bullet$ abstracts hydrogen from cyclohexane, affording cyclohexyl radicals, which could react with molecular oxygen from air to form the cyclohexylperoxy radicals. The cyclohexyl radical could also react with *tert*-butylperoxyl (*t*BuOO$^\bullet$) radical to afford **4**, as already reported in the literature.[27] With regards to recent literature,[42–44] we could presume that the spontaneous decomposition of the unstable product formed by α-H abstraction of the cyclohexylhydroperoxide by radical species (*t*BuO$^\bullet$ and CyOO$^\bullet$) is the major ketone source and could also explained the formation of alcohol. We could suggest a catalytic mechanism for the cyclohexylhydroperoxide decomposition to ketone, because high cyclohexanone/cyclohexanol ratio were observed.[38] Moreover, in the absence of O_2, a very low yield (4%) of cyclohexanone was observed, proving the role of O_2 in the proposed mechanism. Finally, during the catalytic process, the cyclohexanol **3** could be further oxidized into the corresponding ketone **2** under the investigated reaction conditions.

Finally, the catalytic performances of the ruthenium(0) colloids developed in the present paper were compared with those of heterogeneous catalysts (Table 3), already reported in the literature, considering the cyclohexane oxidation with classical oxidants (*t*-BHP, H_2O_2, O_2). Compared with these various catalytic systems, the present ruthenium(0) nanocatalyst demonstrated promising performances in terms of conversion and selectivity, using an inexpensive organic oxidant (*t*-BHP), at ambient temperature, and in water as a benign and environment-friendly reaction media. Based on these results, our system proved to be an advanced model and thus, this easily prepared, active, stable, and reusable catalyst could be promising to develop more sustainable hydrocarbon compounds oxidations.

Conclusions

An easy-to-handle, stable, and highly efficient ruthenium(0) nanocatalyst has been developed for the oxidation of saturated cyclic hydrocarbons, possessing 5 to 10 carbon atoms, in a pure biphasic (water/substrate) medium. High conversions and nearly quantitative selectivities toward the formation of the high-value-added ketone product were achieved according

Entry	Catalyst	Oxidant	Solvent	T [°C]	Conv. [%]	Ketone [%]	Alcohol [%]	Ref.
1	Ru nanoparticles	t-BHP	H_2O	20	97	90	–	this work
2	Pt/Al_2O_3	t-BHP	CH_3COOH	70	96	4	17	[45]
3	Fe–MIL-101	t-BHP	–	70	38	24	25	[46]
4	H–K–OMS-2	t-BHP	CH_3CN	80	59.9	56.3	34.3	[27]
5	Ru colloids	t-BHP	cyclohexane	20	1.75	64	28	[32]
6	CuPd/TiO_2	H_2O_2	CH_3CN	50	88	61	39	[47]
7	$CuCr_2O_4$	H_2O_2	CH_3CN	50	70	85	–	[23]
8	AuPd/MgO	O_2	–	140	11	37	58	[48]
9	AuPd/MIL-101	O_2	CH_3CN	150	50.8	50.2	27.7	[22]
10[a]	Fe nanowires	O_2	acetone	125	36.7	9.9	19.1	[49]

Table 3. Catalytic activities of different catalysts in the cyclohexane oxidation.

[a] Adipic acid was also observed with 60.5 % selectivity.

to the substrate. Furthermore, the ruthenium(0) colloidal suspension could be easily recovered and reused, maintaining a high activity and selectivity over the recycling experiments under the investigated reaction conditions, which constitutes sine qua non conditions for industrial applications. Mechanistic investigations proved that radical intermediates are likely to be involved in the oxidation reaction. This sustainable and mild route to cyclohexanone production may be a potential alternative to the existing conventional processes.

Experimental Section

Materials

Ruthenium(III) trichloride hydrate, $RuCl_3 \cdot 3H_2O$, was obtained from Strem Chemicals. All cyclic alkanes and the aqueous t-BHP solution (70 %) were purchased from Aldrich or Acros and used without further purification. Water was distilled twice before use through usual method. All the oxidation reactions were performed in a Radleys Discovery Technologies carousel.

Preparation of the colloidal ruthenium suspension

The $RuCl_3 \cdot 3H_2O$ (0.1 mmol) was dissolved in 5 mL H_2O, affording a homogeneous colloidal suspension with 0.02 mol L^{-1} concentration. The so-obtained ruthenium species were directly used in the oxidation reaction.

Catalytic experiments

In a 25 mL reactor, a sample of 892 µL of a 0.02 M colloidal ruthenium suspension (0.01784 mmol) was introduced, in addition to 3 mL of distilled water. Then, cycloalkane (2.23 mmol) was added, giving a substrate/catalyst molar ratio of 125, as well as the desired amount of aqueous t-BHP solution. The reaction mixture was vigorously stirred at RT. At the end of the reaction, the reaction products were extracted with diethyl ether and mass balance controlled. Conversion and selectivity were determined from GC analysis using a Hewlett 5890 (Packard Series II) apparatus with an FID detector, equipped with a O.V.1 capillary column (15 m, inner diameter = 0.32). The injector and detector temperatures were at 250 °C. Products identification was performed by comparison of their retention times with commercial products.

Recycling experiments

For the durability experiments, after reaction, the Ru colloids were extracted from the reaction mixture. The catalytic system was reused for a next run, by adding the desired amount of cycloalkane and aqueous t-BHP solution.

TEM experiments

TEM analyses were performed on a JEOL TEM 100CXII electron microscope at an accelerating voltage of 100 kV. The samples were prepared by the addition of a drop of the ruthenium colloidal solution on a copper grid coated with a porous carbon film. The size distributions were determined through a manual analysis of enlarged micrographs with ImageJ software using Microsoft Excel to generate histograms of the statistical distribution and a mean diameter.

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