

Cyclohexane oxidation with dioxygen catalyzed by supported pyrazole rhenium complexes

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Abstract

The pyrazole complexes $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$ **2** (Hpz = pyrazole), $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ **3** and $[\text{ReClF}\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ **4**, and their precursor $[\text{ReOCl}_3(\text{PPh}_3)_2]$ **1**, immobilized on 3-aminopropyl functionalized silica, catalyze the cyclohexane oxidation with dioxygen, to cyclohexanol and cyclohexanone (the main product), in the absence of solvent and additives and under relatively mild conditions. Complex **4**, whose synthesis and characterization are reported herein for the first time, provides the best activity (*ca.* 16% overall conversion towards the ketone and alcohol, at the O₂ pressure of 19 atm, at 150 °C, 8 h reaction time). The reaction is further promoted by pyrazinecarboxylic acid. TGA analysis shows that the supported complexes are stable up to *ca.* 200 °C. The use of radical traps supports the involvement of a free-radical mechanism via carbon- and oxygen-centred radicals. The effects of various factors were studied towards the optimization of the processes. Complex **4** also catalyzes the oxidation of other cycloalkanes to the corresponding cycloalkanols and cycloalkanones.

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1. Introduction

In spite of the very rich coordination chemistry that has been expanded for rhenium [1–4], the use of complexes with this metal as catalysts is still an underdeveloped field of research. However, the wide application of $[(\text{Me})\text{ReO}_3]$ (MTO) in oxidation catalysis [4–6] clearly demonstrates the ability of this metal to form highly active catalysts for oxidation reactions of olefins and other unsaturated substrates.

Recently we have found that some rhenium complexes with O- or N-ligands can catalyze, in homogeneous systems, alkane functionalization reactions, under mild or moderate conditions. Hence, MTO and other Re oxides [6], benzoylhydrazido- and benzoyldiazenido-Re complexes [7], and trispyrazolylmethane and pyrazole complexes of Re [8], can act as homogeneous cat-

alysts for the peroxidative oxidation [6–8], or carboxylation [6] of some alkanes.

For these Re systems, dioxygen was not an adequate oxidant, but we have observed that, when supported on suitably modified silica gel, some bis(maltolato)oxovanadium complexes could catalyze the partial oxidation, with O₂, of cyclic [9–11] and linear [12] alkanes to the corresponding alcohols and ketones. Hence, the extension of this type of study to rhenium complexes, by immobilizing them on a silica gel support, towards the development of rhenium heterogeneous catalytic systems (with the normal advantages over the homogeneous ones *e.g.* in terms of easy catalyst separation and recovery) that could operate with the ideal “green” oxidant, *i.e.* dioxygen, for oxidative functionalization reactions of alkanes, constitute main aims of the current study. A contribution towards widening the use of Re complexes in catalysis is also an objective of this work.

We have selected cyclohexane as the substrate in view of the relevance of its partially oxidized products (cyclohexanol and cyclohexanone) for the production of adipic acid and caprolac-

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tam, which are further used in the manufacture of nylon-6,6 and nylon-6, respectively [13–17]. Normally, Co compounds (cobalt naphthenate or cobalt acetate) have been used for the industrial oxidation reaction, with dioxygen as oxidant, at a temperature above 150 °C, and only a low conversion (*ca.* 4%) is achieved to obtain a high selectivity (*ca.* 85%) towards a mixture of cyclohexanone and cyclohexanol [17]. Studies have been undertaken to develop new selective catalytic systems with a higher activity under mild conditions and using different oxidizing agents (*e.g.* hydrogen peroxide, *t*-butyl hydroperoxide, molecular oxygen and ozone). Heterogeneous catalysts are often oxides or metal cations incorporated in inorganic supports (*e.g.* silica, alumina, zirconia, active carbon, zeolites or aluminophosphates), while promoters can be used to reduce the induction period and to increase the selectivity for the target products [18–24]. Other oxidation catalysts are transition metal-substituted heteropoly compounds (heteropolyoxometalates), which can show activity in the oxidation of alkanes [14,24–28].

In the current study, the new pyrazole rhenium compound [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)] **4** (Hpz = pyrazole), whose synthesis and characterization are reported herein for the first time, and other rhenium complexes, *i.e.* [ReOCl₃(PPh₃)₂] **1**, [ReCl₂{N₂C(O)Ph}(Hpz)(PPh₃)₂] **2** and [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)] **3**, have been supported on 3-aminopropyl functionalized silica and used as heterogeneous catalysts in an efficient and selective oxidation of cyclohexane (mainly to cyclohexanone), by dioxygen in the absence of solvent and additives, under relatively mild reaction conditions.

2. Experimental

2.1. Synthesis of the rhenium complexes (1–3)

Complexes [ReCl₂{η²-*N,O*-N₂C(O)Ph}(PPh₃)₂] **1** [29], [ReCl₂{N₂C(O)Ph}(Hpz)(PPh₃)₂] **2** (Hpz = pyrazole) [30], [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)] **3** [30], and the precursor [ReOCl₃(PPh₃)₂] **1** [31,32] were prepared according to published procedures. Reaction of **1** with an excess of PPh₃ and PhCONHNH₂ led to the formation of [ReCl₂{η²-*N,O*-N₂C(O)Ph}(PPh₃)₂] **1** [29], whereas complexes **2** and **3** were synthesized by treatment of the latter with pyrazole or tris(pyrazolyl)methane (HCp₃) [30] (reactions a–d, Scheme 1).

2.2. Synthesis of the pyrazole fluoro-rhenium complex 4

The newly synthesized pyrazole fluoro-rhenium complex [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)] **4** was obtained (reaction e, Scheme 1) upon a slow addition of a methanol (15 mL) solution of Ti[BF₄] (24 mg, 0.084 mmol) to a dichloromethane (20 mL) solution of [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)] **3** (57 mg, 0.073 mmol). The mixture was stirred under reflux for *ca.* 48 h and filtered to remove TiCl₄. Concentration under vacuum of the dark green solution followed by slow addition of Et₂O resulted in the precipitation of complex **4** as a dark green solid which was filtered-off, washed with Et₂O and dried under vacuum (0.040 g, 56% yield).

Analysis. Found: C, 45.4; H, 3.3; N, 9.8%. ReC₃₁H₂₆N₆POClF_{1/2}CH₂Cl₂ requires C, 45.3; H, 3.5; N, 9.6.

FT-IR (KBr pellet): 3239 [s, ν(NH)], 1588 [s, ν(C=O)], 1538 [vs, ν(N=N) N₂COPh and/or ν(N=C) Hpz], 430 [w, Re–F].

¹H NMR (CDCl₃): δ 15.18 and 12.66 [s, 1H + 1H, H(1) Hpz], 7.95 [dd, 2H, ³J_{HH} = 7.2, ⁴J_{HH} = 2.0, *o*-COPh], 7.63 [m, 1H, H(3) or H(5) Hpz], 7.62–7.55 [m, 6H (*o*- or *m*-PPh₃)], 7.53 [m, 1H, *p*-COPh], 7.50 [m, 1H, H(3) or H(5) Hpz], 7.42 [m, 2H, *m*-COPh], 7.38–7.32 [m, 9H, {(*m*- or *o*-) + *p*}-PPh₃], 7.29 [s, 1H, H(3) or H(5), Hpz], 7.0 [m, 1H, H(3) or H(5), Hpz], 6.35 [q, 1H, J_{HH} = 2.4, H(4), Hpz], 6.18 [q, 1H, J_{HH} = 2.4, H(4) Hpz].

³¹P-{¹H} NMR (CDCl₃): δ 4.43 [d, ²J_{PF} = 26.8].

¹³C-{¹H} NMR (CDCl₃): δ 171.12 [s, C=O], 139.69 and 137.93 [s, C(3) Hpz], 134.0 [d, J_{CP} = 9.8, C_o or C_m (PPh₃)], 133.9 [s, C_p (COPh)], 132.14 [s, C(5) Hpz], 132.0 [s, C_o or C_m (COPh)], 131.46 [s, C(5) Hpz], 130.7 [d, J_{CP} = 2.5, C_p (PPh₃)], 129.91 [d, J_{CP} = 9.4, C_i (PPh₃)], 129.76 [s, C_i (COPh)], 128.78 [s, C_m or C_o (COPh)], 128.14 [d, J_{CP} = 10.6, C_m or C_o (PPh₃)], 106.94 and 106.50 [s, C(4) Hpz].

¹³C NMR (CDCl₃): 171.12, 139.69 and 137.93 [d, J_{CH} = 184.2 and 187.4 C(3) Hpz], 134.0 [dd, J_{CH} = 158.9, C_o or C_m (PPh₃)], 133.9 [d, J_{CH} = 135.6, C_p (COPh)], 132.14 [s, J_{CH} = 162.6 C(5) Hpz], 132.0 [d, J_{CH} = 172.5, C_o or C_m (COPh)], 131.46 [d, J_{CH} = 157.6 C(5) Hpz], 130.7 [dd, J_{CH} = 159.1, C_p (PPh₃)], 129.91, 129.76, 128.78 [dm, J_{CH} = 150.8, C_m or C_o (COPh)], 128.14 [dd, J_{CH} = 162.5, C_m or C_o (PPh₃)], 106.94 and 106.50 [d, J_{CH} = 183.5 and 186.2, C(4) Hpz].

FAB⁺-MS: *m/z* 772 ([M]⁺), 639 ([M–N₂COPh]⁺), 753 ([M–F]⁺), 737 ([M–F–Cl]⁺), 704 ([M–Hpz]⁺), 571 ([M–N₂COPh–Hpz]⁺), 517 ([M–N₂COPh–Hpz–F]⁺).

2.3. Immobilization of the Re complexes on chemically modified silica

We have used the wet-impregnation method [33] for immobilization of the rhenium complexes on the surface of 3-aminopropyl modified silica gel (available from Sigma). Each of the above rhenium complexes (25 mg) was separately dissolved in methanol (10 mL), the solution added to the 3-aminopropyl modified silica (1.0 g) and the mixture refluxed at 80 °C for 5 h.

The modified silica gel with the supported rhenium complexes was filtered-off, washed several times with methanol, dried at 40 °C for 6 h, under dinitrogen, and then at 50 °C for 4 h, in an oven. After drying we found that 19 mg of [ReOCl₃(PPh₃)₂] **1**, 21 mg of [ReCl₂{N₂C(O)Ph}(Hpz)(PPh₃)₂] **2**, 20 mg of [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)] **3** or 23 mg of [ReClF{N₂C(O)C₆H₅}(Hpz)₂(PPh₃)] **4** were separately loaded per gram of 3-aminopropyl functionalized silica support. The colours of the 3-aminopropyl functionalized silica supported catalysts are as follows: light green for **1** and yellow for **2–4**.

The immobilization of the metal compounds possibly occurs via hydrogen-bonding between the NH₂ (and/or OH) groups of the silica support and ligands of the complexes (halides, ben-

2.5. Typical oxidation reaction procedure

The oxidation reactions were performed in a high pressure stainless steel cylindrical rocking batch reactor (22 mL capacity), provided with a gas delivery inlet and a pressure gauge. The inside temperature was controlled by an on/off controller with a suitable thermocouple for temperature sensing. In typical conditions, 3.0 mL (27.8 mmol) of neat cyclohexane and 20 mg of supported rhenium catalyst were used for 8 h. At the end of the reactions, the supported catalysts, whose colours (see above) had turned into light brown, were separated from the solutions by filtration, using a filter paper, and washed three times with acetone. The supported catalysts could be reactivated for further use by heating in an air oven at 60 °C for 6 h. In the experiments with unsupported Re catalysts, the reactions were carried out in a similar way to that of the supported ones, but by using the former (1.2 mg) instead of the latter (20 mg) catalysts.

The oxidation products were analyzed by gas chromatography (GC) (30 μ L of cyclopentanone added as internal standard to 1.0 mL of the filtered final reaction solution). The temperature of injection of the chromatograph (see above) was 240 °C. The initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min to 180 °C, and held at this temperature for 1 min. Helium was used as the carrier gas. They were further analyzed by GC–MS measurements. The turnover numbers (TONs) (moles of product per mole of catalyst) and yields (moles of product per mole of cyclohexane) were estimated. Blank experiments with silica gel or the 3-aminopropyl modified silica gel, but without the Re catalyst, were also performed, giving maximum conversions to cyclohexanol and cyclohexanone of 1.7 and 0.6%, respectively (under the same conditions of entry 3, Table 1). This low, although detectable, activity can result, at least in part, from the effect of the stainless steel reactor walls [36], but this was not investigated further, in the current study, in view of its low significance.

3. Results and discussion

The supported complexes (1–4) act as selective catalysts (or catalyst precursors) for the oxidation of neat cyclohexane, by molecular oxygen, to cyclohexanol and, mainly, cyclohexanone, under relatively mild conditions, without any solvent or additive (Table 1). The pyrazole fluoro-complex [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)] **4** provides the most active system, in a typical run (entry 3, Table 1) leading, after 8 h reaction time, to yields (moles of product/mole of cyclohexane) of cyclohexanone and cyclohexanol of 8.3 and 2.5% (10% overall for these products, within a total 11.3% of cyclohexane conversion, including the by-products), for $p(\text{O}_2) = 13.6$ atm, at 150 °C. The activity corresponds to a TON (estimated simply as the number of moles of cyclohexanone + cyclohexanol per mole Re-complex loaded on the silica) of 5.0×10^3 and is much higher than those of the other catalysts (see entries 18–20, Table 1).

The strong smell at the end of the reaction, when carried out in the presence of the catalyst, indicated the products formation, what was further confirmed by GC and GC–MS analyses that allow to quantify the amounts of cyclohexanone and cyclohex-

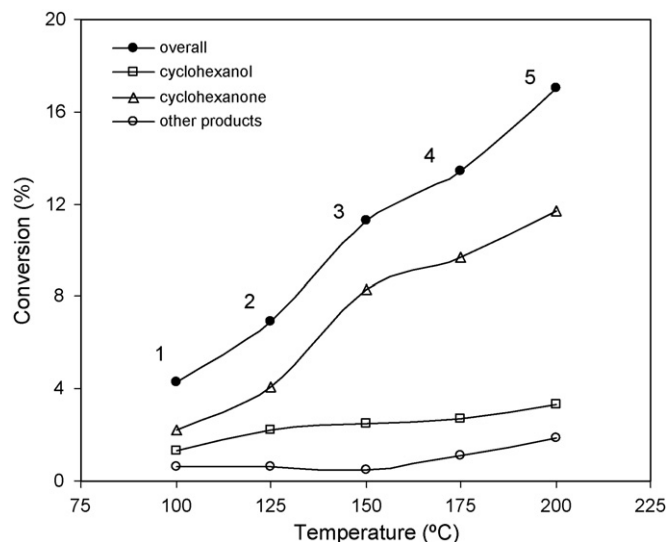


Fig. 1. Effect of temperature on the conversion of cyclohexane, upon oxidation by molecular O₂, in the presence of [ReClF{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] **4** supported on 3-aminopropyl modified silica ($p(\text{O}_2) = 13.6$ atm, time = 8 h). Point numbering corresponds to runs of Table 1.

anol, the main products. As a result of the chemical reaction, the colour of the supported catalysts changes to brown.

After being used, the supported catalysts can be reactivated upon washing (three times) with acetone and drying in an air oven at 60 °C for 6 h, showing usually a comparable activity to that of the initial run.

The effects of various factors (temperature, oxygen pressure, reaction time, amount of catalyst, presence of a co-catalyst) on the catalytic activity and selectivity, as well as the activity towards other substrates, were further studied (Tables 1–3 and Figs. 1–7) for the case of the supported complex **4** which pro-

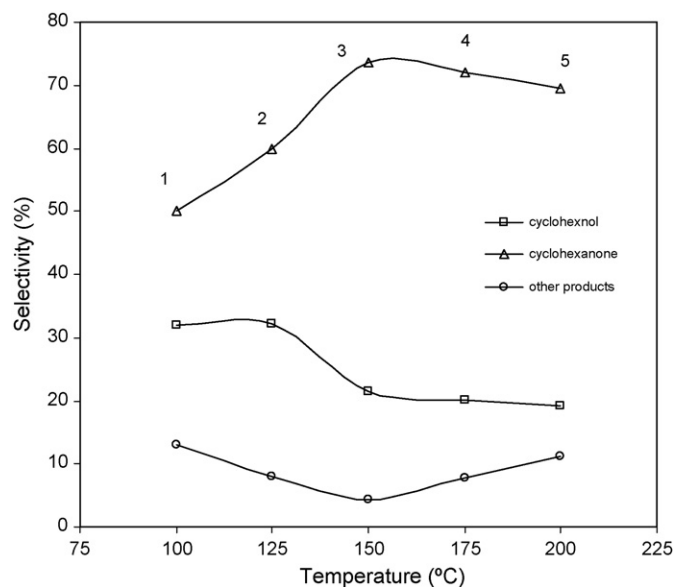


Fig. 2. Effect of temperature on the selectivity of the oxidation of cyclohexane by molecular O₂, in the presence of [ReClF{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] **4** supported on 3-aminopropyl modified silica ($p(\text{O}_2) = 13.6$ atm, time = 8 h). Point numbering corresponds to runs of Table 1.

Table 1
Cyclohexane oxidation with dioxygen catalyzed by supported rhenium complexes^a

Entry	Catalyst	$p(\text{O}_2)^b$ (atm)	Time (h)	Catal (mg)	Temperature ($^\circ\text{C}$)	Conversion (%) ^c			
						Cyclohexanone	Cyclohexanol	Others	Overall
1	4	13.6	8	20	100	2.2	1.3	0.6	4.1
2	4	13.6	8	20	125	4.1	2.2	0.6	6.9
3	4	13.6	8	20	150	8.3	2.5	0.5	11.3
4	4	13.6	8	20	175	9.7	2.7	1.1	13.5
5	4	13.6	8	20	200	11.7	3.3	1.9	16.9
6	4	5.5	8	20	150	1.3	0.8	0.0	2.1
7	4	8.2	8	20	150	4.3	2.2	0.4	6.9
8	4	11.0	8	20	150	6.4	2.8	0.5	9.7
9	4	16.3	8	20	150	10.4	2.9	1.2	14.5
10	4	19.0	8	20	150	12.8	3.3	2.2	18.3
11	4	13.6	4	20	150	1.9	0.5	0.0	2.4
12	4	13.6	6	20	150	3.8	1.4	0.1	5.3
13	4	13.6	12	20	150	10.0	2.3	1.4	13.7
14	4	13.6	24	20	150	11.2	3.2	3.5	17.9
15	4	13.6	8	10	150	2.4	1.1	0.0	3.5
16	4	13.6	8	30	150	11.7	3.5	0.8	16.0
17	4	13.6	8	50	150	13.1	3.7	1.6	18.4
18	1	13.6	8	20	150	3.0	2.3	0.0	5.3
19	2	13.6	8	20	150	5.0	2.1	0.0	7.1
20	3	13.6	8	20	150	5.6	3.0	0.2	8.8

^a Supported Re catalyst = 20 mg, cyclohexane = 27.8 mmol, in an autoclave (22 mL capacity).

^b Measured at 25 $^\circ\text{C}$ (1 atm = 1.01 bar = 101 kPa).

^c Percentage molar yield (moles of product per mole of cyclohexane).

Table 2
Effect of various heteroaromatic carboxylic acids (as co-catalysts) on the cyclohexane oxidation with dioxygen catalyzed by $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ 4^a

Co-catalyst	Entry	Conversion (%) ^b		
		Cyclohexanone	Cyclohexanol	Overall
3-Amino-2-pyrazinecarboxylic acid	1	10.3	3.1	14.3
2,6-Pyrazinedicarboxylic acid	2	10.6	3.0	14.9
2,3-Pyrazinedicarboxylic acid	3	11.5	3.4	15.6
Pyrazinecarboxylic acid	4	12.7	3.3	16.8
Picolinic acid	5	8.8	2.8	11.9

^a Same conditions as those indicated for the entry 3 in Table 1.

^b Percentage molar yield (moles of product per mole of cyclohexane).

vides the most active catalytic system. TGA analysis of this freshly supported catalyst shows that it is stable up to ca. 200 $^\circ\text{C}$ (Fig. 8).

The unsupported Re complexes do not lead to amounts of products considerably above those obtained in blank assays,

Table 3
Oxidations of various cycloalkanes and of benzene with dioxygen catalyzed by supported $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ 4^a

Entry	Substrate	Conversion (%) ^b	
		Cyclohexanone	Cyclohexanol
1	Cyclopentane	4.7	2.8
2	Cycloheptane	7.5	3.8
3	Cyclooctane	8.8	3.3
4	Benzene	0.0	0.5

^a Same conditions as those for the entry 3 in Table 1.

^b Percentage molar yield (moles of product per mole of cyclohexane).

what suggests the involvement of a heterogeneous catalytic process, the Re complexes, under homogeneous reaction conditions, conceivably undergoing decomposition into inactive species.

3.1. Effect of temperature

The temperature effect on the oxidation of cyclohexane was examined in the range from 100 to 200 $^\circ\text{C}$ (Table 1, entries 1–5, and Fig. 1, for $p(\text{O}_2) = 13.6$ atm and 8 h reaction time). The reaction temperature was not allowed to go beyond 200 $^\circ\text{C}$ due to the formation of an unidentified black material. Although the conversion of cyclohexane to cyclohexanol increases rather slowly, a sharp increase occurs towards cyclohexanone (11.7% yield at 200 $^\circ\text{C}$, with an overall conversion of 16.9%). In order to test if this behaviour could reflect the conversion of cyclohexanol to cyclohexanone, we have checked if this alcohol could be oxi-

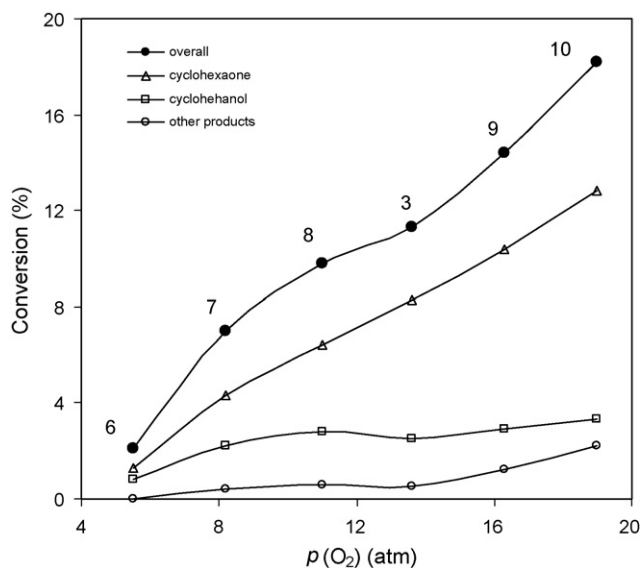


Fig. 3. Effect of O_2 pressure on the conversion of cyclohexane, upon oxidation by molecular O_2 , in the presence of $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ **4** supported on 3-aminopropyl modified silica (temperature = 150°C , time = 8 h). Point numbering corresponds to runs of Table 1.

dized to the ketone by performing an experiment at 175°C , under identical conditions to those of run 4 (Table 1), but using cyclohexanol as the substrate instead of cyclohexane. We have then observed a conversion of the alcohol into the ketone of only 4.3% (49% selectivity), what suggests that most of the ketone derived from the oxidation of the alkane is not formed via oxidation of free cyclohexanol.

The dependence of the selectivity on the temperature is shown in Fig. 2 which indicates that a maximum selectivity towards cyclohexanone is achieved at *ca.* 150°C .

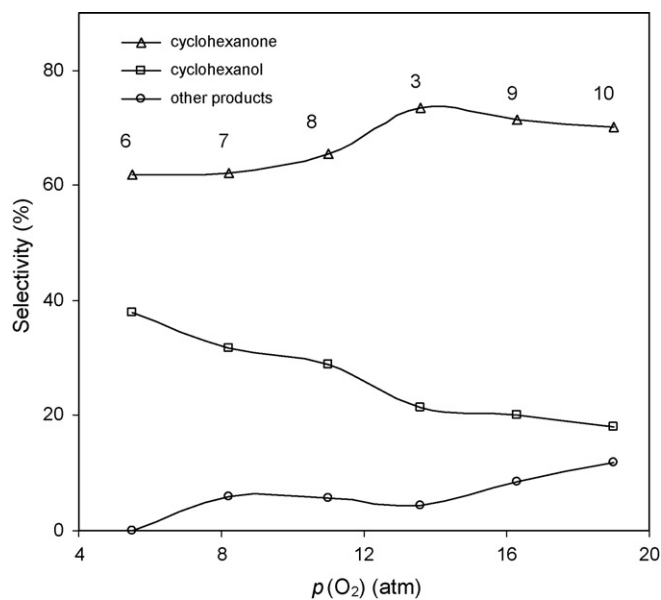


Fig. 4. Effect of O_2 pressure on the selectivity of the oxidation of cyclohexane by molecular O_2 , in the presence of $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ **4** supported on 3-aminopropyl modified silica (temperature = 150°C , time = 8 h). Point numbering corresponds to runs of Table 1.

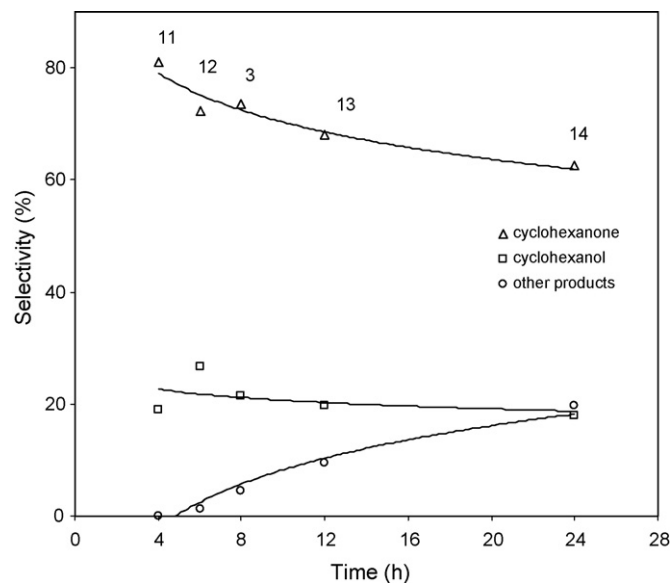


Fig. 5. Effect of time on the selectivity of the oxidation of cyclohexane by molecular O_2 , in the presence of $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ **4** supported on 3-aminopropyl modified silica (temperature = 150°C , $p(\text{O}_2) = 13.6$ atm). Point numbering corresponds to runs of Table 1.

3.2. Effect of dioxygen pressure

The effect of O_2 pressure on cyclohexane oxidation was studied in the range from 5.5 to 19 atm $p(\text{O}_2)$ at constant temperature (150°C) and time (8 h) (entries 3 and 6–10, Table 1). The increase of this pressure results in an enhancement of the conversions of cyclohexane (Fig. 3), *e.g.* the overall conversion increases from 2.1 to 18.3% upon changing $p(\text{O}_2)$ from 5.5 to 19 atm, what is consistent with the promotion of the solubility of this gas in the system. The selectivity towards cyclohexanone

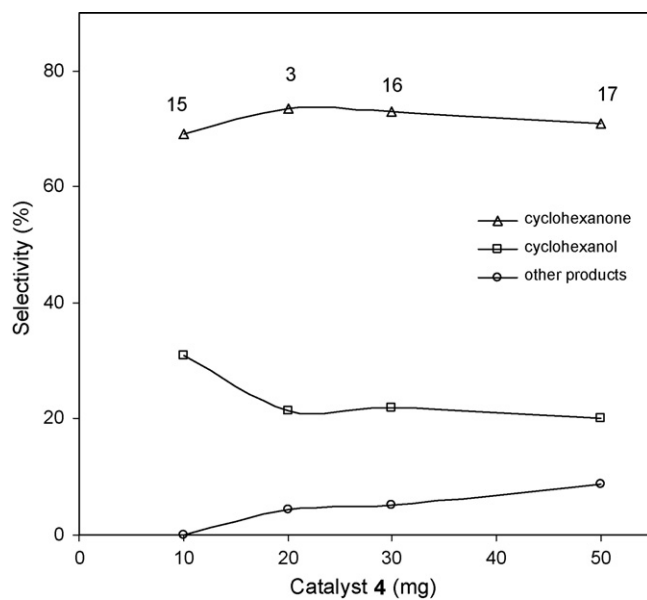


Fig. 6. Effect of the amount of 3-aminopropyl modified silica with supported $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ **4** on the selectivity of the oxidation of cyclohexane by molecular O_2 (temperature = 150°C , $p(\text{O}_2) = 13.6$ atm, time = 8 h). Point numbering corresponds to runs of Table 1.

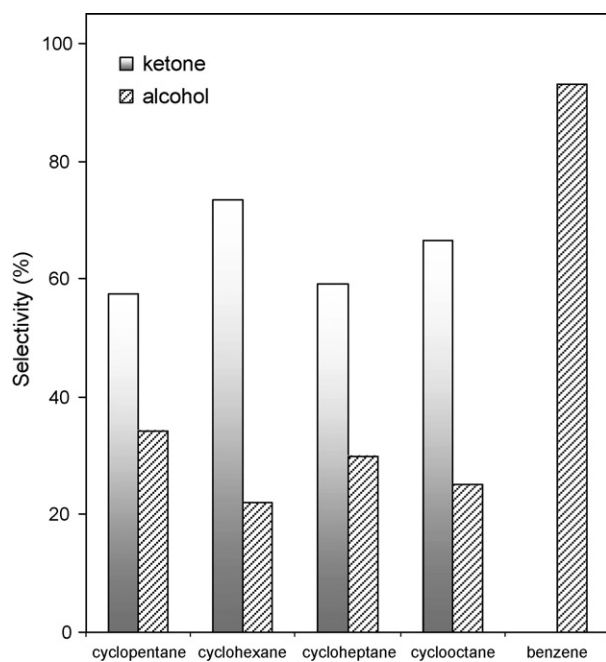


Fig. 7. Selectivities of the oxidations of various cycloalkanes and benzene with molecular O_2 , in the presence of $[ReClF\{NNC(O)C_6H_5\}(Hpz)_2(PPh_3)]$ **4** supported on 3-aminopropyl modified silica (temperature = $150^\circ C$, $p(O_2) = 13.6$ atm, time = 8 h, catalyst = 20 mg).

also increases with $p(O_2)$, but only until 14 atm, while that for cyclohexanol decreases with the pressure increase due to the promotion of the relative amount of by-products. Hence, the use of O_2 pressures above *ca.* 14 atm is not advantageous in terms of selectivity.

3.3. Effect of the reaction time

The effect of the reaction time was studied (entries 3 and 11–14, Table 1) in the range 4–24 h (at constant temperature, $150^\circ C$, and $p(O_2) = 13.6$ atm) and it was observed that the con-

versions towards the desired cyclohexanone and cyclohexanol products does not greatly increase after the first 8 h (*e.g.* the overall conversion of cyclohexane into the ketone and the alcohol increases from 10.8 to 14.4%, for 8–24 h reaction time). Moreover, extending the reaction time above 8 h results in a decrease of the selectivity (Fig. 5) towards such products, concomitant with a more pronounced increase of the formation of by-products.

3.4. Effect of the amount of supported catalyst

The increase of the amount of the supported $[ReClF\{N_2C(O)Ph\}(Hpz)_2(PPh_3)]$ **4** catalyst leads to a growth of the overall conversion (3.5–18.4% for 10–50 mg, respectively, entries 3 and 15–17, Table 1). The selectivity towards the main product, *i.e.* cyclohexanone, remains nearly invariant, *ca.* 70%, but the relative amount of by-products increases (Fig. 6).

3.5. Effect of co-catalysts

Some heteroaromatic acids were tested as possible co-catalysts (Table 2). Pyrazinecarboxylic acid promotes considerably the reaction, increasing the overall conversion (from 11.3 to 16.8%, entries 3, Table 1, and 4, Table 2). A promoting effect of the same acid was also observed by us [11,12] for related alkane oxidations catalyzed by supported V-complexes, and by Shul'pin and Süß-Fink [37,38] in the peroxidative oxidation of alkanes, in various homogeneous systems with V-species. 2,3-Pyrazinedicarboxylic acid, 2,6-pyrazinedicarboxylic acid and 3-amino-2-pyrazinecarboxylic acid have a less pronounced effect, while picolinic acid is almost inactive (11.9% overall conversion *vs.* 11.3% in the absence of this acid). Picolinic acid is also less effective than pyrazinecarboxylic acid [11,37,38] in the above V-catalyzed alkane oxidations.

3.6. Oxidation of other cycloalkanes

The supported $[ReClF\{N_2C(O)Ph\}(Hpz)_2(PPh_3)]$ **4** complex was also tested as a catalyst for the oxidation, with O_2 , of some other cycloalkanes (cyclopentane, cycloheptane and cyclooctane) and benzene (Table 3, Fig. 7). In the cases of these cycloalkanes, the corresponding cycloalkanones and cycloalkanols are formed with conversions and selectivities comparable to those for cyclohexane oxidation (Fig. 7). In contrast, the oxidation of benzene only leads to phenol in a rather lower yield.

3.7. Mechanism

Alkane oxidation reactions can occur [39] via different types of mechanisms. In the current study, the involvement of a free-radical process is supported by the inhibition of the catalytic activity when performing the reactions in the presence of bromotrichloromethane or diphenylamine, *i.e.* a carbon- and an oxygen-radical trap, respectively.

Hence, the oxidation is proposed to proceed via the cyclohexyl radical (Cy^\bullet) obtained by reaction of cyclohexane (CyH)

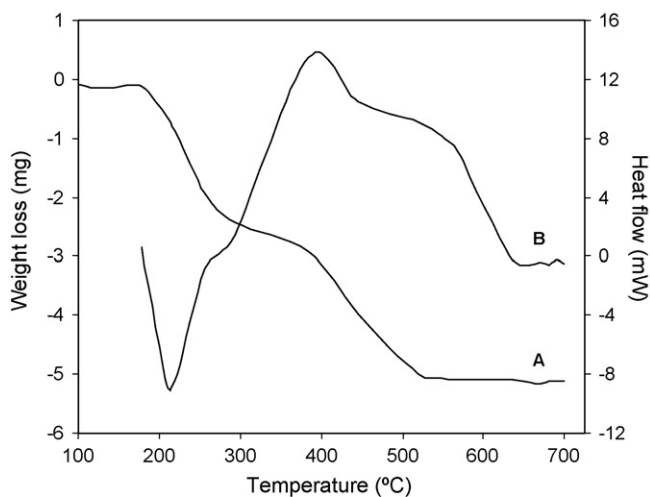


Fig. 8. Thermogravimetric analysis of 3-aminopropyl modified silica with supported $[ReClF\{NNC(O)C_6H_5\}(Hpz)_2(PPh_3)]$ **4** catalyst: (a) weight loss and (b) heat flow.

with O₂ upon homolytic C–H bond cleavage (slow induction period). Oxidation of Cy• by O₂ would form the alkylperoxy radical CyOO• which could react in two ways: (i) decomposition to the final products, *i.e.* cyclohexanol (CyOH) and cyclohexanone (Cy(–H)=O), also with formation of O₂; (ii) H-atom abstraction from the alkane to form the alkyl hydroperoxide CyOOH, whose homolytic decomposition to alkyloxy (CyO•) (O–O bond cleavage) and alkyl peroxy (CyOO•) (O–H rupture) could be catalyzed by a rhenium catalyst. The alcohol (CyOH) could then be formed either by H-abstraction from the alkane (CyH) by CyO• or (see (i) above) by decomposition of the CyOO• to yield also cyclohexanone.

This type of mechanism has been proposed [10–12,39,40] for catalysts in which the metal has two available oxidation states of comparable stability, a property that is not unusual in Re coordination chemistry [1]. The involvement of the hydroperoxide CyOOH is substantiated by the promotion of the detected amount of CyOH with a decrease of that of the ketone Cy(–H)=O, when the final reaction solution is treated with an excess of PPh₃ prior to GC analysis, according to a method reported by Shul'pin [41,42]. The CyOOH still present in the final reaction solution (which did not undergo the above mentioned decomposition in (ii)) is then deoxygenated by PPh₃ to give CyOH (with formation of phosphine oxide), thus eliminating the CyOOH decomposition to both CyOH and Cy(–H)=O in the gas chromatograph [41,42]. In the absence of PPh₃, the overall GC detected amounts of cyclohexanol and cyclohexanone comprise those derived from CyOOH during the reaction (see (ii) above) and those formed upon decomposition, at the GC operating conditions, of the remaining CyOOH in the final reaction solution.

Another point that deserves a comment is that in the present study cyclohexanone always predominates over cyclohexanol, what shows that the ketone can also be formed by other reactions apart from those mentioned above. They can include (i) metal-assisted decomposition of CyOOH to Cy(–H)=O, or (ii) metal-assisted oxidation of the alcohol CyOH to the ketone Cy(–H)=O. In our case, pathway (ii) does not appear to be a relevant one, in view of the observed limited conversion of the alcohol into the ketone, under typical reaction conditions.

Reactions of those types have been proposed for cyclohexane oxidation with O₂ catalyzed by a photoexcited polyoxodectungstate immobilized on amorphous or MCM-41 silicas [43], which also usually lead to a higher amount of the ketone in comparison with the alcohol. A different CyOOH decomposition path, via adsorbed intermediates without formation of free radicals, has been recently proposed [44], on the basis of kinetic studies, for the CyH oxidation with O₂ on MnAPO-5 catalysts (APO-5 = aluminophosphate molecular sieves). However, it is not expected to be followed in the current study since it would account for a ketone/alcohol product ratio of only 0.5.

4. Conclusions

The work shows that pyrazole rhenium complexes, when supported on 3-aminopropyl functionalized silica gel, catalyze the cyclohexane oxidation with O₂ (the ideal “green”

oxidant) to cyclohexanone (the major product) and cyclohexanol, under moderate conditions. The fluoro-complex [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)] **4** provides the system with the best activity and selectivity towards those products, reaching, under typical conditions (*p*O₂ = 13.6 atm, at 150 °C, 8 h reaction time), an overall conversion of 11% and an overall selectivity of 95%. The conversion increases to *ca.* 16–17% upon increasing the O₂ pressure to 19 atm or duplicating the catalyst amount or using pyrazinecarboxylic acid (an heteroaromatic acid) as a promoter. The higher activity of the fluoro-complex **4**, in comparison with the related chloro-complexes **1–3**, is in accord with the observed [8] behaviours for the oxidation of ethane (to acetic acid or acetaldehyde) and of cyclohexane (to cyclohexanone and cyclohexanol), and possibly concerns the overall stronger electron-donor character [45] of the fluoride ligand, relatively to chloride, thus promoting the oxidation (by O₂) of the complex to a higher metal oxidation state, more favourable to the alkane reaction. A related behaviour was reported [46] for cycloalkanes oxidation catalyzed by the metaloporphyrins [Mn(X)(TTP)] [X = halide, OH[–], CH₃COO[–]; TTP = meso-tetrakis(*p*-tolyl)porphyrinato dianion], the fluoro–Mn complex acting as the best catalyst.

The reaction is proposed to proceed via a radical mechanism involving both carbon- and oxygen-centred radicals, as substantiated not only by assays with radical traps, but also by the inactivity (or very low activity) of the complex **4** to catalyze the oxidation of benzene. The oxidations with O₂ of the related C₅, C₇ and C₈ cycloalkanes, as catalyzed by complex **4**, lead similarly to the corresponding cycloalkanones and cycloalkanols, the former also as the main products, showing the generality of the catalytic behaviour of that complex for the oxidation of such a type of substrates (cycloalkanes). Further catalytic studies with those cycloalkanes and also with linear alkanes are under way.

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