

Article

Highly Active and Selective Supported Rhenium Catalysts for Aerobic Oxidation of *n*-Hexane and *n*-Heptane

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Abstract: A series of derivative C-scorpionate rhenium complexes, i.e., $[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2]$ (**A**) (where Hpz is pyrazole), $[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ (**B**), $[\text{ReCl}(\text{F})\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ (**C**), and their precursor $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (**D**), immobilized on 3-aminopropyl-functionalized silica have been prepared and used for neat O_2 oxidation of *n*-hexane and *n*-heptane mainly to the corresponding alcohols and, in lower amounts, ketones. The supported catalyst **C**, with fluoro- and diazenido-ligands, exhibits the highest activity for both alkanes (overall turnover numbers (TONs) up to 3.8×10^3 and 2.5×10^3 , for *n*-hexane and *n*-heptane, respectively) and can be reused in consecutive catalytic cycles. Improved conversion was observed after addition of hetero-carboxylate co-catalysts. A free-radical-based mechanism is proposed to explain the product formation.

Keywords: rhenium; scorpionate derivative; immobilization; supported catalysis; *n*-alkane; oxidation; molecular oxygen; product selectivity; radical mechanism

1. Introduction

Hydrocarbon oxy-functionalizations constitute very important industrial processes due to the huge worldwide demand for oxidized products [1–5]. Homogeneous metal complex catalysts have been successfully applied in various oxidation reactions but their separation from the liquid-phase reaction mixture is often a big challenge [6–9]. Thus, we aim to develop supported catalysts that combine the adaptability and activity of homogeneous ones with the ease of separation and catalyst recyclability of heterogeneous ones, making them potentially more appealing for chemical industry [10,11]. Oxidation with molecular oxygen (or air) is very attractive due to its abundant availability in the atmosphere and from an economical point of view in comparison with other oxidants. Aerobic alkane oxidations normally require, apart from suitable catalysts, the use of high temperatures and pressures, and, under such conditions, alkanes usually undergo competitive reactions—cracking, isomerization, dehydrogenation, cyclization, metathesis, oligomerization, and polymerization [12–14]. These types of difficulties are encountered, e.g., in the case of linear and liquid C_6 (*n*-hexane) and C_7 (*n*-heptane) alkanes [13,14] which are important components of naphtha, with oxy-functionalized derivatives that have commercial interest and, therefore, have been selected for the current study.

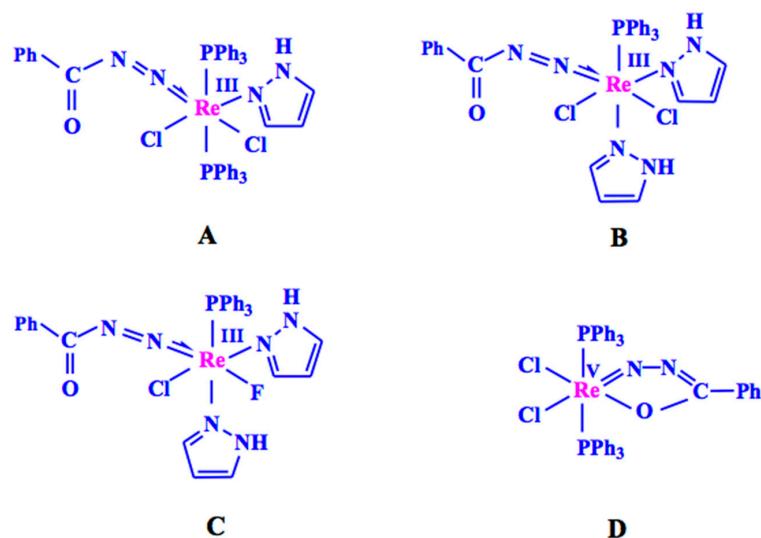
Many metal complex catalysts have been successfully used for C–H bond activation of alkanes with molecular oxygen [12,13,15–20]—in particular, MTO (methyltrioxorhenium trioxide), which is a commercial catalyst that also has high activity for olefin oxidations [21].

The heterogeneous partial oxidation of *n*-hexane with O₂ was reported for a Pt–10% Rh catalyst in a single-gauze auto-thermal reactor, at a typical preheat temperature of the feed gases of 200 °C, producing various oxygenates (70% selectivity) including 2,5-dimethyltetrahydrofuran (ca. 35% selectivity), with *n*-hexane and oxygen conversions of 20 and 100%, respectively [22]. In another case, the oxidation of *n*-hexane with O₂ catalysed by Mn-exchanged zeolites at 130 °C [23] led to a diversity of oxidation products (e.g., 3-hexanone, 2-hexanone, hexanal, 3-hexanol, 2-hexanol, acetic, propionic, butyric, valeric, and hexanoic acids). Other cases include the oxidation of *n*-hexane (and cyclohexane) by air and oxygen mixtures, in the absence and in the presence of Al₂O₃, Ni₂O₃, MoO₃, CuCl₂, and ZSM-5 + 1.2% Fe₂O₃, in a bubble plasma reactor, leading to a diversity of hydroxylated and carbonyl compounds such as alcohols, aldehydes, and ketones [24]. In the case of *n*-heptane, SiO₂–Zr complex catalysts also show a broad product distribution [19]. Vanadium complex catalysts supported on carbamate-modified silica gel originate several oxygenates (2- and 4-heptanone, 2- and 1-heptanol, *trans*-3-hepten-2-one, octan-2-ol, octanoic acid, heptaldehyde, and heptanoic acid) from *n*-heptane [11]. Several types of nonmetallic molecular sieves (e.g., BEA, MCM-41, SAPO-5, and SAPO-11) have also been used as catalysts for *n*-heptane aerobic (with oxygen) oxidation, between 300 °C and 400 °C, leading to a mixture of heterocyclic compounds (2-methyl-5-ethyl furan and 2,6-dimethylpyran), heptanones, 4-methyl-1,4-hexadiene, 2,4-dimethyl-1,3-pentadiene, and 1-hepten-4-ol [24].

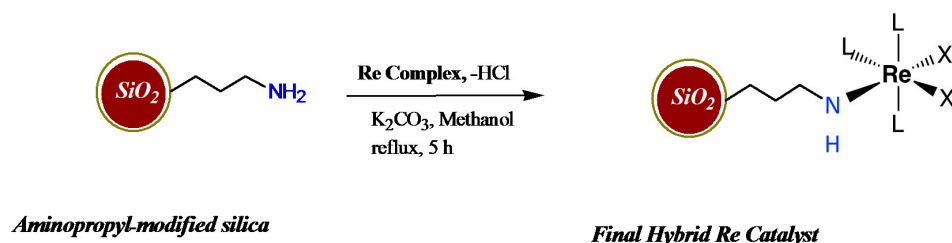
Recently, we have also reported SBA-15–Co complex catalysts for the O₂ oxidation of *n*-hexane and *n*-heptane at 150–200 °C (conversion of 19.6% and 17.3%, respectively) [20]. SBA-15–Re metal catalysts have been also used for direct *n*-hexane (and other *n*-alkanes) oxidation in the presence of O₂ with a high selectivity to hexane-2-one (up to 62%) at 150 °C [25]. Other metals were also investigated for catalysed *n*-hexane oxidation with O₂, namely modified SiO₂–oxovanadium complexes, leading mainly to hexan-2-one with high 58% selectivity at 160 °C [26]. A Schiff base isocyanate-modified SiO₂/V catalyst was used for the same reaction, with an overall conversion of ca. 10% to alcohols, ketones, and acids at 150 °C [27].

Previously, we had found that the rhenium pyrazole complex [ReClF{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] (C) (where Hpz is pyrazole) supported on modified SiO₂, is a catalyst for the oxidation of cycloalkanes with a good overall conversion of 16% at 150 °C [17]. This complex is part of a set of pyrazole derivatives of C-scorpionate complexes. In fact, attempts to synthesize a rhenium complex with a hydrotris(1-pyrazolyl)methane ligand from the reaction with the benzoylhydrazido rhenium(V) chelate (in stoichiometric amounts) in refluxing methanol led to the formation of the corresponding pyrazole derivatives [28,29]. The pyrazole ligand is derived from the rupture of a C(sp³)–N bond in the hydrotris-(1-pyrazolyl)methane compound—conceivably by hydrolysis of the C-scorpionate.

Herein, we address the anchorage of the pyrazole Re-complexes, [ReCl₂{NNC(O)C₆H₅}(Hpz)(PPh₃)₂] (A), [ReCl₂{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] (B), and [ReClF{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] (C), and their precursor [ReOCl₃(PPh₃)₂] (D) [17,28–31] on 3-aminopropyl-functionalized SiO₂ (Schemes 1 and 2), and evaluate them as reusable heterogeneous catalysts for the neat oxy-functionalization of *n*-hexane and *n*-heptane in the presence of molecular oxygen under pressure in a batch reactor under low temperature.



Scheme 1. Schematic representations of rhenium complexes A to D.



Scheme 2. Formation of hybrid materials by immobilization of rhenium complexes at 3-aminopropyl-modified silica.

2. Results

2.1. Catalyst Synthesis and Characterization

The aim of the current study was to assess the catalytic activity and the recyclability of the rhenium complexes $[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2]$ (**A**) (where Hpz is pyrazole), $[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ (**B**), $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ (**C**), and $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (**D**) anchored on 3-aminopropyl-functionalized silica (Schemes 1 and 2) for the partial oxidation of *n*-alkanes. Therefore, *n*-hexane and *n*-heptane were chosen for oxidation with a cheap and green oxidant (molecular oxygen).

Complexes A–D (Scheme 1) were synthesized according to a reported procedure [17,29,31] and characterized by spectroscopic and analytic techniques. Then, they were supported on 3-aminopropyl-functionalized silica by replacement of a chloride ligand by the N-donor silica via a condensation reaction in the presence of K_2CO_3 [15]. The loss of one chloride ligand from the Re coordination sphere was confirmed by far-IR spectroscopy ($400\text{--}200\text{ cm}^{-1}$): the spectra of A, B, and D display only one ($280\text{--}325\text{ cm}^{-1}$ range) of the two Re–Cl bands found in the non-immobilized complexes; in the spectrum of C, no band could be detected for the Re–Cl bond in the range $400\text{--}200\text{ cm}^{-1}$.

Morphological characterization of the respective chemical compositions [using scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS)] and thermal stability [using thermogravimetric analysis (TGA)] of the most active Re catalyst **C** are presented. SEM images (Figure 1A) of the Re complex **C** supported on modified SiO_2 show light clusters of Re complex on the

dark background, i.e., the silica surface. The presence of metal complex over the SiO_2 support matrix was confirmed in the EDS detector of SEM (showing 0.23% of Re, Figure 1B).

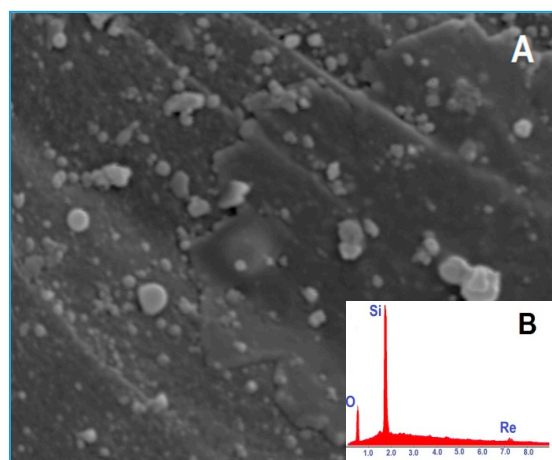


Figure 1. Scanning Electron Microscopy (SEM) image of C (A) and presence of Re on support surface, confirmed by SEM/EDS spectrum (B).

The thermal stability of the hybrid materials was tested by TGA (Figure 2). Initially and below 100 °C, a slight weight loss was observed, most likely due to absorbed moisture. After that, a significant weight loss was observed only in the range of ca. 200 to 245 °C, most likely due to decomposition of the anchored metal complex species over the silica support. The order of stability is $C > D > A > B$. No more complex decay was observed above that temperature range. These Re catalysts are stable under the operating temperature range of 100–200 °C for the current catalytic study.

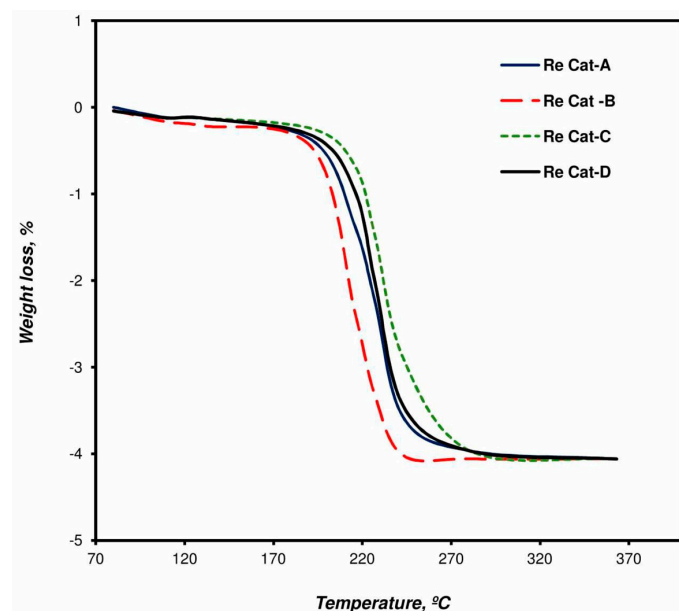


Figure 2. Thermal gravimetric analysis (TGA) graph of supported rhenium complex catalysts A–D.

2.2. Catalytic Batch Oxidation of Alkanes

We have found that the above supported Re complexes A to D act as catalysts for the partial oxidation of neat *n*-hexane and *n*-heptane by molecular oxygen, under relatively mild conditions

(typical temperature of ca. 150–160 °C and typical O₂ pressure of ca. 10–12 atm), to the corresponding alcohols and, in lower amounts, ketones, without needing any additional solvent or additive.

Normally, saturated hydrocarbons require harsh reaction conditions for oxy-functionalization, but we have achieved a high catalytic conversion rate at a relatively low temperature, as shown in Table 1, in the presence of **A–D** supported on functionalized silica—namely, 5.2–12.6% conversion for *n*-hexane and 4.0–10.0% for *n*-heptane.

Table 1. Selected data ^a for neat C₆ and C₇ *n*-alkane oxidations with di-oxygen catalysed by hybrid Re catalysts.

Alkane	Run	Catalyst	Conversion (%)				
			2-Hexanol	3-Hexanol	2-Hexanone	Hexanoic Acid	Total
<i>n</i> -hexane	1	A	3.0	1.5	1.7	0.6	7.4
	2	B	3.9	2.0	2.2	0.8	9.3
	3	C	5.1	2.5	3.1	1.0	12.6
	4	D	2.1	1.1	1.3	0.4	5.2
<i>n</i> -heptane			2-Heptanol	4-Heptanol	2-Heptanone	3-Heptanone	
	5	A	1.1	3.0	1.0	0.4	5.9
	6	B	1.6	4.0	1.3	0.6	8.2
	7	C	2.0	5.5	1.4	0.7	10.0
	8	D	0.8	2.2	0.6	0.3	4.0

^a Reaction conditions: catalyst = 25 mg, 8 h; for *n*-hexane (23.0 mmol): 150 °C, *p*(O₂) = 12 atm; for *n*-heptane (17.6 mmol): 160 °C, *p*(O₂) = 10 atm.

For both substrates, the heterogenized pyrazole–fluoro Re complex [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)] **C** provides the most active catalyst leading to overall *n*-hexane conversion of 12.6% (5.1% to 2-hexanol, 2.5% to 3-hexanol, 3.1% to 2-hexanone, and 1.0% to hexanoic acid, entry 3, Table 1 and Figure S1, ESI) and overall *n*-heptane conversion of 10% (2.0% to 2-heptanol, 5.5% to 4-heptanol, 1.4% to 2-heptanone, 0.7% to 3-heptanone, entry 7, Table 1 and Figure S1, ESI), for *p*(O₂) of 12 or 10, at 150 or 160 °C, respectively, upon 8 h reaction time. Such conversions correspond to overall selectivities towards the alcohols of 60% and 75% for the oxidations of *n*-hexane and *n*-heptane, respectively.

Moreover, remarkable overall turnover numbers (TONs) (number of moles of products per mole of Re complex **C** loaded on the modified silica gel) of ca. 3.8×10^3 for *n*-hexane and 2.5×10^3 for *n*-heptane (for runs 3 and 7, Table 1, respectively) were achieved. Hexanoic acid, in small amounts, was a minor observed product of the *n*-hexane oxidation, whereas no isomerization, dehydrocyclization, or cracking products were found. Identical product distribution was found for *n*-hexane when subject to oxidation catalyzed by tricarbonyl Re(V) complexes anchored on modified SBA-15 [25].

Good *n*-alkanes conversions with the supported complex **C** were also reported [32] for the following homogeneous systems: (i) peroxidative oxidation of cyclohexane with H₂O₂ oxidant, and (ii) ethane oxidation to acetic acid with K₂S₂O₈ oxidant in trifluoroacetic acid.

The catalytic activity of the **A–D** complexes for the oxidation of *n*-hexane and *n*-heptane was also checked under homogeneous conditions, but the conversions were lower than those achieved in the heterogeneous system. The fluoro–chloro complex [ReClF{N₂C(O)Ph}(Hpz)₂(PPh₃)] **C** still provides the most active catalyst (maximum overall conversions of ca. 4% and 3% with respect to *n*-hexane and *n*-heptane oxidations, respectively) within the studied Re species. The overall selectivity towards alcohols was maintained. The higher activity of the fluoro complex **C** in comparison with the related chloro complexes **A**, **B**, and **D** is in accord with the observed [33] catalytic behaviors for ethane and cyclohexane oxidations [17,32]. It possibly concerns the overall stronger electron-donor character of the fluoride ligand relative to chloride, as found by a previous detailed electrochemical study [29], thus favoring the oxidation (by O₂) of the complex to a higher metal oxidation state and promoting the alkane oxidation.

Blank experiments for both *n*-alkanes were run in the absence of catalyst and led to lower overall conversion of 2.2 and 1.6% for C₆ and C₇, respectively. This confirms that our catalysts are playing a key role for this aerobic oxidation process.

The most active supported catalyst C was selected for optimizing and recycling studies and the percentage of metal variation was measured by Atomic Absorption Spectroscopy (AAS) analysis. The AAS shows that the fresh Re catalyst has $0.29 \pm 0.02\%$ weight Re content.

The effect of various parameters such as temperature, O₂ pressure, reaction time, and catalyst amount were examined for the most active supported catalyst C. Improved conversion results with an heteroaromatic acid (as a co-catalyst) and catalyst recycling are also discussed (see below). All the catalytic results are summarized in Table 1 and Figures 3–12.

2.3. Optimization of Reaction Conditions for the Oxidations

2.3.1. Effect of the Temperature

The reaction temperature study was performed within the range of 90–190 °C or 100–200 °C for the oxidation of *n*-hexane (Figure 3) or *n*-heptane (Figure 4), at $p(\text{O}_2) = 12$ atm or 10 atm, respectively, with 8 h duration. An increase of temperature leads to an enhancement of the overall conversion of the alkanes, which reaches the values of 19.1% and 16.2%, respectively, under those conditions. The conversions into the alcohol and ketone products also increase with the temperature. However, the reaction temperature was not allowed to go beyond 190 °C for hexane and 200 °C for heptane, since an unidentified black charring material appeared.

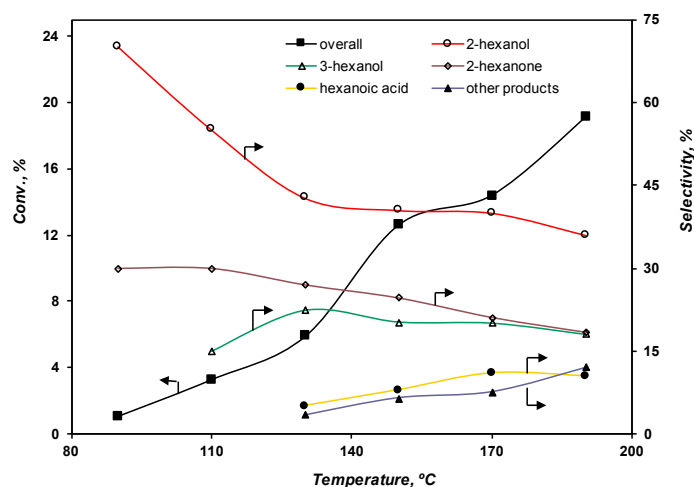


Figure 3. Reaction temperature effect on the conversion and selectivity of *n*-hexane oxidation with O₂ catalyzed by C ($p(\text{O}_2) = 12$ atm, 8 h). Conv.: conversion.

The best overall selectivity of 93% (overall conversion 12.6%) of the main products (alcohols, ketone, and acid; Table 1) was obtained at 150 °C for hexane oxidation, with the following selectivities: 2-hexanol, 40.5%; 3-hexanol, 20.2%; 2-hexanone, 24.6%; and hexanoic acid, 8.0%. A mixture of unidentified minor or by-products (6.5%) was also obtained. For *n*-heptane, the highest overall selectivity of 96% of the main products (alcohols and ketones, Table 1) and overall conversion 10% was observed at 160 °C. The main product selectivities at this temperature are 2-heptanol, 20.0%; 4-heptanol, 55%; 2-heptanone, 14%; and 3-heptanone, 7.0%. Above this temperature—170 °C for hexane and 180 °C for *n*-heptane—the overall conversion increases to 14.4% and 12.4% but the selectivity of the main products falls to 92.1% and 90.1% for hexane and heptane oxidation, respectively. At the higher temperature of 190 °C, the main product (alcohols, ketone, and acid) selectivities decreased significantly (2-hexanol, 36.0%; 3-hexanol, 18.0%; 2-hexanone, 18.3%; and hexanoic acid, 10.5%) due

to an increasing amount (12.0%) of by-products. The same trend was also observed for heptane at 200 °C, where the overall conversion increased to 16.2% but the main product (alcohols and ketones) selectivity (84.0%) decreased significantly.

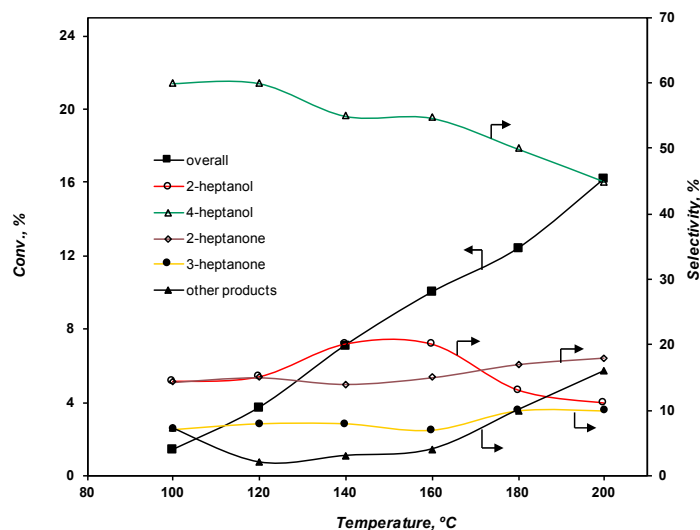


Figure 4. Reaction temperature effect on the conversion and selectivity of *n*-heptane oxidation with O₂ catalyzed by C ($p(\text{O}_2) = 10$ atm, 8 h).

The best selectivity (40.5%) and conversion (12.6%) of the main *n*-hexane product, i.e., 2-hexanol, was obtained at 150 °C. For *n*-heptane, the best selectivity (55%, with the conversion of 10.0%) for the main product, i.e., 4-heptanol, was observed at 160 °C. Above those temperatures, the generation of by-products increased with the subsequent drop in the formation of the above main products. Hence, temperature effect plays a lead role for both *n*-alkane selectivity and conversion: lower temperatures correspond to lower conversions but higher selectivities towards alcohols and ketones.

2.3.2. Effect of the O₂ Pressure

The effect of O₂ pressure was examined from 6 atm to 20 atm for the oxidation of *n*-hexane (Figure 5) and *n*-heptane (Figure 6) and Table 1. The overall conversions and the conversions into the main products markedly increase with $p(\text{O}_2)$, the former reaching values of 20.8% and 16.8%, at maximum 20 atm pressure, respectively. However, the selectivities of the main products do not follow this trend: that of 2-hexanol decreases from 50.1% to 38.0% for $p(\text{O}_2)$ of 10 and 20 atm, while that of 4-heptanol decreases from 56% to 51%, on account of the increasing amount of by-products produced upon increasing the O₂ pressure. A good overall conversion of 12.6% with a high selectivity of 93% of main products (alcohols, ketone, and acid; Table 1) was obtained at 12 atm for hexane oxidation. For the *n*-heptane oxidation, the overall conversion of 10.0% with the high selectivity 96% of main products (alcohols and ketones, Table 1) was obtained at 12 atm pressure. The promotion of the overall conversion with the oxygen pressure is consistent with the increase of the solubility of this gas with pressure.

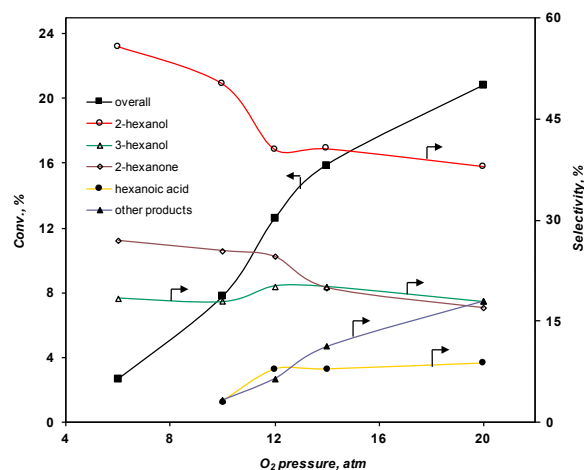


Figure 5. O₂ pressure effect on the conversion and selectivity of *n*-hexane oxidation catalyzed by C (150 °C, 8 h).

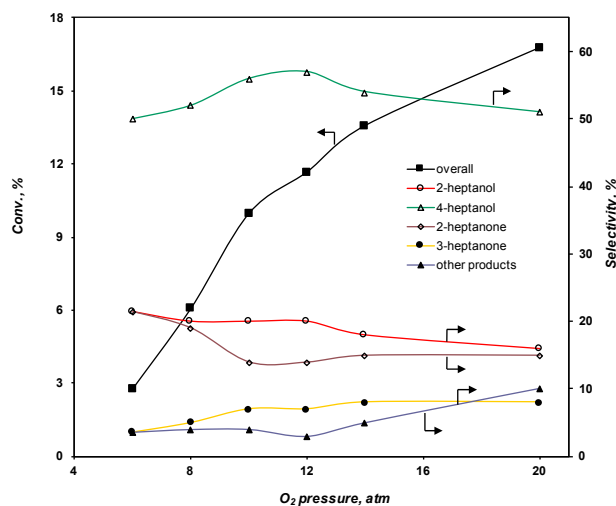


Figure 6. O₂ pressure effect on the conversion and selectivity of *n*-heptane oxidation catalyzed by C (160 °C, 8 h).

2.3.3. Effect of the Reaction Time

The reaction time study concerned the period from 4 h to 16 h at 150 °C for *n*-hexane (Figure 7) and from 4 h to 24 h at 160 °C for *n*-heptane (Figure 8), under constant $p(\text{O}_2)$ (12 or 10 atm, respectively). Similar trends for both alkanes can be recognized, i.e., the overall conversions increase with the time e.g., from 2.9% to 17.3% for hexane and 1.9% to 22.1% for heptane. Initially (4 h time), the main product selectivity was very high (2-hexanol, 56%; 4-heptanol 58%). It reduces from 47.0% (at 6 h) to 22.5% (at 16 h) for 2-hexanol. In the 4-heptanol case, there was no change observed till 10 h (58% selectivity). Afterward, it reduces from 51.0% to 38% selectivity at the reaction times of 16 h and 24 h, respectively. The formation of by-products increases along with the time; hence, the selectivities towards the main products tend to decrease.

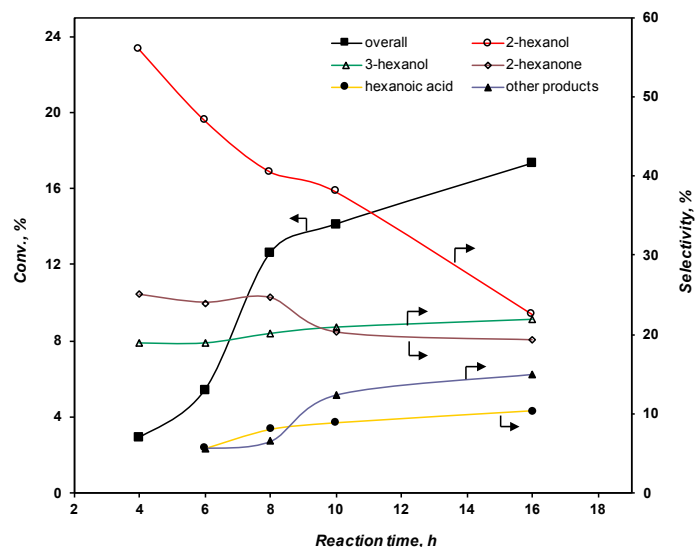


Figure 7. Reaction time effect on the conversion and selectivity of *n*-hexane oxidation with O₂ catalyzed by C (150 °C, $p(\text{O}_2) = 12$ atm).

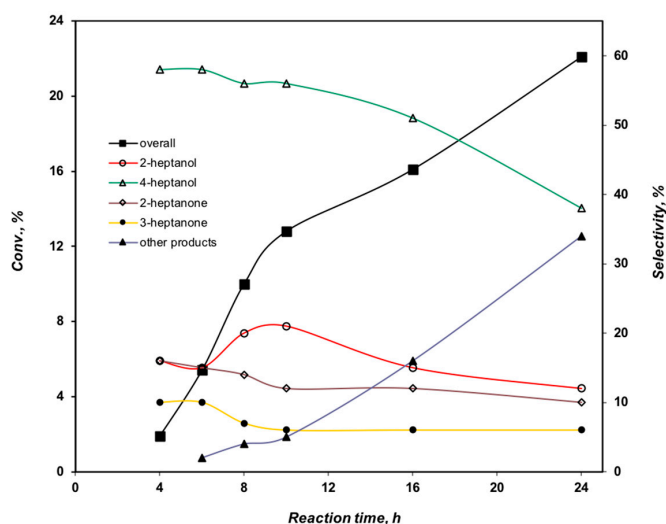


Figure 8. Reaction time effect on the conversion and selectivity of *n*-heptane oxidation with O₂ catalyzed by C (160 °C, $p(\text{O}_2) = 10$ atm).

2.3.4. Effect of the Catalyst Amount

The conversions of both *n*-alkanes into the oxidation products are promoted by increasing the amount of the supported catalyst C (Figure 9 for *n*-hexane and Figure 10 for *n*-heptane). Therefore, increasing the amount of catalyst from 5 mg to 45 mg led to a growth of overall conversion from 2.7% to 20.8% (for *n*-hexane) and from 4.2% to 18.3% (for *n*-heptane). However, and as expected, the alcohol and ketone selectivity (2-hexanol, 54%; 3-hexanol, 26% and 2-hexanone, 20%, for *n*-hexane) decreased as the amount of catalyst increased (Figure 9). In the case of *n*-heptane, this change is not so evident (Figure 10).

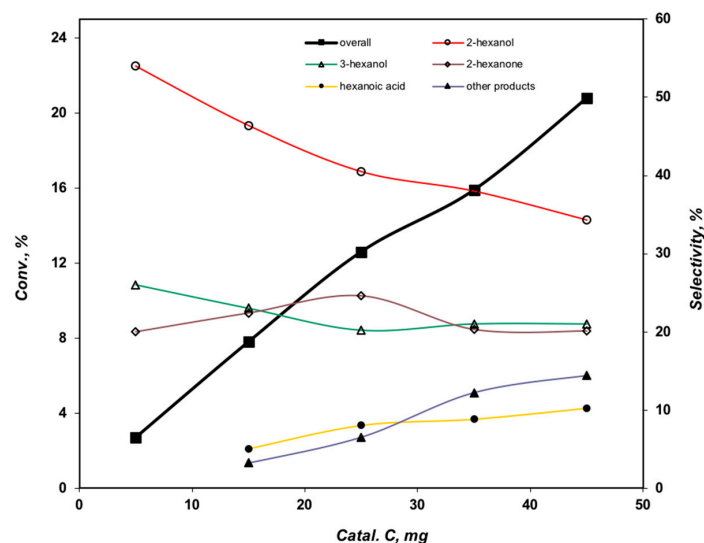


Figure 9. Effect of amount of C on the conversion and selectivity of *n*-hexane oxidation with O₂ (150 °C, $p(\text{O}_2) = 12$ atm, 8 h). Catal.: catalyst.

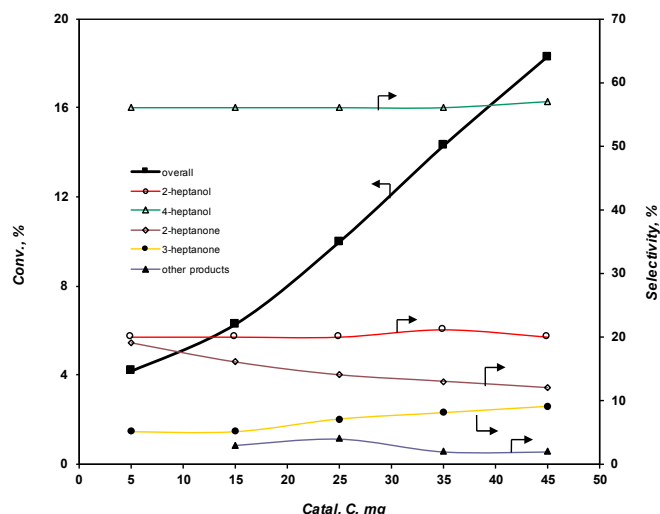


Figure 10. Effect of amount of C on the conversion and selectivity of *n*-heptane oxidation with O₂ (160 °C, $p(\text{O}_2) = 10$ atm, 8 h).

2.3.5. Effect of the Co-Catalyst

To improve the conversion, some heteroaromatic carboxylic acids, i.e., 3-amino-2-pyrazinecarboxylic acid, 2,6-pyrazinedicarboxylic acid, 2,3-pyrazinedicarboxylic acid, pyrazinecarboxylic acid (PCA), and picolinic acid, were tested as co-catalysts (Figure 11 for *n*-hexane and Figure 12 for *n*-heptane). The best conversion was observed with pyrazinecarboxylic acid for both alkanes. Under similar conditions (Table 1, run 3) PCA quite significantly promotes the overall conversion from 12.6% to 17.5% for *n*-hexane oxidation. The main products, 2- and 3-hexanol, increased from 7.6% to 12.7%, and 2-hexanone from 3.1% to 3.7%. For *n*-heptane, a similar PCA effect was observed: the overall conversion increased from 10.0% to 15.9%. The conversions to the major products, i.e., to alcohols (2- and 4-heptanol), increased from 7.5% to 11.8%, and to ketones (2- and 3-heptanone) increased from 2.1% to 3.2%. The other tested acids were less active for both alkanes.

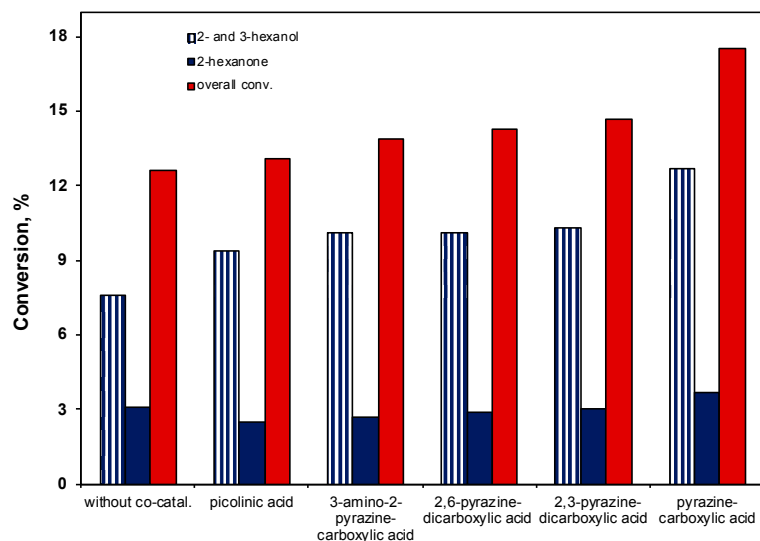


Figure 11. Effect of hetero-aromatic carboxylic acids (as co-catalysts) on conversion of *n*-hexane oxidation with O₂ catalyzed by C (under conditions of run 3, Table 1).

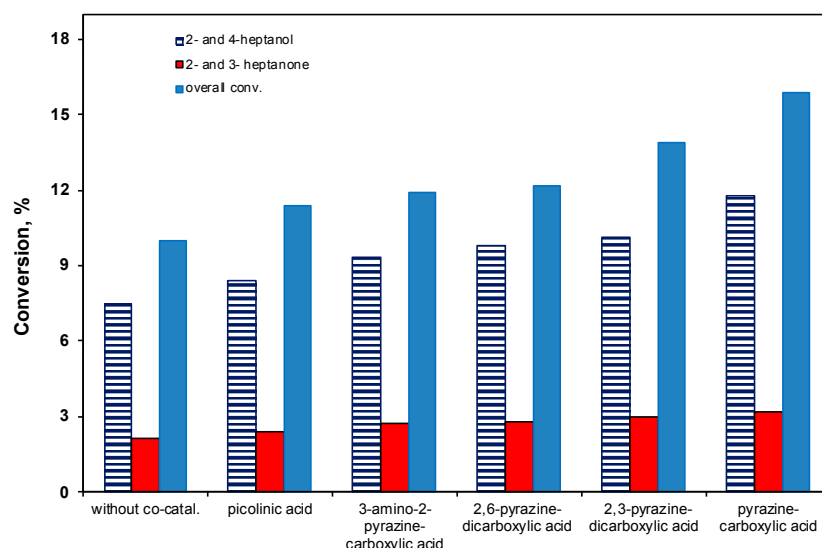


Figure 12. Effect of hetero-aromatic carboxylic acids (as co-catalysts) on conversion of *n*-heptane oxidation with O₂ catalyzed by C (under conditions of run 7, Table 1).

The promoting effect of an acid co-catalyst was already observed for other systems in the oxidative transformation of alkanes [7,8,18,34–40] and conceivably consists of assisting proton transfer from a ligated H₂O₂ to an oxido-ligand via the carboxylate group of the pyrazinecarboxylate ligand, as suggested for homogeneous catalyst systems [41].

2.4. Catalyst Stability and Recyclability

The used catalyst C (runs 3 and 7, Table 1) was selected for the recycling studies. After the first essay, the reactor was degassed. O₂ was then admitted (12 and 10 atm, for hexane and heptane, respectively) and the reaction was left to proceed (2nd cycle) for a further 8 h reaction period. The overall conversions of *n*-hexane and *n*-heptane increased relative to the first cycle, from 12.6% to 14.8% and from 10.0% to 12.5%, respectively, thus showing that the catalyst lost most of its initial activity.

For additional reuse essays, the supported catalyst C, after being used in a cycle of 8 h under the above typical (for *n*-hexane and *n*-heptane oxidation) conditions, was reactivated by heating (see

Section 3) and used for a second catalytic run with fresh reagents under the conditions of runs 3 and 7 of Table 1, for a duration of 16 h. Then, the supported catalysts were separated from the reaction mixtures by filtration, carefully washed, and analysed for Re content. AAS analyses showed that the fresh catalyst C had $0.29 \pm 0.02\%$ weight of Re metal content. After being used in the first cycle (for 8 h), the Re content has decreased to $0.24 \pm 0.02\%$ and $0.22 \pm 0.02\%$ weight for the cases of *n*-hexane and *n*-heptane oxidation, respectively. In the second cycle (after 16 h), only a negligible or minor loss of metal was observed, i.e., the Re content was $0.22 \pm 0.02\%$ weight for *n*-hexane and $0.21 \pm 0.02\%$ weight for *n*-heptane essays. After the second cycle, the overall conversions of *n*-hexane and *n*-heptane were 8.7% and 7.3%, respectively, confirming the loss of activity of the catalyst. As the Re leaching was insignificant, the inactivation of the catalyst could involve the formation of Re=O species over a long period under such an oxidative atmosphere, on account of the known affinity with Re by oxygenated species [29,31].

2.5. Proposed Reaction Mechanism for *n*-Alkanes Oxidation

Additional experiments under the same conditions as runs 3 and 7 of Table 1 were carried out in the presence of the carbon-radical trap bromotrichloromethane (CBrCl₃) or of the oxygen-radical trap diphenylamine (Ph₂NH). The overall conversion dropped significantly for both *n*-alkanes. Consequently, we assume that the oxidation of the *n*-alkanes can proceed via a radical mechanism [7,8,18,35–40]. Free alkyl radicals (R•) could be obtained by reaction of the alkane (RH) with O₂ upon homolytic cleavage of a C–H bond (slow reaction). Reaction of free alkyl R• with di-oxygen would form the alkylperoxy radical ROO•, which could undergo metal-assisted decomposition to the alkoxy radical RO•. The alcohol (R–OH) could be formed either by H-abstraction from the alkane (RH) by RO• or by Re-promoted decomposition of ROO• to yield also the ketone R(–H)=O.

The co-catalyst (PCA) could assist in these metal-induced ROOH cleavage reactions by promoting proton transfer from the ROOH ligand to an oxido (or hydroxido) ligand, to form the coordinated alkylperoxido (ROO) species subject to bond cleavage as proposed [6,40,42,43] for oxido-vanadium/H₂O₂ systems.

The presence of alkyl hydroperoxides was detected by gas chromatography using the well-known Shul'pin's method [42,43]. Additional gas chromatographic (GC) injections of the samples after treatment with triphenylphosphine were performed to ensure the precise quantification of the oxidation products present in the reaction solution, as alkyl hydroperoxides can be converted quantitatively to the corresponding alcohols by reduction with triphenylphosphine. In fact, when the triphenylphosphine was added to a sample (from the reaction at the optimized conditions) prior to the GC analysis a significant increase of ca. 30% of the alcohols obtained was observed for both substrates (*n*-hexane and *n*-heptane), indicating that the alkyl hydroperoxide is formed as the primary product.

3. Materials and Methods

Complexes [ReCl₂{NNC(O)C₆H₅}(Hpz)(PPh₃)₂] (A) (where Hpz is pyrazole), [ReCl₂{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] (B) [29], [ReClF{NNC(O)C₆H₅}(Hpz)₂(PPh₃)] (C) [17], and [ReOCl₃(PPh₃)₂] (D) [31] (Scheme 1) were prepared according to previous published methods, under an N₂ atmosphere using standard Schlenk techniques.

A silica surface was modified by the reaction of 20 µL of 3-aminopropyl trimethoxysilane, NH₂(CH₂)₃Si(OCH₃)₃ with 400 mg of silica gel (200–400 mash size) in 25 mL of toluene in a round-bottom flask. This mixture was refluxed overnight. The NH₂-functionalized silica was separated from the solution and washed with deionized water in order to remove unanchored amino-silane species.

The prepared 3-aminopropyl-modified silica gel was used for anchoring the above Re complexes (Scheme 2). Each of the Re complexes A–D (25 mg) was separately dissolved in methanol (10 mL); the solution was then added to the 3-aminopropyl-modified silica (1.00 g) and the mixture was refluxed for 5 h in the presence of K₂CO₃ and methanol. Hybrid Re catalysts were separated by filtration, washed

several times with methanol, dried at 40 °C for 6 h under nitrogen, and then at 50 °C for 4 h in an oven. Quantities of 21 mg of $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$ **A**, 20 mg of $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ **B**, 23 mg of $[\text{ReClF}\{\text{N}_2\text{C}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ **C**, and 19 mg of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ **D** were loaded per gram of 3-aminopropyl-functionalized silica support. The colors of the hybrid materials are as follows: yellow for **A–C** and light green for **D**.

Far-infrared spectra FIR ($400\text{--}200\text{ cm}^{-1}$) of supported **A–D** were recorded on a Vertex 70 spectrophotometer in CsI pellets (Bruker, Bremen, Germany).

The morphology of the prepared hybrid materials was examined by Scanning Electron Microscopy (SEM) on a FEI Quanta 400 (JEOL, Tokyo, Japan), and energy-dispersive EDS studies were also performed in the same analysis. The C, H, N elemental analyses were carried out by the Micro-Analytical Service at Instituto Superior Técnico (IST). TGA of the catalysts were performed using a Setaram TG/DTA/DSC-92 instrument (Setaram Instrumentation, Caluire, France).

All the oxidation reactions were conducted in a cylindrical-shaped SS pressure reactor (18 mL capacity). Internal temperature and pressure of the reactor were monitored by a thermocouple and a pressure gauge, respectively. In typical oxygenation reaction conditions, 3.0 mL of neat *n*-alkane and the supported Re catalyst were added to the reactor where molecular O_2 was introduced. The system was heated to the desired temperature. After reaction, the solid catalyst was separated from the liquid product by filtration, washed several times with acetonitrile and dried at 60 °C overnight. The dried used catalyst was collected for further recycling studies. The color of the used catalyst turned into light brown.

The formed products were quantitatively analysed by gas chromatography (GC) in a FISIONS Instruments GC 8000 series gas chromatograph (Jasco, Tokyo, Japan) equipped with a FID detector and a DB-WAX capillary column (length: 30 m; internal diameter: 0.32 mm) using helium as a carrier gas and 2-pentanone as internal standard (added to a 1 mL sample). The products were identified, and their retention times confirmed with those of commercially available (Aldrich) samples. The product peaks were further confirmed in a GC-MS Carlo Erba Instruments Auto/HRGC/MS (Jasco, Tokyo, Japan) with a DB-Wax column. Reaction products were identified by comparison of their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

TONs (turnover numbers) were calculated as the number of moles of products per mole of Re complex supported on silica and the yield values were calculated as moles of the desired product per mole of substrate. The selectivity was calculated as moles of product per mole of total yield of all products [17].

4. Conclusions

We have successfully used four 3-aminopropyl silica-supported Re complex catalysts (**A–D**) for the industrially important oxidation of *n*-alkanes by molecular oxygen (an ideal “green” oxidant) to obtain valuable oxidized products. Among them, the fluoro-containing $[\text{ReClF}\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)]$ (**C**) catalyst achieved the highest TONs up to 3.8×10^3 and 2.5×10^3 , overall conversion of 12.6% and 10%, and selectivity of 84.9% (2- and 3-hexanol and 2-hexanone) and 96.0% (2- and 4-heptanol, 2- and 3-heptanone) for C_6 and C_7 -alkanes, respectively. Among the main oxidation products, the best selectivities were attained for 2-hexanol (40.5%) and 4-heptanol (54.7%), after 8 h at $p(\text{O}_2) = 12$ or 10 atm and at 150 or 160 °C, for *n*-hexane and *n*-heptane, respectively. TGA results indicate that catalysts **A–D** are stable at the applied temperature range (100–200 °C); however, recycled **C** is much less active in subsequent catalytic cycles, suggesting its deactivation under the oxidative reaction conditions. Tests with both C- and O-centered radical traps indicate that the products are formed through free-radical reactions.

Supplementary Materials: Supplementary materials are available online at www.mdpi.com/2073-4344/8/3/114/s1. Figure S1: (a1) Exemplary GC-MS chromatogram from the *n*-hexane oxidation with O₂ catalyzed by C [*p*(O₂) = 12 atm, 8 h]; internal standard: 2-pentanone; (a2) integrated chromatogram; (b) fragmentation patterns of selected retention times, obtained from the NIST spectral library stored in the computer software of the mass spectrometer; Figure S2: (a) Exemplary GC-MS chromatogram from the *n*-heptane oxidation with O₂ catalyzed by C [*p*(O₂) = 10 atm, 8 h]; internal standard: 2-pentanone; (b) fragmentation patterns of selected retention times, obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

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