Catal Lett (2009) 129:79–84
DOI 10.1007/s10562-008-9830-9

Oxidation of Benzene Catalyzed by 2,2′-Bipyridine and 1,10-Phenantroline Cu(II) Complexes

**Chaline Detoni · Nakédia M. F. Carvalho ·
Rodrigo O. M. A. de Souza · Donato A. G. Aranda ·
O. A. C. Antunes**

Received: 7 November 2008 / Accepted: 16 December 2008 / Published online: 8 January 2009

Abstract The use of mononuclear Cu(II) 2,2′-bipyridine and 1,10-phenantroline complexes as catalysts in the oxidation of benzene, using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidant in CH_3CN/H_2O solution is presented. The reactions were carried out at 25 and at 50 °C. The complexes $[Cu(bipy)_3]Cl_2 \cdot 6H_2O$ (**1**), $[Cu(bipy)_2Cl]Cl \cdot 5H_2O$ (**2**), $[Cu(bipy)Cl_2]$ (**3**), $[Cu(phen)_3]Cl_2 \cdot 7H_2O$ (**4**), $[Cu(phen)_2Cl]Cl \cdot 5H_2O$ (**5**), $[Cu(phen)Cl_2]$ (**6**) were able to oxidize benzene into phenol, hydroquinone and p-benzoquinone. Highest conversion (22%) was obtained using $[Cu(Phen)Cl_2]$ (**6**) as catalyst.

Keywords Selective benzene oxidation · Mononuclear Cu(II) complexes · 2,2′-Bipyridine · 1,10-Phenantroline · Peroxides · Biomimetic catalyst

1 Introduction

In previous work we exploited the oxidation of monoterpenes based principally in systems related to P450 monooxygenase [1–5]. Our successes lead us to go through the oxidation of cyclohexane also via P450 based systems [6, 7]. The success of that enterprise made our attention turn to the use of Fe(III) and Cu(II) complexes functional models of biomimetic non-heme monooxygenase systems [8–11].

Phenol is one of the most important feedstocks in the production of resins, fibers and related materials. More than 90% of the phenol consumed is produced via the so called cumene process [12] which is a three step process and coproduces acetone in 1:1 molar ratio with respect to phenol. However, due to the inherent environmental and energetic issues related to this process, many efforts are in progress for the development of new route for phenol production via a one step process through direct oxidation of benzene [13].

The direct and catalytic transformation of arenes to various useful chemicals via C–H activation is of considerable interest to chemical industries and remains a challenge to chemists [14]. The aromatic nucleus is resistant to oxidation because of its stabilization and the energy strength of the $C(sp^2)$–H bond, so oxygenation almost invariably requires a highly reactive oxidant under severe conditions. In the last years, several papers regarding the use of transition metal complexes as catalysts for aromatic C–H oxidation have been published [15].

Parida and Dash [16] have reported the liquid phase oxidation of benzene using hydrogen peroxide as oxidant and acetic acid as solvent, with manganese nodule leached residue (WMNLR) calcinated at different temperatures. The results showed about 13% of conversion and 98% of selectivity to phenol. However, high temperatures are required to treat WMNLR. Liu et al. [17] reported the benzene oxidation with Cu substituted polyoxometalate ($TBA-PW_{11}Cu$) as catalysts and molecular oxygen as oxidant, showing 9.2% of conversion and 91.8% of selectivity to phenol at 50 °C. Esmelindro et al. [18] showed the benzene oxidation to phenol and 1,4-benzoquinone with a

---

C. Detoni · D. A. G. Aranda
Escola de Química, Universidade Federal do Rio de Janeiro,
Cidade Universitária CT Bloco E, Rio de Janeiro,
RJ 21941-909, Brazil

C. Detoni · N. M. F. Carvalho · R. O. M. A. de Souza ·
O. A. C. Antunes (✉)
Instituto de Química, Universidade Federal do Rio de Janeiro,
Cidade Universitária CT Bloco A-641, Rio de Janeiro,
RJ 21945-970, Brazil
e-mail: octavio@iq.ufrj.br

mononuclear Cu(II) complex, [Cu(BMTEA)$_2$Cl]Cl (BMTEA = bis(2-thienylmethyl)-1,2-ethylenediamine), as catalyst and hydrogen peroxide as oxidant.

Copper is present in the active site of several enzymes and plays fundamental roles in living systems. This metal is coordinated to the protein residues, as found in tyrosinase, enzyme responsible for the hydroxylation [19]. Copper is also found in particulated methane monooxygenase (pMMO), an enzyme responsible for the oxidation of methane to methanol [20].

Based in the work developed by Canhota et al. [10] which showed the cyclohexane oxidation with the complexes **1**, **2** and **3** as catalysts, furnished yields of about of 43% using complex **3** and H_2O_2 at 50 °C and that yields are strongly related to the number of ligands coordinated to Cu(II) we envisaged the use of the present systems in the oxidation of benzene. Therefore, the aim of the present paper is to report the catalytic activity of 2,2′-bipiridine and 1,10-phenantroline Cu(II) complexes as catalyst in benzene oxidation. The studied complexes were in addition to [Cu(bipy)$_3$]Cl$_2$ · 6H$_2$O (**1**), [Cu(bipy)$_2$Cl]Cl · 5H$_2$O (**2**), [Cu(bipy)Cl$_2$] (**3**), the previously undisclosed [Cu(phen)$_3$]Cl$_2$ · 7H$_2$O (**4**), [Cu(phen)$_2$Cl]Cl · 5H$_2$O (**5**) and [Cu(phen)Cl$_2$] (**6**), were bipy is 2,2′-bipyridine and phen is 1,10-phenantroline. The oxidation reactions were carried out using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidant and acetonitrile–H$_2$O (3.5:1) solution as solvent, in mild conditions (temperature of 25 or 50 °C at atmospheric pressure).

2 Experimental

2.1 Materials and Methods

All solvents and reagents were purchased from Aldrich or Merck. Hydrogen peroxide (H_2O_2, 30% in water) and *tert*-butyl hydroperoxide (*t*-BuOOH, 70% in water) were titrated by the iodometric method before using. Fourier-transform infrared spectra (FT-IR) were recorded on a Nicolet Spectrometer 760 (in CsI pellets). Elemental analyses were obtained using Perkin–Elmer 2400 CHN and a microbalance Perkin–Elmer AD-4 autobalance. Benzene oxidations were monitored by GC. The products retention times were compared with standards. A HP5890 chromatograph equipped with a DB-5 column was used. Hydrogen was used as the carrier gas at 1.0 mL/min and 20 psi. The detector (FID) temperature was set to 260 °C while the injector temperature was set at 240 °C. The lower temperature was raised from 50 to 60 °C at 1.5 °C/min and from 60 to 200 °C at 10 °C/min. Retention time and mass spectra were compared with standards and used to characterize most of the reactions products. Relative yields were calculated taking into account the response factors of the substrate (benzene) and of the products (phenol, 1,4-benzoquinone and hydroquinone) through the use of an external standard [10].

Mass spectrometry data (electron impact): phenol: *m*/*z* 94 (M^{+}), 66 (M^{+}-CO), 65 (M^{+}-$H^{\cdot}$), 39 (M^{+}-C_2H_2); Hydroquinone: *m*/*z* 110 (M^{+}), 81 (M^{+}-$^{\cdot}$CHO), 55 (M^{+}-C_2H_2), 3 (M^{+}-H_2); 1,4-Benzoquinone: *m*/*z* 108 (M^{+}), 82 (M^{+}-C_2H_2), 54 (M^{+}-$CO^{\cdot}$), 26 (M^{+}-CO).

2.2 Synthesis of the Complexes

The complexes were synthesized according to the procedures previously described [10]. The synthesis of the complex [Cu(L)$_3$]Cl$_2$ was carried out by the addition of 3 equivalents of the ligand (2,2′-bipyridine or 1,10-phenatroline) in 50 mL of ethanol to one equivalent of $CuCl_2 \cdot 2H_2O$ in 15 mL of methanol. The mixture was stirred for 10 min at room temperature after 5 min was formed a precipitate. The solvent was evaporated slowly at room temperature and the complex was collected. The complexes **2**, **3**, **5** and **6** were synthesized as described above for the [Cu(L)$_3$]Cl$_2$, with different ligand and salt ratios (2:1 and 1:1).

(**1**) [Cu(bipy)$_3$]Cl$_2$ · 6H$_2$O: Turkish blue solid. IR (KBr disc, cm^{-1}): 3069, 3051, 3028, 1604, 1597, 1566, 1492, 1442, 776. Elemental analysis calculated for $C_{30}H_{36}N_6O_6Cl_2Cu$: C, 50.60; H, 5.06; N, 11.80%. Found: C, 49.51; H, 5.41; N, 11.33%. UV–Vis λ (ε, dm^3 mol^{-1} cm^{-1}) 237 nm (3.7 × 104), 287 nm (3.3 × 104).

(**2**) [Cu(bipy)$_2$Cl]Cl · 5H$_2$O: Light blue solid. IR (KBr disc, cm^{-1}): 3062, 3048, 3034, 1604, 1597, 1565, 1492, 1471, 1443, 772. Elemental analysis calculated for $C_{20}H_{26}N_4O_5Cl_2Cu$: C, 44.69; H, 4.84; N, 10.43%. Found: C, 44.75; H, 4.70; N, 10.35%. UV–Vis λ (ε, dm^3 mol^{-1} cm^{-1}) 240 nm (2.5 × 104), 298 nm (2.3 × 104), 309 nm (1.7 × 104).

(**3**) [Cu(bipy)Cl$_2$]: Light green solid. IR (KBr disc, cm^{-1}): 3068, 3053, 3037, 1602, 1551, 1497, 1473, 1446, 777. Elemental analysis calculated for $C_{10}H_8N_2Cl_2Cu$: C, 41.27; H, 2.75; N, 9.63%. Found: C, 41.10; H, 2.59; N, 9.52%. UV–Vis λ (ε, dm^3 mol^{-1} cm^{-1}) 245 nm (3.0 × 104), 300 nm (2.8 × 104), 310 nm (2.7 × 104).

(**4**) [Cu(phen)$_3$]Cl$_2$ · 7H$_2$O: Turkish-green blue solid. IR (KBr disc, cm^{-1}): 3055, 1626, 1605, 1587, 1518, 1495, 1425, 724. Elemental analysis calculated for $C_{36}H_{38}N_6O_7Cl_2Cu$: C, 53.90; H, 4,74; N, 10.40%. Found: C, 53.64; H, 4.96; N, 10.34%. UV–Vis λ (ε, dm^3 mol^{-1} cm^{-1}) 228 nm (1.1 × 105), 264 nm (8.1 × 104).

(**5**) [Cu(phen)$_2$Cl]Cl · 5H$_2$O: Green solid. IR (KBr disc, cm^{-1}): 3088, 3054, 3032, 1606, 1587, 1495, 1427, 723. Elemental analysis calculated for $C_{24}H_{26}N_4O_5Cl_2Cu$: C, 49.26; H,4.44; N, 9.58%. Found: C, 49.25; H, 4.40; N, 9.43%. UV–Vis λ (ε, dm^3 mol^{-1} cm^{-1}) 224 nm (4.8 × 104), 268 nm (4.3 × 104), 293 nm (1.3 × 104).

(**6**) [Cu(phen)Cl_2]: Light green solid. IR (KBr disc, cm^{-1}): 3080, 3058, 3012, 1607, 1586, 1516, 1495, 1423, 722. Elemental analysis calculated for $C_{12}H_8N_2Cl_2Cu$: C, 45.78; H, 2.54, N, 8.9%. Found: C, 45.59; H, 2.53; N, 8.78%. UV–Vis λ (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 223 nm (2.6 × 104), 271 nm (2.6 × 104), 294 nm (9.0 × 103).

Complexes **1**, **4**, **5** and **6** kept the same absorptions on changing the solvent from acetonitrile to acetonitrile/water and to water, therefore showing no ligand exchange to water.

2.3 General Procedure for Benzene Oxidation

The oxidation reactions were performed in a 10 mL round-bottomed flask sealed with a silicone septum under argon atmosphere, using acetonitrile: H_2O (3.5:1) solution as solvent, H_2O_2 or *t*-BuOOH as oxidant and the Cu(II) complexes as catalysts. Solvent, catalyst (7.0×10^{-4} M), substrate (0.77 M) and oxidant (0.77 M) were successively added. The total volume was 5 mL. The reaction mixture was stirred at 25 or 50 °C for 24 h. The reaction was quenched by the addition of 3.0 g of Na_2SO_3 and then the mixture was filtered in a silica bed to retain the catalyst. The products were analyzed by gas chromatography.

3 Results and Discussion

3.1 Complexes Characterization

In this study, we have synthesized six Cu(II) complexes containing 2,2′-bipyridyl (bipy) or 1,10-phenantroline (phen) as ligand. The complexes differ from one another by the number of ligand molecules coordinated to Cu(II) center. The complexes were synthesized using $CuCl_2 \cdot 2H_2O$ and 1, 2 or 3 equivalents of ligands, forming the complexes **1**, **2**, **3**, **4**, **5** and **6**, as shown in Fig. 1. In complex number **1**, copper is hexacoordinated assuming an octahedral geometry [21] and in **2**, it is pentacoordinated and has trigonal bipyramidal geometry [22]. According to literature, complex **3** can be found in two geometries: a distorted square pyramidal geometry, in which one chlorine atom is interacting with the copper center of another complex molecule, forming a supramolecular structure [23], or a distorted octahedral geometry, where the two chlorine atoms are interacting with the neighbor copper center [24]. It is reported, for complex **4**, that copper is hexacoordinated and has an octahedral arrangement with six Cu–N bonds and in addition to the copper coordinated cation, there are two chloride ions [25]. For number **5**, copper is pentacoordinated and presents trigonal bipyramidal geometry [26], while in complex number **6** copper is probably hexacoordinated with a phen and two chlorines in a plane and with two chlorines perpendicular to this plane and shared by other copper ions [27].

3.2 Catalytic Tests

The catalytic activity of the complexes in the benzene oxidation was investigated. The reactions were carried out using H_2O_2 or *t*-BuOOH as oxidant, acetonitrile–H_2O as solvent (the presence of water is important for the complete solubilization of the complexes) and at room temperature or at 50 °C. The products—phenol, hydroquinone and benzoquinone—were formed when hydrogen peroxide was

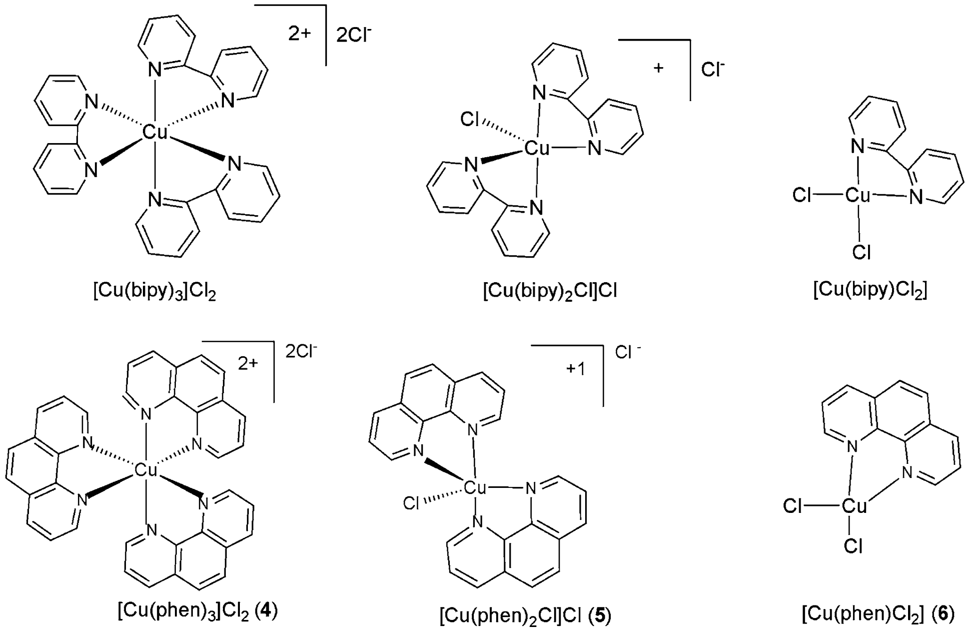

Fig. 1 Schematic representation of the Cu(II) complexes

used as oxidizing agent. *t*-BuOOH was found to be a suitable oxidant. Highest conversions were obtained using H_2O_2 as oxidant at 50 °C.

In literature there are several papers showing 1,4-benzoquinone as a product of the hydroquinone oxidation [28–30] and to better understand the reaction's pathways hydroquinone oxidation was investigated. These reactions were conducted under the same conditions stated above for the benzene oxidation. The complex **1** was used as catalyst and H_2O_2 as oxidizing agent at 50 °C. When phenol was used as substrate, hydroquinone was the only product formed, with the yield about 22%, while in the hydroquinone oxidation, just 1.3% of yield for 1,4 benzoquinone was obtained.

Table 1 shows the results obtained in the oxidation reactions. The highest conversion was observed when the complex $[Cu(phen)Cl_2]$ was used at 50 °C (entry 12) where yield of about 22% was obtained, with reasonable selectivity to phenol. The highest selectivity to phenol was found with $[Cu(bipy)_3]Cl_2$ (entries 1 and 2) at much lower conversions. The phen complexes are more active to benzene oxidation, but with lower selectivities.

Analyzing the results in Table 1, it is possible to observe that the three Cu(II) bipy complexes showed practically the same activity, with a smooth tendency to decrease conversion and increasing selectivity to phenol with increasing number of ligands (Table 1, entries 1–6). The same behavior was observed for the phen complexes (Table 1, entries 7–12). The most active complex was $[Cu(phen)Cl_2]$ (entry 12) with a 22% of conversion (entry 12). It was obtained a 15% of conversion when using the $[Cu(phen)_2Cl]Cl$ complex (entry 10) and 12%, with $[Cu(phen)_3]Cl_2$ (entry 8). Therefore, it is possible to relate the catalytic activity of the complexes with the number of ligands coordinated to the copper ion. These results are similar to those published by Canhota et al. [10]. The low conversion values obtained for the complex **1** could be probably due to the full-filled coordination positions around the copper center, where the ligands are strongly coordinate to the metal. The saturation of the first coordination sphere also obstructs the access of the oxidant or the electron transfer to the metal center, and consequently, the oxidation does not take place so efficiently. Another possibility is that the stabilization of the copper oxidation state (Cu^{2+}) by the tris-ligands, seriously hinders a rapid electron transfer, which is necessary for the oxidation. On the other hand, complexes $[Cu(L)_2Cl]Cl$ and $[Cu(L)Cl_2]$ that have vacant and more labile positions occupied by the chloride ions are more susceptible to suffering rapid electron transfer. In these cases, although possible, a mechanism of inner sphere electron transfer is unlikely to occur due to an inherent difficulty of to have a link between complex and substrate. Although the complexes with only one ligand (**3** and **6**) showed higher conversions, complexes with three ligands (**1** and **4**) coordinated to the metal ion showed higher selectivity values. So it was demonstrated in the present paper the general expectation where minor conversion values result in greater selectivities.

In order to evaluate the selectivity and conversion dependence on time, tests were carried out using H_2O_2 as

Table 1 Results for the benzene oxidation catalyzed by Cu(II) complexes and hydrogen peroxide after 24 h

Entry	Catalyst	*T* (°C)	Conversion (%)[a]	Selectivity (%)[b]			TON[c]
				Phenol	BQ	HQ	
1	$[Cu(bipy)_3]Cl_2$	25	4.0	100	0.0	0.0	44
2	$[Cu(bipy)_3]Cl_2$	50	7.0	100	0.0	0.0	77
3	$[Cu(bipy)_2Cl]Cl$	25	5.0	59	0.0	41	55
4	$[Cu(bipy)_2Cl]Cl$	50	8.0	77	23	0.0	88
5	$[Cu(bipy)Cl_2]$	25	4.0	49	17	34	44
6	$[Cu(bipy)Cl_2]$	50	9.0	59	0.0	33	99
7	$[Cu(phen)_3]Cl_2$	25	4.0	85	15	0.0	44
8	$[Cu(phen)_3]Cl_2$	50	12.0	64	20	0.0	132
9	$[Cu(phen)_2Cl]Cl$	25	6.0	40	13	38	66
10	$[Cu(phen)_2Cl]Cl$	50	15.0	57	0.0	14	165
11	$[Cu(phen)Cl_2]$	25	8.0	34	41	25	88
12	$[Cu(phen)Cl_2]$	50	22	48	0.0	35	242

Yields percentage was calculated according to the formula $\text{Area(product)}/[\text{Area(substrate + products)}] \times 100$. All chromatographic data were corrected considering the corresponding response factors of benzene, benzoquinone and hydroquinone

[a] Conversion percentage was calculated according to the formula $\text{Area(products)}/[\text{Area(substrate + products)}] \times 100$

[b] Selectivity percentage was calculated according to the formula $\text{Yield}/\text{Conversion} \times 100$

[c] Turnover number (TON) was calculated according to the formula $\text{no. of mols}_{\text{products}}/\text{no. of mols}_{\text{catalyst}}$

oxidizing agent. It was observed that higher yield values were obtained with greater reaction times. However, byproducts formation competed with the phenol production. This was due to the fact that the oxidation products are more easily oxidized than the substrate. Table 2 shows the progress of the reaction along the time for complexes **1** and **4**. It is possible to observe the conversion grow up with the reaction time and the reaction can continue after 24 h, which indicates that the catalyst remained active until this time. So, it would be possible to get higher conversions, at higher reaction times.

The Cu(II) phen complexes showed higher conversions than the Cu(II) bipy complexes. However, they were not very selective for benzene oxidation into phenol, leading preferentially to hydroquinone and 1,4-benzoquinone.

Temperature has an important role in the benzene conversion into phenol, increasing conversion and selectivity of the reaction. In the reactions using bipy complexes, it is possible to observe a 7% conversion with 100% selectivity to phenol at 50 °C (entry 1), and 4% at 25 °C (entry 2). The reactions using the complex **6** as catalyst confirm the importance of the temperature in the conversion. Conversion values around 8% were obtained at 25 °C, but in the same reaction submitted to 50 °C the conversion had a threefold increase (entries 11 and 12).

The turnover number (TON) is a measurement of the efficiency of the catalyst (number of moles of substrate per mol of the catalyst). Table 1 shows TON for each catalyst at 25 and 50 °C. For every reaction condition, the TON increases as expected when higher temperature is used. This result ratifies the importance of the temperature control in the catalyst activity.

The fact that the ligands do not appear to suffer oxidation during the reactions reinforce the biomimetic nature of these catalysts since it is very unlikely to observe autooxidation of monooxygenases.

Table 2 Progress of the reaction with time at 50 °C and H_2O_2

Catalyst	Time (h)	Conversion (%)	Selectivity (%)		
			Phenol	BQ	HQ
$[Cu(bipy)_3]Cl_2$	1	2.8	100	0.0	0.0
$[Cu(bipy)_3]Cl_2$	2	4.1	100	0.0	0.0
$[Cu(bipy)_3]Cl_2$	4	4.6	100	0.0	0.0
$[Cu(bipy)_3]Cl_2$	8	5.4	100	0.0	0.0
$[Cu(bipy)_3]Cl_2$	24	7.0	100	0.0	0.0
$[Cu(phen)_3]Cl_2$	1	2.3	100	0.0	0.0
$[Cu(phen)_3]Cl_2$	2	4.4	93	7	0.0
$[Cu(phen)_3]Cl_2$	4	6.0	95	5	0.0
$[Cu(phen)_3]Cl_2$	8	8.1	72	4	14
$[Cu(phen)_3]Cl_2$	24	12	64	20	0.0

4 Conclusions

The mononuclear complexes **1**, **2**, **3**, **4**, **5** and **6** used as catalysts were active in benzene selective oxidation. The complexes **3** and **6** presented better conversions than **1**, **2**, **4**, and **5**. However, the highest selectivity was obtained with complexes that have three ligands coordinated to the metal ion, complexes **1** and **4**. Complexes with phen ligands (**4**, **5**, and **6**) showed the highest conversions, but low selectivity to phenol. The system composed by the complex number **1** and the hydrogen peroxide as oxidizing agent showed good results with conversions of about 7% and selectivity of 100%. In general the present results were better than that previously obtained by our group in the oxidation of benzene with biomimetic complexes analogous to pMMO [18, 31].

Acknowledgments Financial support from CNPq, CAPES, FAPERJ and FINEP are gratefully acknowledged.

References

1. Gomes MFT, Antunes OAC (1996) Catal Lett 38:133
2. Gomes MFT, Antunes OAC (1996) Catal Lett 42:213
3. Lima LF, Corraza ML, Cardozo-Filho L, Alvarez HM, Antunes OAC (2006) Braz J Chem Eng 23:83
4. Lima LF, Cardozo-Filho L, Arroyo PA, Alvarez HM, Antunes OAC (2005) Kinet Catal Lett 84:69
5. Silva AD, Patitucci ML, Bizzo HR, D'Elia E, Antunes OAC (2002) Catal Commun 3:435
6. Salomão GC, Olsen MHN, Drago V, Fernandes C, Cardozo Filho L, Antunes OAC (2007) Catal Commun 8:69
7. Olsen MNH, Salomão GC, Drago V, Fernandes C, Horn A Jr, Cardozo Filho L, Antunes OAC (2005) J Supercrit Fluids 34:119
8. Silva GC, Parrilha GL, Carvalho NMF, Drago V, Fernandes C, Horn A Jr, Antunes OAC (2008) Catal Today 133–135:684
9. Carvalho NMF, Horn A Jr, Antunes OAC (2006) Appl Catal A 305:140
10. Canhota FP, Salomão GC, Carvalho NMF, Antunes OAC (2007) Catal Commun 9:182
11. Silva AC, Fernández TL, Carvalho NMF, Herbst MH, Bordinhão J, Horn A Jr, Wardell JL, Oestreicher EG, Antunes OAC (2007) Appl Catal A 317:154
12. Schimidt RJ (2005) Appl Catal A 280:89
13. Lücke B, Narayana KV, Martin A, Jähnisch K (2004) Adv Synth Catal 346:1407
14. Shilov AE, Shul'pin GB (1997) Chem Rev 97:2879
15. Punniyamurthy T, Velusamy S, Iqbal J (2005) Chem Rev 105:2329
16. Parida KM, Dash SS (2007) J Coll Interface Sci 316:541
17. Liu Y, Murata K, Inaba M (2005) Catal Commun 6:679
18. Esmelindro MC, Oestreicher EG, Caovilla M, Lessa JA, Fernandes C, Dariva C, Egues SM, Bortoluzzi AJ, Antunes OAC (2006) J Braz Chem Soc 17:1551
19. Jolley RL, Evans LH, Makino N, Mason HS (1974) J Biol Chem 249:335
20. Chan SI, Yu SS-F (2008) Acc Chem Res 41:969
21. Sotomayor MDP, Tanaka AA, Kubota LT (2003) Electrochim Acta 48:855
22. Stephens FS, Tucker PA (1973) J Chem Soc Dalton Trans 2293
23. Hérnandez-Molina M, González-Platas J, Ruiz-Pérez C, Lloret F, Julve M (1999) Inorg Chim Acta 284:258

24. Garlan MT, Grandjean D, Spodine E, Atria AM, Manssur J (1988) Acta Crystallogr Sect C Cryst Struct Commun 44:1209
25. Jian FF, Lin JH, Zhang SS (2001) Chin J Chem 19:772
26. Murphy G, O'Sullivan C, Murphy B, Hathaway B (1998) Inorg Chem 37:240
27. Faye GH (1966) Can J Chem 44:2165
28. Quintanilla A, Casas JA, Mohedano AF, Rodríguez JJ (2006) Appl Catal B 67:206
29. Duprez D, Delanoë F, Barbier J Jr, Isnard P, Blanchard G (1996) Catal Today 29:317
30. Alejandre A, Medina F, Fortuny A, Salagre P, Sueiras JE (1998) Appl Catal B 16:53
31. Olsen MNH, Salomão GC, Fernandes C, Drago V, Horn A Jr, Cardozo-Filho L, Antunes OAC (2007) Acta Scientiarum Technol 29:43