

Review

Cyclohexane oxidation continues to be a challenge

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Abstract

Many efforts have been made to develop new catalysts to oxidize cyclohexane under mild conditions. Herein, we review the most interesting systems for this process with different oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide and molecular oxygen. Using H₂O₂, Na-GeX has been shown to be a most stable and active catalyst. Mesoporous TS-1 and Ti-MCM-41 are also stable, but the use of other metals such as Cr, V, Fe and Mo leads to leaching of the metal. Homogeneous systems based on binuclear manganese(IV) complexes have also been shown to be interesting. When *t*-BuOOH is used, the active systems are those phthalocyanines based on Ru, Co and Cu and polyoxometalates of dinuclear ruthenium and palladium. Microporous metallosilicates containing different transition metals showed leaching of the metal during the reactions. Molecular oxygen can be used directly as an oxidant and decreases the leaching of active species in comparison to hydrogen peroxide and *tert*-butyl hydroperoxide. Metal aluminophosphates (metal: Mn, Fe, Co, Cu, Cr V) are active and relatively stable under such conditions. Mn-AIPO-36 yields directly adipic acid, but large amounts of carboxylic acids should be avoided, as they cause metal leaching from the catalysts. Rare earth exchanged zeolite Y also shows good selectivity and activity. In the last part of the review, novel alternative strategies for the production of cyclohexanol and cyclohexanone and the direct synthesis of adipic acid are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In 1993, we published a review article entitled “*Why is it Interesting to Study Cyclohexane Oxidation*” [1],

where we gave a detailed description of the industrial process and concluded that a profound study of the *Gif* systems should give new ideas on how to improve the industrial cyclohexane oxidation process. Barton [2] attributed the name *Gif* to oxidation systems that have the particular characteristic of functionalizing saturated hydrocarbons to ketones, preferentially at

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secondary positions, following a non-radical process. Further studies in our [3] and Barton's [4,5] labs have shown that the singular behavior of *Gif* systems is lost when pyridine is substituted by other solvents. We believe [6] that *Gif* oxidation processes have as a crucial step the insertion of singlet oxygen into the metal–carbon bond to form an alkylperoxo-metal intermediate, a reaction step that is probably only possible in pyridine. As the use of this solvent is prohibitive for industrial chemistry, we review here important results on cyclohexane oxidation with hydrogen peroxide, *tert*-butyl hydroperoxide and molecular oxygen, published after our first review and describe alternative processes to obtain the principal oxidation products of cyclohexane.

2. Hydrogen peroxide as oxidant

The oxidation of cyclohexane (Fig. 1) under mild conditions is a topic of great interest [1]. Many attempts have been made to substitute the classical process (cyclohexane (*ane*) conversion of 4% with a concentration of cyclohexanone (*one*) plus cyclohexanol (*ol*) of 0.40 mol l^{-1} after 40 min), by biomimetic systems that can catalyze the selective oxidation of alkanes at room temperature with different oxidants. Hydrogen peroxide is the preferred oxidant as it only produces water as a by-product in an environmentally friendly reaction and has a high oxygen uptake (47%) [7,8]. Unfortunately, cyclohexane oxidation with H_2O_2 catalyzed by biomimetic systems still gives low conversions and turnovers [9–19], thus making its industrial use difficult. Furthermore, the relative prices of hydrogen peroxide (US\$ 0.58/kg) and adipic acid (US\$ 1.43/kg) should be considered

[20]. Thus, if the efficiency of the reaction is less than 40%, the value of the oxidant is higher than that of the product. Recently, better results were obtained by Shul'pin et al. [21] using a binuclear manganese(IV) complex ($[\text{LMn}^{\text{IV}}(\text{O})_3\text{Mn}^{\text{IV}}\text{L}]^{2+}$, L: 1,4,7-trimethyl-1,4,7-triazacyclononane) as catalyst, in the presence of acetic acid that prevents the decomposition of H_2O_2 to water and oxygen. The reaction initially forms cyclohexyl hydroperoxide (CHHP), as the predominant product, which is later decomposed to cyclohexanone and cyclohexanol. At 293 K, using a catalyst concentration of 0.03 mol l^{-1} in acetonitrile as a solvent, the total concentration of oxidation products was 0.10 mol l^{-1} after 2 h (cyclohexane conversion of 46% with a turnover of 3300), but the H_2O_2 efficiency is as low as 30%. Ru catalysts are also used to oxidize cyclohexane [22]. Working at 343 K, 0.3 MPa air pressure, with the sterically hindered complex *cis*-Ru(dmp) $_2$ (CH $_3$ CN) $_2$ (PF) $_6$, (dmp: 2,9-dimethyl-1,10-phenanthroline), a turnover of 1900 was obtained, but the only product is cyclohexanol (0.38 mol l^{-1}). We also have oxidized cyclohexane using methyltrioxorhenium (CH_3ReO_3) as a catalyst [23]. Anhydrous hydrogen peroxide was used as an oxidant and acetonitrile was found to be the most appropriate solvent for this reaction. Addition of pyrazine-2-carboxylic acid (PCA) accelerates the reaction (the optimal CH_3ReO_3 :PCA ratio is 1:4), giving 0.5 mol l^{-1} of cyclohexanone, 4.9 mol l^{-1} of cyclohexanol and 7.18 mol l^{-1} of CHHP (turnover = 126). When the reaction is carried out under argon, the total concentration of oxidized products was 50% lower, showing that atmospheric oxygen is also consumed during the reaction.

The incorporation of organic metal complexes into molecular sieves pores and cavities, leading to

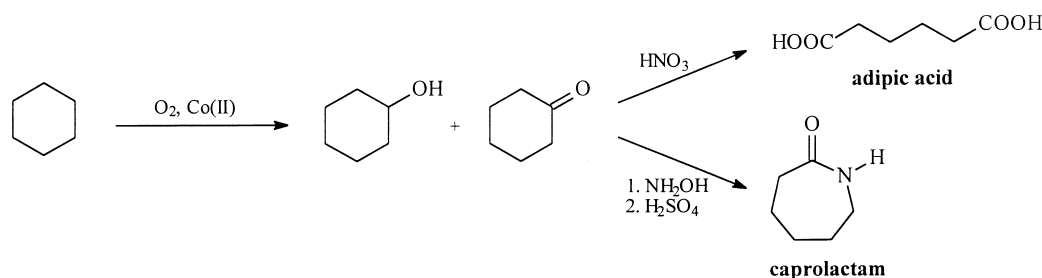


Fig. 1. Conversion of cyclohexane to adipic acid or ϵ -caprolactam.

systems that mimic the unique characteristics of enzymes, are also used to oxidize cyclohexane. Armengol et al. [24] described the use of Cu^{2+} -phthalocyanine and Co^{2+} -perfluorophthalocyanine incorporated in faujasite or mesoporous MCM-41 using H_2O_2 as an oxidant to give cyclohexanone and cyclohexanol as the only products. In this case, MCM-41 was functionalized with 3-aminopropyltrimethoxysilane and suspended in solutions of iron and copper salts to form the respective supported catalysts. Despite the higher activity shown by supported catalysts in comparison to free complexes and its stability towards leaching, conversions and H_2O_2 efficiency are still low. In cyclohexane oxidation, best results were obtained at 373 K in the presence of $\text{Fe}(\text{CH}_3\text{O})_3$ $\text{Si}(\text{CH}_2)_3\text{NH}_2$ -MCM-41 as catalyst [25]. Using acetone as solvent, a conversion of cyclohexane of 19.5% with a turnover of 88 was obtained after 12 h. Cyclohexanone and cyclohexanol were obtained in a concentration of 0.19 mol l^{-1} with an *one:ol* ratio of 8. On the other hand, the H_2O_2 efficiency was only 34% and leaching of the metal occurred progressively.

In 1983, Enichem researchers discovered titanium silicalite-1 (TS-1), a silicalite that has the MFI structure with a small fraction of silicon atoms substituted by titanium. TS-1 efficiently catalyzes a large variety of reactions using H_2O_2 as oxidant [26]. Alkane oxidations catalyzed by TS-1 were firstly studied by Clerici [27], who showed that TS-1 is an active catalyst and can discriminate between linear, branched or cyclic alkanes. Since then much effort has been employed to incorporate other transition metals in a variety of molecular sieves to give the so-called redox molecular sieves [28]. The use of redox molecular sieves as catalysts in cyclohexane oxidation with H_2O_2 is summarized in Table 1. We also studied cyclohexane oxidation with H_2O_2 catalyzed by TS-1 [29] and the best results were obtained at 373 K using acetone as solvent. Under these conditions, cyclohexanone and cyclohexanol were obtained with a turnover of 76 and an *one:ol* ratio of 1.3 after 24 h. H_2O_2 is almost completely consumed and the H_2O_2 efficiency for cyclohexanone and cyclohexanol is 22%. The *one:ol* ratio increases during the reaction, which can be explained by over-oxidation of cyclohexanol under the reaction conditions. Mechanistic studies have shown that cyclohexanol is selectively oxidized to cyclohexanone inside the pores of

TS-1 and non-selectively oxidized to several other oxidation products on the external surface. This non-selective oxidation could be suppressed by the addition of BHT (2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger), which does not enter into the molecular sieve pore system due to its larger kinetic diameter. Although cyclohexane oxidation by TS-1 is very selective, the quantities of *one* and *ol* obtained (0.15 mol l^{-1} after 24 h) and the H_2O_2 efficiency (22%) are too low for industrial applications. Zahedi-Niaki et al. [30] compared the catalytic properties of titanium aluminophosphates (TAPO-5, TAPO-11 and TAPO-36) with those of TS-1. Using TS-1 as a catalyst, they obtained a conversion of 6.3% with an *one:ol* ratio of 0.23 after 5 h and a H_2O_2 conversion of 13% with an efficiency of 65% relative to oxidation products. At the same conditions, TAPO-5 and TAPO-11 showed activities and selectivities only slightly lower than those of TS-1. TAPO-36 showed the smallest conversion (3.7%). In all cases, no leaching of titanium was observed. We synthesized and tested mesoporous metallosilicates [31] with pore diameters of ca. 3.0–4.0 nm. As can be seen from Table 1, the medium-pore silicalite TS-1 (pore diameter of 0.55 nm) is more active and shows a turnover of 76 after 24 h (approximately 52% after 12 h), which is higher than the mesoporous Ti-MCM-41 (42%, after 12 h). This higher activity was attributed to the more restricted environment in the TS-1 pore system, thus favoring the abstraction of hydrogen from cyclohexane, which is the first step of the oxidation process. The lower activity of Ti-MCM-41 was also attributed to its lower hydrophobicity, which makes the adsorption of the hydrophobic substrate and the desorption of the polar oxidation product more difficult. The results obtained for Mn-, Fe- and Co-MCM-41 were similar to those observed for Ti-MCM-41. High activities were observed for V- and Cr-MCM-41, however, H_2O_2 efficiency was lower. Besides Ti-MCM-41, all metallosilicates suffer leaching of the metal and the observed catalytic activity is mainly due to the homogeneous species. Iron and chromium containing silico-aluminumphosphates (Fe-, CrAPSO-37) which have faujasite structures like zeolites X and Y, were also synthesized and tested [32,33]. The iron containing zeolite was not active in cyclohexane oxidation with H_2O_2 , whereas the chromium containing molecular sieve appeared to be active, giving a turnover of

Table 1
Cyclohexane oxidation with H₂O₂ catalyzed by redox molecular sieves

Catalyst (wt.% metal)	Catalyst (g)	<i>T</i> (K)	<i>t</i> (h)	Solvent (ml)	ane/H ₂ O ₂ (mmol)	Conversion: ane (%)	Ratio of one:ol	H ₂ O ₂ cons- umed (%)	H ₂ O ₂ eff. (%)	Turnover ^a	Reference
TS-1 (1.76)	0.10	373	24	Acetone (15)	18.5/20.0	15.0	1.3	98	22	76	[29]
TS-1 (1.90)	0.20	350	5	Acetone (6.3)	118.8/88.2	6.3	0.23	13	65	94	[30]
TAPO-5 (2.00)	0.20	350	5	Acetone (6.3)	118.8/88.2	4.4	0.09	11	52	63	[30]
TAPO-11 (2.00)	0.20	350	5	Acetone (6.3)	118.8/88.2	4.2	0.12	13	42	60	[30]
TAPO-36 (4.00)	0.20	350	5	Acetone (6.3)	118.8/88.2	3.7	0.15	15	34	26	[30]
Ti-MCM-41 (1.48)	0.10	373	12	Acetone (15)	18.5/20.0	7.0	2.25	98	11	42	[31]
V-MCM-41 (0.39)	0.10	373	12	Acetone (15)	18.5/20.0	11.3	1.33	99	17	274	[31]
Cr-MCM-41 (1.10)	0.10	373	12	Acetone (15)	18.5/20.0	13.5	1.78	97	21	118	[31]
Mn-MCM-41 (1.17)	0.10	373	12	Acetone (15)	18.5/20.0	7.0	1.17	97	10	61	[31]
Fe-MCM-41 (1.64)	0.10	373	12	Acetone (15)	18.5/20.0	8.1	0.88	99	11	51	[31]
Co-MCM-41 (2.15)	0.10	373	12	Acetone (15)	18.5/20.0	8.1	1.50	100	13	41	[31]
Cr-APSO-37 (0.04)	0.02	373	24	Acetonitrile (3)	5.0/5.0	13.2	7.6	100	23	390	[32,33]
Mo-MCM-41 (0.05)	0.10	150	3	Acetone (15)	2/1 ^b	–	5.95	–	–	49 ^c	[34]
NaGe-X	0.10	343	3	Without	120/240	66.5	0.66	79	59	798 ^d	[38]
Sulfated GeX	0.10	343	1.5	Without	120/240	42.0	3.00	88	40	504 ^d	[38]

^a Millimole of oxidized products per millimole of metal in the catalyst.

^b Molar ratio cyclohexane:H₂O₂.

^c Turnover frequency (millimole of oxidized products per millimole of metal in the catalyst per minute).

^d Millimole of oxidized products per gram of catalyst.

390. However, in this case the H_2O_2 efficiency was also low and catalysis was mainly due to leaching of small quantities of chromium into the solution [33]. Rana et al. [34] and Rana and Viswanathan [35] synthesized and tested Mo-MCM-41 as a catalyst at 423 K. They obtained a turnover frequency (TOF) of 49 min^{-1} , which corresponds to a turnover of 8820 after a reaction time of 3 h. However, H_2O_2 oxidizes cyclohexane at 423 K, principally in the presence of acetone, which forms peroxy complexes. They compared this catalyst with Ti-MCM-41 (0.06 wt.% TiO_2) and obtained a TOF of 21 min^{-1} , which correspond to a turnover of 3780 after 3 h. The temperature used (423 K) is too high and leads to thermal decomposition of H_2O_2 , inducing a radical chain process. Working at this temperature, we observed that the amounts of cyclohexanone and cyclohexanol obtained were principally due to uncatalyzed reactions, initiated by homolytic cleavage of H_2O_2 [36]. Sn-ZSM-48 catalysts were also used in cyclohexane oxidation [37], but the results were not satisfactory. Working at 353 K, a turnover of 12.6 (*one:ol* ratio of 1.5) and a 18.9% H_2O_2 efficiency were obtained.

Pârvulescu et al. [38] tested highly crystalline faujasite like Na-GeX (exhibits tetracoordinated Ge) and its modified sulfated form (a solid with properties resembling those of sulfated zirconia), that give best results under autogenic pressure. Using Na-GeX as a catalyst, a conversion of 66.5% with an *one:ol* ratio of 0.66 were obtained after 3 h at 343 K. The H_2O_2 conversion was 79% with an efficiency of 58.7% corresponding to the oxidation products. For sulfated GeX, after 1.5 h, a cyclohexane conversion of 42% and a H_2O_2 conversion of 88% with an efficiency of 24% were achieved. The recycling of the catalysts in successive experiments gave reproducible results. When the same experiments were carried out under a N_2 atmosphere, conversions were 50% lower than those obtained under autogenic conditions, while the H_2O_2 conversion remained constant. Thus, the oxidation occurs not only with H_2O_2 as an oxidizing agent, but also with O_2 formed in situ, resulting in turnovers and conversions considerably higher than those reported for TS-1 [29,30]. A concentration of 2.5 mol l^{-1} of cyclohexanone and cyclohexanol was obtained after 3 h using Na-GeX as a catalyst, which is similar to those obtained in the industrial process (ca. 0.40 mol l^{-1} after 40 min), but the H_2O_2 efficiencies have to be improved.

Metal-substituted polyoxometalates have many similarities to metal complexes with macrocyclic ligands as metalloporphyrines and related species, because they also have rigid coordination sites surrounding the metal center. The advantage of using polyoxometalates in oxidation reactions is their great stability towards oxygen donors and the possibility of incorporation of several transition metals [39–41]. The results of the cyclohexane oxidation with H_2O_2 using transition metal polyoxometalates are shown in Table 2. Mizumo et al. [39,40] compared the catalytic activity of tetrabutylammonium salts of mono-, di- and triiron-substituted silicotungstates and observed that the structures of the active sites have a remarkable influence on the catalytic activity. Best results were obtained with the diiron species and the main products were cyclohexanone and cyclohexanol. No induction period was observed for product formation and only a negligible amount of dicyclohexyl as by-product was observed. It is remarkable that the H_2O_2 efficiency to oxidation products was 95% and the addition of a second portion of H_2O_2 to the system showed that the catalyst was not deactivated. The *one:ol* ratio of approximately 1 is different from a Haber-Weiss based mechanism and the results for *n*-hexane, *n*-pentane and adamantane oxidation indicate that the reactivity follows the order secondary > tertiary > primary and differs from that of radical reactions. Thus, a non-radical process prevails, that can be related to catalytic pathways found in methane monooxygenase and *Gif* systems [39]. Despite of the high efficiency (95%) of H_2O_2 observed, the amount of cyclohexane and cyclohexanol (ca. 0.10 mol l^{-1}) is low and the reaction time is too long (96 h). Simões et al. [41] used Keggin-type heteropolytungstates $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{M}(\text{L})\text{O}_{39}]^{(7-m)-}$ (where M^{m+} is a first row transition metal cation and L is H_2O or CH_3CN), as catalysts in cyclohexane oxidation with H_2O_2 (Table 2). Using Co, Mn or Ni, only cyclohexanone and cyclohexanol were produced, while with Fe or in the absence of a transition metal CHHP was also formed. The polyanions $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$ showed a higher catalytic activity. With iron species, a conversion of 76% with a concentration of oxygenated products of ca. 0.8 mol l^{-1} was obtained after 9 h and CHHP was the predominant product. If the reaction was left for more than 9 h under reflux, a much

Table 2
Cyclohexane oxidation with H₂O₂ catalyzed by polyoxometalates

Catalyst	Catalyst (μmol)	<i>T</i> (K)	<i>t</i> (h)	Solvent (ml)	<i>ane</i> /H ₂ O ₂ (mmol)	Conversion: <i>ane</i> (%)	Ratio of <i>one:ol</i>	H ₂ O ₂ con- sumed (%)	H ₂ O ₂ eff. (%)	Turnover ^a	Reference
[γ -SiW ₁₀ {Fe(OH ₂) ₂ O ₃₈ }] ⁶⁻	8	356	96	Acetonitrile (6)	1.0/1.0	66	0.82	100	95	120	[39,40]
[α -SiW ₁₁ Fe(OH ₂)O ₃₉] ⁵⁻	8	356	96	Acetonitrile (6)	1.0/1.0	7	1.38	27	41	14	[39,40]
[α -SiW ₉ {Fe(OH ₂) ₃ O ₃₇ }] ⁷⁻	8	356	96	Acetonitrile (6)	1.0/1.0	5	1.08	100	8	10	[39,40]
(TBA) ₄ H ₃ PW ₁₁ O ₃₉	39	353	12	Acetonitrile (10)	18.5/39.2	35 ^b	2.63	–	–	166	[41]
(TBA) ₄ HPW ₁₁ CuO ₃₉	40	353	12	Acetonitrile (10)	18.5/29.4	11	0.57	100	–	51	[41]
(TBA) ₄ HPW ₁₁ Co(H ₂ O)O ₃₉ ·2H ₂ O	38	353	12	Acetonitrile (10)	18.5/39.2	5	0.67	75 ^c	–	24	[41]
(TBA) ₄ HPW ₁₁ Mn(H ₂ O)O ₃₉ ·3H ₂ O	38	353	12	Acetonitrile (10)	18.5/39.2	8	1.67	100	–	40	[41]
(TBA) ₄ HPW ₁₁ Ni(H ₂ O)O ₃₉ ·H ₂ O	39	353	12	Acetonitrile (10)	9.3/39.2	20	4.00	20–40 ^c	–	48	[41]
(TBA) ₄ HPW ₁₁ Fe(H ₂ O)O ₃₉ ·2H ₂ O	42	353	9	Acetonitrile (10)	18.5/39.2	76 ^d	2.20	20–40 ^c	~100	335	[41]

^a Millimole of oxidized products per millimole of heteropolyoxometalates.

^b 35% conversion (6% cyclohexylhydroperoxide, 21% *one* and 8% *ol*).

^c H₂O₂ consumed after 6 h.

^d 76% conversion (57% cyclohexylhydroperoxide, 13% *one* and 6% *ol*).

higher conversion was observed (96% after 10 h). On the other hand, a very complex product mixture is obtained, resulting in a significant loss in selectivity. When the reaction was carried out under a nitrogen atmosphere, similar results are obtained, excluding the possibility of autoxidation. However, in the presence of BHT the reaction was inhibited indicating that a radical process is operative. The monitoring of H_2O_2 consumption during the reaction showed that for $PW_{11}Fe$ after 6 h, 60–80% of initial H_2O_2 was still present giving the high efficiency of 100%.

3. *tert*-Butyl hydroperoxide as oxidant

Klein et al. [42] reported that amorphous, microporous, homogeneously mixed oxides (AMM) based on Ti or V in silica can be prepared by an acid catalyzed sol-gel process and catalyze cyclohexane oxidation with *tert*-butyl hydroperoxide (TBHP). Competitive oxygenation reactions of cyclohexane and perdeuterocyclohexane show that AMM-Ti-Si, TS-1 [43], Ti-beta [44] and Ti-MCM-41 [45] exhibit the same kinetic isotope effect and an identical temperature dependence. These results suggest that C–H bond cleavage is rate determining and the hydrogen transfer to the complex is linear and of electrophilic nature. The results of the selective cyclohexane oxidation at 353 K using TBHP as an oxidant can be summarized as follows: AMM-Ti-Si is a remarkable active catalyst and does not suffer deactivation. Compared to other Ti containing materials, such as Ti-MCM-41, Ti-beta or TS-1, higher cyclohexane conversions can be obtained to give cyclohexanone (46.3%), cyclohexanol (18.5%) and adipic acid (32.1%) [46]. The results obtained in the oxidation of cyclohexane catalyzed by microporous metallosilicates containing various transition metals prepared by the acid catalyzed sol-gel process [47,48] are summarized in Table 3. $CuO-SiO_2$ and $Cr_2O_3-SiO_2$ showed a good activity and were studied in more details. The catalyst $CuO-SiO_2$ lost approximately 27 wt.% of Cu in the first catalytic cycle reaction and after five cycles the conversion dropped drastically. However, the leached Cu showed low activity in the homogeneous phase. For $Cr_2O_3-SiO_2$, it was observed that chromium was leached due to the reaction with hydroperoxide.

Table 3

Cyclohexane oxidation with TBHP catalyzed by metallosilicates prepared by the sol-gel method (reaction conditions: 95 mmol of cyclohexane, 9.5 mmol of TBHP, 100 ± 5 mg of catalyst, 24 h, 348 K, [46,47])

Catalyst	<i>one</i> (mmol)	<i>ol</i> (mmol)	CHHP (mmol)	Conversion (%)
$V_2O_5-SiO_2$	0.19	0.80	0.07	1.1
$Fe_2O_3-SiO_2$	0.97	0.25	0.26	1.6
TiO_2-SiO_2	0.99	0.61	0.47	2.2
ZrO_2-SiO_2	0.17	2.59	0.02	2.9
$CuO-SiO_2$	2.70	0.82	0.20	3.9
$Mo_2O_5-SiO_2$	2.30	1.64	0.32	4.4
$Co_2O_3-SiO_2$	2.37	1.93	0.52	5.1
$Cr_2O_3-SiO_2$	4.60	0.42	0.20	5.5

Parton et al. and Vankelecom et al. [49,50] studied the oxidation of cyclohexane at room temperature using TBHP and iron-phthalocyanines occluded in zeolite Y (FePc-Y) as catalysts. The conversion of cyclohexane in the presence of FePc-Y was high (up to 25%) with selectivities for cyclohexanone of 95%. The FePc-Y follows the same mechanism observed for cytochrome P-450; i.e. the cleavage of C–H bonds by a high-valent metal-oxo species is the rate determining step, followed by a rapid recombination of the metal hydroxy and alkyl radicals, thus, avoiding the formation of free radicals. The observed activities are significantly higher than those obtained with homogeneous FePc complexes. The catalytic activity and efficiency of iron-phthalocyanine catalysts was shown to depend strongly on the polarity of the support [51]. Reactant concentrates close to the active sites of the catalyst, and consequently the reaction rates are essentially controlled by the adsorption equilibrium on the solid support. Although FePc-Y showed no leaching, a rapid deactivation was observed under prolonged reaction times, probably due to pore blocking by over-oxidation products. In a tentative effort to circumvent this problem, FePc-Y was embedded in a polydimethylsiloxane membrane [52], but the deactivation of the catalyst due to sorption of hydrophilic compounds formed during the reaction was also observed. Balkus et al. [53] synthesized ruthenium perfluorophthalocyanine encapsulated in NaX ($RuF_{16}Pc-X$), according to the template method, and showed that the material was active as a catalyst in the oxidation of cyclohexane at room temperature. The catalyst showed no sign of

deactivation, contrary to the equivalent iron compound. Raja and Ratnasamy [54] studied the cyclohexane oxidation catalyzed by chloro- and nitro-substituted phthalocyanines of copper, cobalt and iron encapsulated in zeolites X and Y, at ambient conditions using molecular oxygen and alkyl hydroperoxides as oxidants. The catalytic activities of the encapsulated materials are much higher than those of the unsupported complexes. The rate of cyclohexane oxidation, using copper hexadecachloro-phthalocyanine encapsulated in zeolite Y is high (TOF of 6.7 min^{-1}) with TBHP efficiencies up to 90%. Reaction rates decrease with an increase in the molecular cross-section of the oxidant (cyclohexyl > *t*-butyl > cumyl), confirming that the active site is indeed located inside the zeolitic cavities and not on the external surface. A series of Cu^{2+} -phthalocyanine and Co^{2+} -perfluorophthalocyanine complexes, prepared inside the pores of MCM-41 (MPC-MCM-41) or faujasite Y (MPC-Y), was tested in the oxidation of cyclohexane with hydrogen peroxide and *tert*-butyl hydroperoxide. The only products were cyclohexanol and cyclohexanone. Comparative experiments showed that $\text{CoF}_{16}\text{Pc-MCM-41}$ was more active and selective than $\text{CoF}_{16}\text{Pc-Y}$ or unsupported CoF_{16}Pc , while CuPc complex shows higher activity and selectivity when encapsulated in zeolite Y. These results show the influence of pore dimensions of the support that allow the tuning of the catalytic activity and selectivity of these materials. No leaching of the complexes to the homogeneous phase was observed.

Other novel oxidation catalysts, which have been recently investigated are the transition metal-substituted polyoxometalates, with “sandwich” like structures, e.g. dinuclear ruthenium polyoxometalate $[(\text{WZnRu}^{\text{III}})_2(\text{ZnW}_9\text{O}_{34})_2]^{11-}$, and dinuclear palladium polyoxometalate, $[(\text{WZnPd}^{\text{II}})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$. These complexes show high activity and chemoselectivity in the oxidation of alkanes with *tert*-butyl hydroperoxide [55]. Turnovers as high as 720 were obtained using $[(\text{WZnRu}^{\text{III}})_2(\text{ZnW}_9\text{O}_{34})_2]^{11-}$ as a catalyst (molar ratio of cyclohexane/TBHP/catalyst of 10900/27600/1), which means a catalytic activity 10-fold higher than that previously found for transition metal substituted Keggin compounds [55].

The catalytic mechanism using *tert*-butyl hydroperoxide was investigated by Leising et al. [56] and Lee and Bruce [57], who studied the effect of tripodal lig-

ands on $(\mu\text{-oxo})(\mu\text{-carboxylato})\text{diferric}$ catalysts and the variation of the bridge in $\text{Fe}_2\text{O}(\text{TPA})_2$ catalysts (TPA: Tris(2-pyridylmethyl)amine). The efficiency increased with an increase of the nucleophilicity of the ligand. Under the reaction conditions [56] all TBHP is consumed within 0.25 h and afforded the following product distribution: *t*-BuOH (75%), *t*-BuOOCy (11%), MeOH (10%) and *t*-Bu₂O₂ (<1%). These results demonstrated that TBHP reacts with the catalyst via two distinct mechanisms: (1) a heterolytic process, where a high-valent iron-oxo species is responsible for cyclohexanone and cyclohexanol formation; and (2) a homolytic pathway that generates *t*-BuO- and *t*-BuOO-radicals that are responsible for the formation of *t*-BuOOCy. When BHT is added, the yields of oxidation products in the reaction catalyzed by Mn(II)(salen) do not change significantly and no products derived from free radical coupling were detected [58]. On the other hand, Kim et al. [59] observed that when the reaction is carried out under argon in the presence of $[\text{Fe}_2\text{O}(\text{TPA})_2(\text{H}_2\text{O})_2]^{4+}$ as catalyst, a decrease in the concentration of TBHP reduced the yields of ketone and dialkyl peroxide significantly and increased the conversion of TBHP to *tert*-butanol while the *one:ol* ratio is close to 1. This is in agreement with results obtained by Pires et al. [60] where a constant ratio of *one:ol* of 1 is found in the reaction catalyzed by Ce-exchanged zeolite Y and variable amounts of TBHP (4–24 mmol) under air. These results show that alkyl radicals are formed in the reaction and can be trapped by O₂. A similar behavior is observed when either phosphotungstic complexes of Ru(II) or its salts of tetrafluoroborate are used as catalysts in dimethylsulfoxide as a solvent [61].

4. Oxygen as the ultimate oxidant

Gas phase oxidations usually occur under extreme conditions where it is difficult to control product selectivity, either for catalytic or non-catalytic reactions. Thus, liquid phase hydrocarbon transformations are preferred due to the ease of operation under mild conditions [62,63]. The catalytic system currently in use for industrial cyclohexane oxidation employs homogeneous cobalt salts, molecular oxygen and temperatures above 423 K, with conversions around 4% and selectivities of 85% to cyclohexanone and

cyclohexanol [64]. Under these conditions, the rate of cleavage of the C–H bond is high, which favors the formation of significant amounts of CHHP, that decomposes to cyclohexanol and cyclohexanone at the end of the process and also generates carboxylic acids as by-products [65]. However, as observed in other radical processes, the selectivity decreases with higher conversions. Therefore, the industrial process requires a rigid control of the conversion to maintain reasonable selectivity values.

In the last decade, many heterogeneous catalysts have been developed for this reaction, which operate under mild conditions with oxygen as an oxidant resulting in a more selective process with three important advantages: the facility to separate the catalyst after the reaction, lower energy costs and a higher stability of the catalytic species, as its deactivation is caused by the irreversible reaction of over-oxidation products [66]. In order to accelerate the initiation step of the autoxidation process using oxygen as oxidant, most of the new catalytic systems use H_2O_2 or TBHP as a co-catalyst. However, molecular oxygen can be used directly in the presence of transition metals, such as Fe [67], Zn [68] or alkaline metals like Na and K [69]. The absence or the use of a catalytic amount of H_2O_2 or TBHP minimizes leaching of active species, which can be severe when they are used in stoichiometric amounts where they are the main reason for removal of the metal from the support [70]. The activation of dioxygen by external agents has also been observed using enzymatic oxidative systems like the cytochrome P-450 or the metanomonooxygenase, which is found in soil metanotropic bacteria [71]. Biomimetic metalloporphyrin catalysts, based on the iron complex present in cytochrome P-450, gave promising results in selective oxidation, but their activity decreases rapidly due to the self-destruction of the active species [71].

Solvent free systems, operating with soluble Fe(III) and Cu(II) catalysts were firstly investigated by Barton et al. [72], and later reinvestigated by Schuchardt et al. [73]. These complexes are interesting in that they can activate molecular oxygen and that activity is dependent on oxygen pressure. The systems based on iron are more selective for oxygenated products, while copper based catalysts favor cyclohexene formation. The presence of TBHP as an initiator is fundamental for the reactivation of the system, as the addition of new portions of TBHP reinitiates the process and the

activity of the catalyst reaches almost the same values observed at the beginning of the reactions.

Heterogeneous oxidation catalysts can be either oxides or metal cations and complexes incorporated on inorganic matrixes such as silica, alumina, zirconia, active carbon, zeolites or aluminophosphates [28]. The activity of these systems is mainly based on the correct choice of the solvent, which determines the polarity of the medium and the size of the substrate that needs to be adsorbed at the catalytic surface. Using amorphous supports such as silica, the metallic species are normally found as oxide particles, e.g. vanadium oxide supported on silica, employed in the selective oxidation of butane by O_2 [74]. Zeolites with high Si content and SiO_2 -based materials that have a hydrophobic character favor the adsorption of hydrocarbons such as cyclohexane. The hydrophobicity of these supports results in a low affinity for oxidation products, which are expelled from the catalytic active sites as soon as they are formed. Thus, over-oxidation of the products is reduced and high selectivities are maintained. An example of these systems is the (Ti, Al) zeolite β , which has the same hydrophobicity of the crystalline TS-1, and is able to oxidize cyclohexane and larger substrates with oxygen in the presence of TBHP. However, efficiencies are normally low [75]. Other crystalline supports that could be used are metalloaluminophosphates (MAPO, M: Cr, Co, Fe, Cu and V), which can be obtained directly by adding a metallic source to the gel of synthesis during their preparation. Considering the kinetic diameter of the substrate, the best structures for cyclohexane oxidation are MAPO-18, MAPO-36, MAPO-5 and MAPO-VFI [76]. Using MAPO-VFI in the presence of TBHP and without solvent, Luna et al. [77] were able to oxidize cyclohexane with molecular oxygen to give cyclohexanol and cyclohexanone. The ability to activate molecular oxygen was also investigated in the absence of hydroperoxides as a co-catalyst. Thomas et al. [78] prepared isolated four-coordinate metal ions (Mn(III), Fe(III) and Co(III)) containing aluminophosphate molecular sieves. These catalysts were used in the cyclohexane oxidation with air as oxidant. Mn-AlPO-36 was the most active system, giving after 24 h at 403 K and 1.5 MPa air pressure, 13% conversion and a turnover of 233, with the following product distribution: 15% cyclohexanol, 47% cyclohexanone and 33% adipic acid [78]. They also observed [79] that using

molecular sieves with smaller pore diameter, the selectivity to adipic acid can be increased. Using FeAPO-5 (pore diameter of 0.73 nm), 14% of adipic acid is obtained after 24 h (370 K, 1.5 MPa air pressure), but if FeAPO-31 (pore diameter of 0.54 nm) is used, the selectivity to adipic acid increases up to 65%. As diffusion of cyclohexane and the reaction intermediates within the channel system are severely limited, further oxidation of the cyclic intermediates to linear products as adipic acid is facilitated. However, large amounts of carboxylic acids should be avoided, as they cause extensive metal leaching from the catalysts. TBHP can be used as an initiator in such catalytic systems, decreasing the initial induction period, accelerating the rate of the reaction and giving rise to enhanced activity [80].

Using CoAPO-5, Vanoppen and Jacobs [81] oxidized cyclohexane under O₂ pressure at 418 K, and the typical product distribution of the industrial process was observed. In these experiments, the conversion was kept at 3.5%. Increasing the Co loading of the catalyst also accelerates the rate of decomposition of cyclohexyl hydroperoxide to form the final oxidation products. The efficiency of the oxidation depends on the Co(II):Co(III) ratio. If Co(II) and a weakly bound proton are present, the catalyst exhibits good efficiency in acid catalysis. On the other hand, if Co(III) is the dominant species, the material shows good results for the oxidation of a large variety of substrates in the presence of molecular oxygen. The reaction can be performed with acetic acid or in absence of any solvent (in this case, higher O₂ pressures are required). Using CoAPO-36, under an O₂ pressure of 1.5 MPa and at 423 K, Sankar et al. [76] obtained a very selective system to form cyclohexanone and cyclohexanol during the first 8 h of reaction. After 16 h the conversion reached 9.6% and the turnover was 166. The system remained active after this period, indicating that the over-oxidation products, e.g. acids, are not able to block the active sites of the catalyst. Filtering off the catalyst from the solution, no catalytic activity was observed, proving that the catalyst is heterogeneous. The catalyst could be recycled and after calcination, the CoAPO showed the same catalytic activity, in four consecutive reaction cycles.

Molecular sieves as zeolite Y or MCM-41, are most suitable for the development of ship-in-the-bottle catalysts. Phthalocyanine and porphyrine complexes are mostly used, due to their higher catalytic activ-

ity and selectivity. Phthalocyanine ligands bearing electron-withdrawing groups like Cl or NO₂ showed better stabilities in the oxidation reaction, and the use of Cu, Fe and Co complexes gave good efficiencies in the autoxidation of cyclohexane in the presence or in the absence of TBHP [82]. In homogeneous phase, Co, Fe and Cu phthalocyanine complexes show similar activities. After encapsulation, the copper complex revealed a much higher activity. However, the use of these materials is restricted because of the relative low complex loading and/or high metal leaching [83–85]. On the other hand, rare earth exchanged zeolite Y has been studied in cyclohexane oxidation and showed both good selectivity and activity [86,87].

The generation of radicals in the autoxidation process can also be achieved by photochemical induction. In the presence of photosensitive species and light with an appropriate wavelength, these compounds can transfer electrons to O₂, generating reduced species that are able to abstract hydrogen from the hydrocarbon, starting a radical chain reaction. Oxides like anatase or complex salts such as [(*n*-Bu)₄N]⁺[W₁₀O₃₂]⁻ showed this behavior. Using anatase in the presence of TS-1, Lu et al. [88] converted cyclohexane to cyclohexanol, cyclohexanone and CO₂. The same behavior is observed for the system W₁₀O₃₂⁻/Fe(III) porphyrine complex, where W₁₀O₃₂⁻ acts as a photosensitive species and the Fe(III) complex selectively decomposes the hydroperoxide [89]. Unfortunately, it is not possible to compare its efficiencies and the conversions appear to be much lower than that obtained by chemical activation. Another type of photocatalytic systems is based on the photolysis of a halocompound, generating an active radical species to abstract the hydrogen of the substrate. Shul'pin et al. [90], used this system with FeCl₃ in CH₃CN and obtained a cyclohexane conversion of nearly 8% after 8 h of irradiation. This result is interesting, but the use of catalytic systems based on the generation of halo radicals is not recommendable because of the high environmental impact and the costs of the reactors. There is little data in the literature about the gas phase oxidation of cyclohexane [91]. We observed that using supported Cu(II), Fe(III), Cr(III) and Co(III) salts supported on silica-gel, zeolite Y or MAPO-VFI in an on-line gas reactor, higher temperatures are necessary to generate the catalytically active species compared to the

ruthenium is used as catalyst in a biphasic system consisting of benzene and an aqueous solution of zinc sulfate (423 K and 5 MPa of H₂ pressure) [99], which limits hydrogen diffusion to the surface of the catalyst, and thereby decreases the hydrogenation rate of cyclohexene to cyclohexane. Similar yields are obtained when Ru–B catalyst supported on amorphous silica is used [100], confirming that the high selectivity to cyclohexene in these systems is due to a water layer formed over the outer surface of the catalyst. In contrast to the former case, water now promotes the desorption of cyclohexene by competitive adsorption or by the formation of an adduct with cyclohexene [101]. In the industrial scale process, designed by Asahi, cyclohexene is obtained in 60% yield [102–104].

Despite achieving moderate to good selectivities towards cyclohexene, the partial hydrogenation of benzene is problematic since the complete hydrogenation to cyclohexane is more favorable and the lifetimes of the catalysts are normally short. These problems could be circumvented by the dehydrohalogenation of cyclohexyl halides, a method which has the potential advantage of recycling hazardous halogenated compounds. The hydrogen treatment of cyclohexyl chloride, using a silica supported nickel catalyst at temperatures between 423 and 523 K, produces cyclohexene as the main product with selectivities higher than 97% and a TOF of $3.6 \times 10^5 \text{ min}^{-1}$ in the starting period of the reaction [105]. However, the catalyst suffers from poisoning by HCl formed during the reaction, but the activity can be completely restored after reactivation at 673 K under a stream of hydrogen. When zeolite Y is used as support the activities are slightly reduced, but the catalyst suffers from an irreversible deactivation by coke formation during the reaction [106].

The direct oxidation of cyclohexene to adipic acid by an environmentally friendly process was described first by Noyori and coworkers [107]. The reaction uses hydrogen peroxide as oxidant, produces water as the only by-product and is made possible through the presence of a catalytic amount of a tungsten oxide and a phase transfer catalyst. The reaction mechanism involves the epoxidation of the double bond and hydrolytic epoxide ring opening, followed by an alcohol and a Baeyer–Villiger oxidation to give a hydroxy lactone, which is further oxidized to the anhydride (Fig. 3). Subsequent hydrolysis of the anhydride affords adipic acid in 93% yield. However,

despite the “green” conditions used in this solvent- and halide-free process, its industrial application is still not possible as 4 mol of hydrogen peroxide are consumed per mol of adipic acid formed and it is thus, cost prohibitive. To make it an economically viable process, part of the oxidation would have to be accomplished by molecular oxygen, which enjoys lower production and storage costs than hydrogen peroxide. More recently, the direct oxidation of cyclohexene to adipic acid in a nearly quantitative yield, without the need of a phase-transfer catalyst (PTC), was described [108]. Despite the environmental and economical advantages due to the replacement of an expensive PTC by organic acids, the process still has to be improved in order to become industrially viable, by substituting some of the hydrogen peroxide used with molecular oxygen. Another strategy for the production of adipic acid is the treatment of cyclohexene oxide with the Jones reagent under very mild conditions [109]. This system gives adipic acid in 60% yield as the main product together with some cyclohexanone (20% yield) after 20 min at 293 K. However, as the overall process would generate 1.5 tonnes of toxic chromium containing waste per tonne of adipic acid produced, it cannot be used in industrial scale. Adipic acid can also be obtained by a biocatalytic strategy that uses *Escherichia coli* to convert D-glucose into *cis,cis*-muconic acid, followed by a hydrogenation to afford adipic acid [110]. This procedure suppresses the problems of petroleum-based feedstocks and generation of environmentally incompatible by-products involved in the current synthesis of adipic acid. However, this process is still too expensive to be scaled-up.

The difficulty of producing adipic acid directly from cyclohexene, supports the use of cyclohexanone as an intermediate for this synthesis. Cyclohexanone can be prepared by other methods in addition to the oxidation of cyclohexane, such as the dihydroxylation of cyclohexene, the dehydrogenation of cyclohexanol, the hydrogenation of phenol or by an elegant chloride-free Wacker-type oxidation process (see Fig. 2). The latter is known to be mostly efficient for terminal olefins and it would be attractive to develop a similar process for internal olefins. Recently, Kim et al. [111] described an active catalytic system for the production of cyclohexanone based on the Pd(NO₃)₂–CuSO₄–H₃PMO₁₂O₄₀ system, which gives cyclohexene conversion of 47% with 94% selectivity to cyclohexanone. In this system,

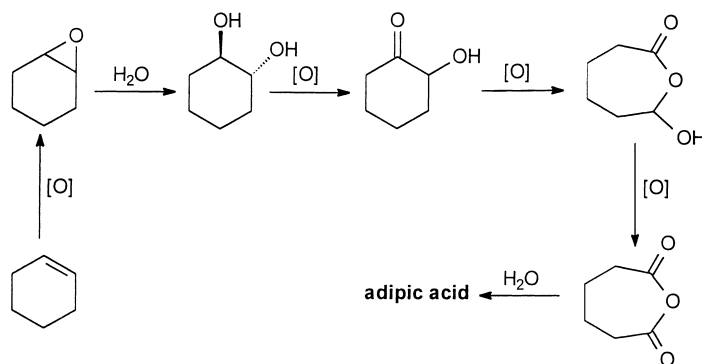


Fig. 3. Direct oxidation of cyclohexene to adipic acid with hydrogen peroxide [107].

chloride ions probably suppress the reaction rate while Cu-heteropolyanion interaction facilitates the oxidation of Pd(0). However, despite the promising features of this process, the turnovers are not higher than 350 and any future industrial application requires turnovers above 10000. Further modification of this catalytic system would probably allow an increase in activity. The oxygenation of cyclohexene to cyclohexanone can also be successfully accomplished by Mn(III) complexes. In this case, *t*-BuOOH induces the activation of molecular oxygen in acetonitrile, giving cyclohexanone as the principal product with efficiencies (mmol of product per mmol of *t*-BuOOH) up to 1650%. Unfortunately, when H_2O_2 is used in place of *t*-BuOOH, all the systems fail to produce detectable amounts of products, as does the absence of dioxygen that strongly decreases the activity of the Mn complexes used [112]. Cyclohexanone can also be obtained by the dihydroxylation of cyclohexene with molecular oxygen in the presence of osmium catalysts to afford the corresponding diol, where both oxygen atoms are used effectively to give the product in 68% yield [113]. The diol can be further dehydroxylated under basic conditions to give cyclohexanone [114].

On its turn, the dehydrogenation of cyclohexanol (obtained by the hydration of cyclohexene in the presence of acid catalysts such as sulfuric, nitric or perchloric acids [115]), to cyclohexanone is an extensively studied system, not only due to the essential conversion of the cyclohexanol formed in the oxidation of cyclohexane, but also as the model for the preparation of other cyclic oxygenated compounds. The dehydrogenation process is normally

accomplished with heterogeneous copper catalysts in a variety of different supports, such as basic oxides in combination with alkaline metals [116], alkali-doped silica [117], carbon covered alumina [118] and dispersions of copper on silica [119] and alumina [120]. The addition of promoters, such as rhodium [121,122] and cobalt [123] to copper catalysts has also shown to increase the selectivity towards cyclohexanone, as does cobalt supported on activated charcoal [124] and platinum on carbon fibers [125]. However, cyclohexene can be obtained as a side product depending on the acidity of the support used, as acid sites promote dehydration [126]. Industrially, the hydrogen obtained as a by-product in the dehydrogenation process is employed in the hydrogenation of benzene to cyclohexane. Copper supported on alumina, prepared by the electroless plating method, gives selectivities higher than 99% for cyclohexanone in a 17% conversion at 493 K, a yield that can be further increased at higher temperatures without a significant loss of selectivity. Bimetallic catalysts, such as Cu–Co/SiO₂ with different metal loadings can also give high yields of cyclohexanone, but these are deactivated after a period of 48 h.

However, one of the most selective methods employed for the manufacturing of cyclohexanone is the partial hydrogenation of phenol. This process is carried out industrially over Pd/Al₂O₃ catalysts modified with alkali or alkali–earth metals [127–129]. Phenol can be partially hydrogenated either in the liquid or the vapor phase, but the latter involves an expensive two-step process, as phenol is first hydrogenated to cyclohexanol over a nickel catalyst to be then

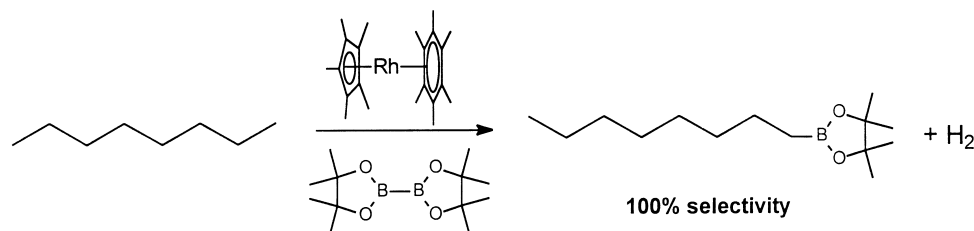


Fig. 4. Functionalization of *n*-octane in the terminal position [137,138].

endothermically dehydrogenated to cyclohexanone. The liquid phase conversion can be accomplished with a large variety of heterogenized catalysts, such as carbon supported platinum alloys [130], nickel supported on silica [131,132] and palladium supported on hydrotalcite [133–135] or magnesium oxide [136]. The choice of the support is essential for both the activity and selectivity of these catalysts. For example, basic oxides such as MgO show higher activities, but their poor mechanical strength limits its industrial application, while alumina alone suffers from severe deactivation during the course of the reaction. Alumina has its activity increased by the addition of alkali or earth-alkali promoters, that can enhance desorption of the cyclohexanone from the support and prevent deactivation due to coke formation. However, the selectivity strongly decreases when conversions higher than 10% are achieved, thus lowering the yields. It appears that the catalysts prepared from hydrotalcite supports are the most promising, as conversions higher than 45% can be achieved while maintaining excellent selectivities for cyclohexanone (>95%).

On the other hand, other starting materials such as hydrocarbons have shown to be a promising answer for the replacement of those already in use. Considering the large volume of these raw mixtures brought annually from beneath Earth's surface, it is a pity that most of it is burned as simple fuels, as a result of their low reactivity, especially in the terminal position. Recent studies on the functionalization of saturated hydrocarbons show a high selectivity to linear alkylboranes, which can be easily further converted to alcohols and then to carboxylic acids. For instance, reactions of *n*-octane and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi-1,3,2-dioxaborolane (pinBBpin) in the presence of 5 mol% of Cp^{*}Rh (η^4 -C₆Me₆) at 423 K (Fig. 4), gives the octyl-borane

as the only product in a 88% yield [137,138]. On the other hand, selective carboxylation of saturated hydrocarbons with carbon monoxide could give adipic acid in a single step. Some good results have already been obtained in this field, i.e. Co(OAc)₂/K₂S₂O₈ in trifluoroacetic acid allows the selective synthesis of different linear carboxylic acids [139,140] as do reactions catalyzed by Mg/K₂S₂O₈ in trifluoroacetic acid [141,142] and polyhalomethane-AlBr₃ [143]. The selective oxidation of linear alkanes has also been successfully accomplished with molecular oxygen on molecular sieves, where those prepared by the isomorphous incorporation of cobalt and manganese atoms to give namely CoAlPO-18 and MnAlPO-18 have given the best results [144].

6. Conclusions

Cyclohexane oxidation with hydrogen peroxide in the presence of homogeneous catalysts or redox molecular sieves shows low efficiency and is, therefore, not interesting for industrial applications. Peroxometalates as catalyst are much more efficient and should be studied in more detail. Cyclohexane oxidation with *tert*-butyl hydroperoxide gives much higher efficiencies in the presence of homogeneous or heterogeneous catalysts or redox molecular sieves, since this oxidant is more reactive. However, its higher price and the need to utilize the *tert*-butanol produced makes this oxidant unattractive for industry. The ideal oxidant is certainly molecular oxygen, which is cheap and quite selective if temperatures not higher than 343 K are used. The challenge is to find active catalysts for these conditions. The combination of redox active solids, like the amorphous cerium containing silica found in our group, with *tert*-butyl

hydroperoxide seems to be an appropriate solution as long as the hydroperoxide is a co-catalyst and not used up in the oxidation process. On the other hand, non-radical oxidation of cyclohexene is an interesting alternative for industry, as cyclohexanone is directly obtained in a Wacker-type oxidation, and the oxidative cleavage of the double bond would directly lead to adipic acid. However, these oxidative transformations of cyclohexene need to be further studied.

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