Korean J. Chem. Eng., 34(3), 701-705 (2017)
DOI: 10.1007/s11814-016-0310-4

pISSN: 0256-1115
eISSN: 1975-7220

Oxidation of tetralin to 1-tetralone over CrAPO-5

Samiran Bhattacharjee*, Yu-Ri Lee, and Wha-Seung Ahn**,†**

*Centre for Advanced Research in Sciences (CARS), University of Dhaka, Dhaka 1000, Bangladesh
**Department of Chemical Engineering, Inha University, Incheon 22212, Korea
(*Received 19 September 2016 • accepted 1 November 2016*)

Abstract−A chromium-incorporated microporous aluminophosphate, CrAPO-5, was tested as a catalyst for the oxidation of tetralin using either a combination of aldehyde and O_2 (1 atm) or *tert*-butyl hydroperoxide as an oxidant system. The former resulted in significantly improved catalytic performance (69.6% yield to 1-tetralone) over the latter (38.5% yield to 1-tetralone) at 80 °C in 8 h, and conversion increased in the sequence of acetaldehyde<<isobutyl aldehyde<pivalaldehyde. CrAPO-5 also exhibited good activity and high selectivity (53.7% yield to 1-tetralone) after 24 h using pivalaldehyde and O_2 at room temperature. Hot filtration and recycle experiments established that oxidation takes place mostly on Cr sites in CrAPO-5. A plausible reaction mechanism involving acylperoxy radicals and oxo-chromium(V) species on CrAPO-5 was proposed for the tetralin oxidation.

Keywords: CrAPO-5, Tetralin Oxidation, Pivalaldehyde, Acylperoxy Radicals, *Tert*-butyl Hydroperoxide

INTRODUCTION

Oxidation of tetralin can lead to 1-tetralone as the primary oxidation product, which is a useful chemical intermediate for dyes, agrochemicals, and pharmaceuticals [1-3]. 1-Tetralone is also used as a diesel fuel additive to promote clean combustion [4]. Oxidation of benzylic compounds has been studied extensively using soluble catalysts such as those chromium-based [5-7], Mn (III) porphyrins [8], and vanadium ion-pairs [9] or using nickel complexes with surface-active ligands in a biphasic mode [10]. For heterogeneous catalysts, Fe/MgO [11], Mn octahedral molecular sieves [12], Cr/Cu/Co MOFs [13,14], LDH-Ni(II)-salen [15], CrAPO-5 and CrAPO-11 [16-19], chromium-exchanged zeolite Y [20], Cr-MCM-41 [21-24], and ZSM-5 [25] have been tested. Among these, chromium-based catalytic systems are generally reported to offer higher catalytic activity and selectivity [25-28].

Benzylic oxidation reactions have been mostly carried out using alkyl hydroperoxide as an oxidant [29,30] and little investigation has been conducted employing other alternative oxidant systems. Recently, we described MIL-101(Cr) [14] or chromium-containing hierarchical material, H-CrAPO-5 [31] for tetralin oxidation, and found that catalytic activity and product selectivity are strongly influenced by the oxidant. These catalysts showed excellent activity with high selectivity for the tetralin oxidation using pivalaldehyde and O_2 (1 atm) as oxidant [14,15,31]. The present paper describes, in more detail, the tetralin oxidation using *in-situ* generated acylperoxy radicals from a mixture of O_2 and a sacrificial aldehyde as an oxidant over a conventional microporous CrAPO-5 catalyst. *tert*-Butyl hydroperoxide (*t*-BuOOH), urea-H_2O, and cumene hydroperoxide were also tested as an oxidant for comparison. To gain further insight into the reaction pathway for the product formation, the catalytic tetralin oxidation was studied as a function of reaction time using both aldehyde/O_2 and *t*-BuOOH as an oxidant. A plausible mechanism was also proposed based on the observed catalytic reaction results.

†To whom correspondence should be addressed.
E-mail: whasahn@inha.ac.kr

EXPERIMENTAL

1. Materials

$Al(OH)_3$, orthophosphoric acid (85 wt%), chromium(III) acetate hydroxide, tetralin (99%), pivalaldehyde (96%), isobutyraldehyde (99.5%), acetaldehyde (99%), cumene hydroperoxide, urea-H_2O_2, and *tert*-butyl hydroperoxide (5-6 M solution in decane) were obtained from Aldrich, and triethylamine (99.5%) from Fluka. These were used without further purification.

2. Catalyst Preparation

Microporous CrAPO-5 (1.6 mol% Cr in the substrate mixture) was prepared as reported by Chen and Sheldon [16], and calcined catalyst was chemically prewashed as suggested by Selvam et al. to remove weakly bound Cr species at the catalyst external surface [32]. The material was prepared and activated as described in our earlier work [31].

3. Catalyst Characterization

The physicochemical properties of the CrAPO-5 catalyst were measured using the instrumentation described in our earlier work [31]. The powder X-ray diffraction of CrAPO-5 involved a Rigaku Miniflex diffractometer with CuK_α (λ=1.54) radiation at a scan rate of 0.5° min^{-1}. The UV-Vis diffuse reflectance spectra were recorded on a Varian CARY 3E double-beam spectrophotometer using MgO as a reference at room temperature. BET surface areas were measured on a Micromeritics ASAP 2020 surface analyzer at −196 °C. Prior to the measurement, the sample was degassed at 200 °C for 6 h. The chemical composition of CrAPO-5 was measured by SEM-EDX (Hitachi S-4200). Metal content in the filtrate of the reaction

product in tetralin oxidation was measured by inductively coupled plasma-Mass spectrometry (ICP-MS, Perkin-Elmer élan 6100).

4. Catalytic Tetralin Oxidation

The catalytic oxidation of tetralin over CrAPO-5 was as described in our earlier work [31]. For *t*-BuOOH, reaction was carried out using a Chemistation PPS-2510 fitted with a condenser (Eyela). Typically, tetralin (8 mmol), chlorobenzene (5 mL), and catalyst (0.05 g) were charged into a glass reactor and heated to the desired temperature. To this reaction mixture, *t*-BuOOH (16 mmol) was introduced and stirred at 600 rpm. In the case of aldehyde/O_2 oxidant system, tetralin (2 mmol), pivalaldehyde (4 mmol), acetonitrile (10 mL), and catalyst (0.01 g) were charged into a two-necked round flask fitted with a condenser. The mixture was heated while bubbling O_2 (1 atm) under constant stirring. Hot filtration tests were performed by quickly removing the catalyst from the reaction mixture after 30 min reaction, and the filtrate was stirred for an additional period up to 450 min at the same reaction temperature. The conversion and selectivity were examined by GC (7890A GC System, 7683B series injector, Agilent Technologies) fitted with an HP-5 capillary column (30 m, 0.32 mm, 0.25 μm) and FID.

RESULTS AND DISCUSSION

1. Characterization of the Catalyst

Characterization results of the CrAPO-5 by XRD, SEM-EDX, N_2 adsorption-desorption isotherms, and UV-Visible diffuse reflectance spectroscopy are summarized in Table 1, which confirmed successful synthesis of high quality microporous material with excellent textural properties.

2. Catalyst Performance in Tetralin Oxidation

2-1. *Tert*-butyl Hydroperoxide as an Oxidant

First, oxidation of tetralin over CrAPO-5 was carried out in chlorobenzene using *t*-BuOOH as an oxidant at 80 °C. The profile of tetralin oxidation as a function of reaction time is shown in Fig. 1. The products, 1-tetralone and 1-tetralol, were detected simultaneously at the beginning of the reaction (after 10 min) with yield of 1.7% and 0.4%, respectively. The yield of 1-tetralone increased progressively and reached 38.5% when the conversion leveled off at 47% after 8 h, whereas the yield of 1-tetralol steadily increased from 0.4 to 2.4% (120 min reaction time and conversion reached to 27%) and then yield of 1-tetralol remained virtually constant afterwards. This reaction trend seems to follow the pathway described in Scheme 1, in which the reaction intermediate 1-*tert*-butylperoxytetralin is transformed into 1-tetralone and 1-tetralol initially, and 1-tetralol is then further converted to 1-tetralone. The unstable intermediate, 1-*tert*-butylperoxytetralin was not detected in the reaction mixture by GC because of its short lifetime [12]. It was also observed that tetralin converts to corresponding products with 14% of tetralin conversion in the presence of *t*-BuOOH without catalyst at 80 °C after 8 h.

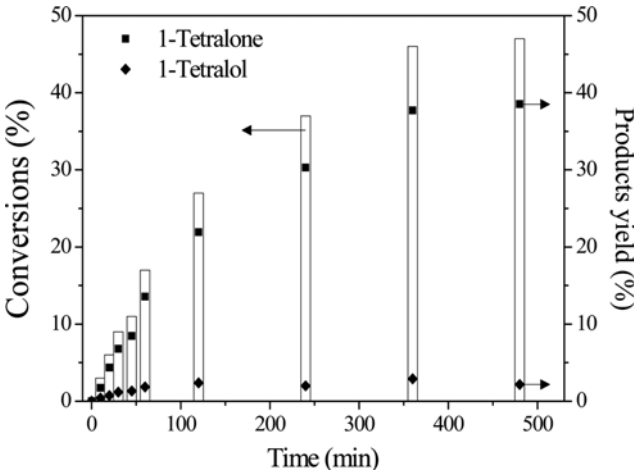
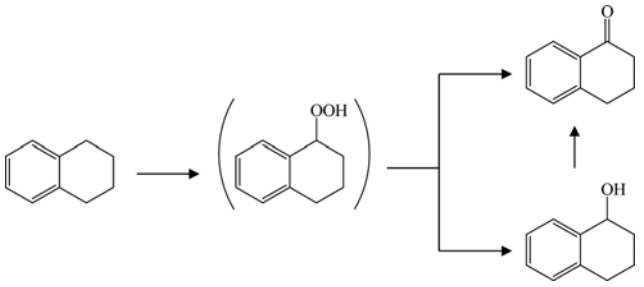


Fig. 1. Conversion of tetralin (white bar) and yield of 1-tetralone (■) and 1-tetralol (◆) as a function of reaction time using *t*-BuOOH at 80 °C (reaction conditions: 8 mmol tetralin, 16 mmol *t*-BuOOH, 5 mL chlorobenzene, and 0.05 g catalyst).



Scheme 1. A reaction path proposed for the tetralin oxidation over CrAPO-5.

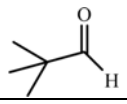
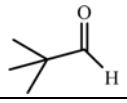
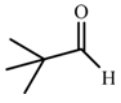
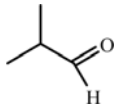
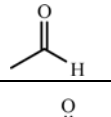
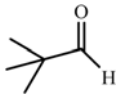
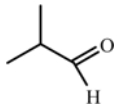
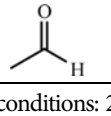
2-2. A Sacrificial Aldehyde and O_2 as an Oxidant System

Tetralin oxidation was also studied using *in-situ* generated acylperoxy radicals via a sacrificial aldehyde and O_2 [14,15,31,33,34]. For this purpose, the reaction was investigated in the range of 25-80 °C using O_2 (1 atm) in the presence of pivalaldehyde in an acetonitrile

Table 1. Summary of the calcined CrAPO-5 characterization results

Techniques	Parameters	Results
X-ray powder diffraction	2θ degree	7.3, 19.6, 21.1, 22.3
SEM-EDX	Cr content	1.64 mol%
	Al content	49.82 mol%
	P content	48.54 mol%
N_2 adsorption-desorption isotherms	BET surface area (m^2g^{-1})	250
	Pore volume (cm^3g^{-1})	0.16
UV-visible diffuse reflectance	λ_{max} (nm)	360, 270

Table 2. Effect of temperature, reaction time and aldehyde species in the tetralin oxidation reaction in aldehyde/O_2 oxidant system[a] along with recycling test results

Temp. (°C)	Aldehyde	Conversion (%)	Selectivity (%)[g]			
			Tlone	Tlol	Nthol	Nlene
25		15.0	92.1	6.1	1.0	0.8
		58.2[b]	92.2	5.1	1.9	0.8
		58.1[c]	92.1	5.2	1.8	0.9
50		46.0	92.4	2.2	2.5	2.9
80		77.0	90.4	5.4	1.9	2.3
		76.1[d]	90.6	5.1	2.2	2.1
		76.1[e]	90.4	5.6	1.9	2.1
		64.0	84.3	2.8	6.2	6.7
		19.0	79.0	15.3	3.1	2.6
80[f]		21.0	90.8	0.3	1.4	7.5
		15.0	81.4	0.7	12.7	5.2
		3.4	77.0	16.1	2.1	4.8

[a]Reaction conditions: 2 mmol tetralin, 4 mmol pivalaldehyde, 10 mL acetonitrile, O_2 (1 atm), 0.01 g catalyst for 8 h
[b]First run after 24 h
[c]Fourth run after 24 h
[d] Second run
[e]Third run
[f]Blank test (using aldehyde and O_2) and reaction time 8 h
[g]1-Tetralone, 1-tetralol, 1-naphthol and naphthalene are denoted as Tlone, Tlol, Nthol and Nlene, respectively

medium. At 25 °C, tetralin was oxidized to 1-tetralone with 92.2% selectivity at 58.2% conversion after 24 h (Table 2). As shown in Table 2, the conversion increased sharply from 15 to 77% with increasing temperature from 25 to 80 °C, while the selectivity to 1-tetralone decreased slightly from 92 to 90% after 8 h. The reaction profile for tetralin oxidation at 80 °C as a function of the reaction time is shown in Fig. 2. At the initial stage, tetralin was converted to 1-tetralone, whereas 1-tetralol was not detected during the reaction even at a trace level. After 45 min, tetralin conversion increased sharply, probably spurred by build-up of the intermediate acylperoxy radicals and the yield to 1-tetralone and 1-tetralol reached 69.6 and 4.2%, respectively; after 8 h reaction with tetralin conversion leveled off at 77%. As shown in Fig. 2, the yield of both 1-tetralone

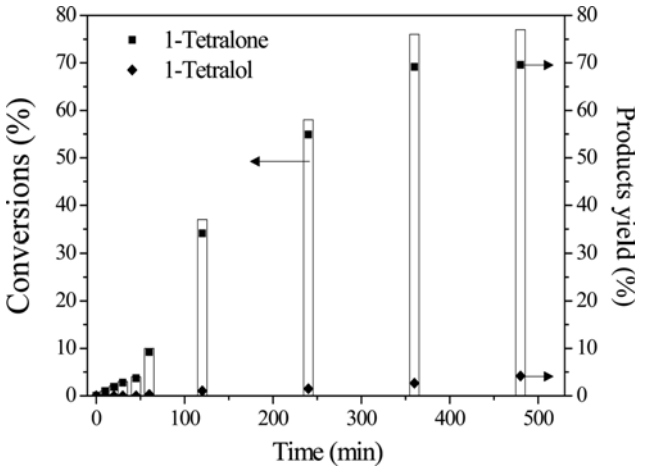


Fig. 2. Conversion of tetralin (white bar) and yield of 1-tetralone (■) and 1-tetralol (◆) as a function of reaction time using pivalaldehyde/O_2 at 80 °C (reaction conditions: 2 mmol tetralin, 4 mmol pivalaldehyde, 10 mL acetonitrile and 0.01 g catalyst with 20 ml/min O_2 bubbling).

and 1-tetralol gradually increased with time. These results indicate that the reaction path for tetralin oxidation in the presence of *in-situ*-generated acylperoxy radicals can also be described by Scheme 1. The present results also demonstrate that *in-situ* generated acylperoxy radicals are significantly more effective for the conversion of tetralin to 1-tetralone compared with *t*-BuOOH. A similar trend in oxidant-dependent activity was also reported by others [33,34]. Interestingly, no oxidation product was formed when either urea-H_2O_2 or cumene hydroperoxide was used as an oxidant under identical reaction conditions, even at an elevated temperature.

To examine the influence of the sacrificial aldehyde species for the tetralin oxidation, reaction was performed using three different kinds of aldehyde: acetaldehyde, isobutyl aldehyde, and pivalaldehyde (Table 2). Tetralin conversion and selectivity to 1-tetralone were found strongly influenced by the type of aldehyde used, and conversion increased in the sequence of acetaldehyde<<isobutyl aldehyde<pivalaldehyde, as reported earlier [31]. It was also observed that this oxidant system exhibits a higher level of non-catalytic thermal conversion than with *t*-BuOOH under identical reaction conditions (Table 2).

2-3. Catalyst Stability

Initially, a recycling test was used to check the stability of catalyst under the identical reaction conditions. The catalyst was isolated by filtration and washed with the respective solvent (chlorobenzene for *t*-BuOOH and acetonitrile for trimethylacetaldehyde/O_2), calcined at 500 °C in air for 5 h, and reused. Using *t*-BuOOH, tetralin conversion dropped slightly from 47 to 46% after the fresh run, but conversion remained virtually constant after the second run. The chromium content in the filtrate was 0.65 and 0.25 ppm after the fresh and second run, respectively. A recycling test over the catalyst was also carried out using the pivalaldehyde/O_2 system. Tetralin conversion decreased from 77 to 76% after the fresh run and remained constant afterwards. The chromium content in the filtrate was 0.24 and 0.19 ppm for the fresh and second run, respectively.

Further investigation into the stability of chromium moiety in

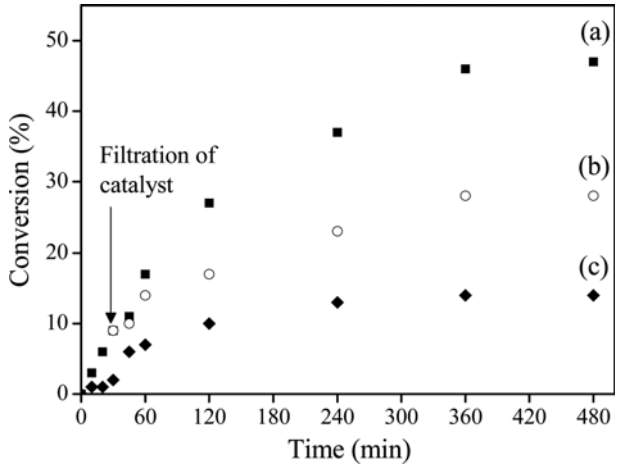


Fig. 3. Tetralin oxidation using *t*-BuOOH at 80 °C, 0.05 g catalyst in chlorobenzene: (a) CrAPO-5 catalyst, (b) filtrate (catalyst filtered off after 30 min reaction), and (c) blank run (using *t*-BuOOH only).

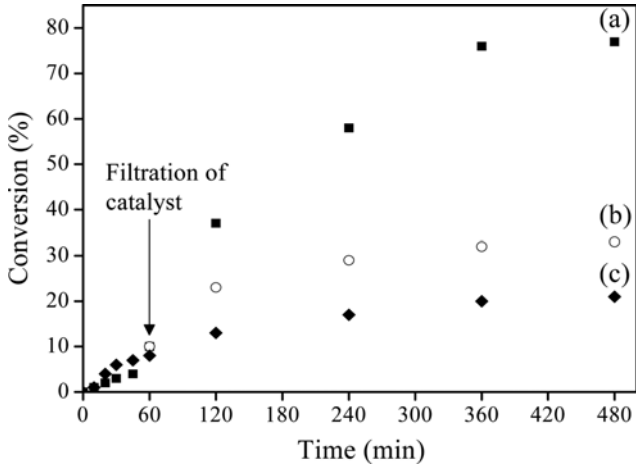


Fig. 4. Tetralin oxidation using pivalaldehyde/O_2 at 80 °C, 0.01 g catalyst in acetonitrile: (a) CrAPO-5 catalyst, (b) filtrate (catalyst filtered off after 60 min reaction), and (c) blank run (using pivalaldehyde/O_2 only).

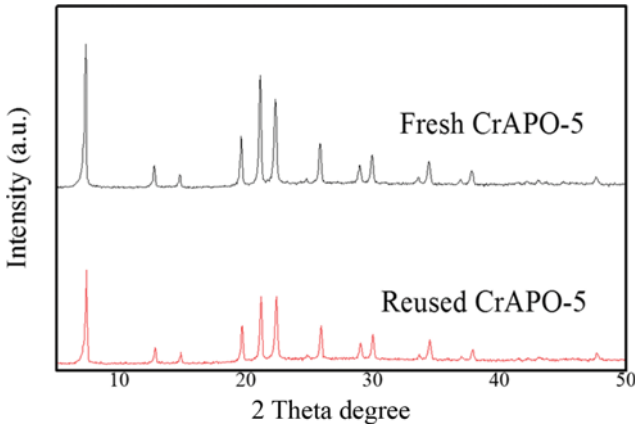
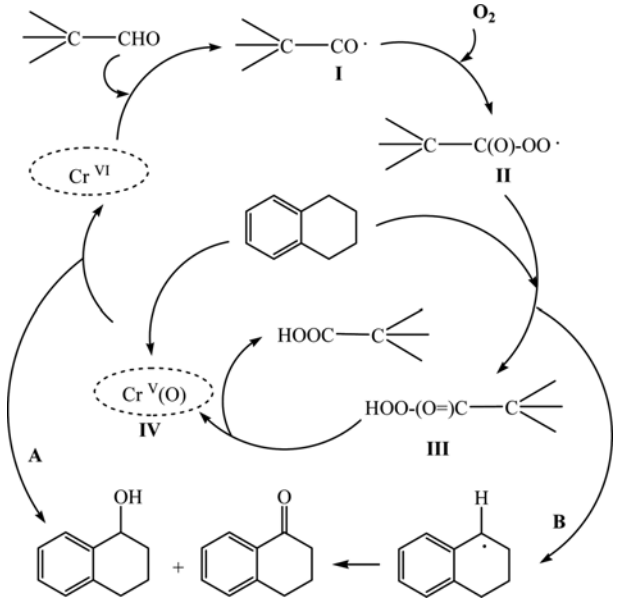


Fig. 5. XRD pattern of the fresh and reused CrAPO-5 catalyst.



Scheme 2. A mechanism proposed for the tetralin oxidation using aldehyde/O_2 system over CrAPO-5.

the framework of CrAPO-5 was done through a hot filtration experiment. In *t*-BuOOH, catalyst was quickly removed after 30 min reaction, and the filtrate was further stirred at 80 °C for an additional period up to 450 min (Fig. 3). The reaction was found still in progress but with a much slower conversion rate compared to that in the presence of catalyst. The selectivity to 1-tetralone was virtually identical (82%) in both cases. As shown in Fig. 4, in the case of pivalaldehyde/O_2 system at 80 °C, the reaction profile of tetralin conversion after hot filtration also showed a trend close to that when *t*-BuOOH was used. The higher conversions (7-10%) after hot filtration compared with a reaction without catalyst after 8 h indicated that the reaction intermediate formed in the presence of catalyst may still present in the filtrate after catalyst removal, which can produce products via thermal reaction [13]. The involvement of small amount of leached Cr in the solution, however, could not be ruled out. As shown in Fig. 5, the XRD pattern of the reused catalyst showed practically identical peaks to those of the fresh catalyst, indicating that the structure of the material remained intact during the reaction.

2-4. Reaction Mechanism

Oxidation reactions by various oxidant sources in chromium-based catalytic system are known to proceed through different reaction pathways, either through the formation of oxo-/-peroxo-metal species in the intermediate stage or through a radical pathway to form corresponding products [6]. Scheme 2 shows a plausible mechanism proposed for the tetralin oxidation using aldehyde/O_2 system over CrAPO-5. It was suggested that aldehyde reacts with O_2 to form initially a highly active acylperoxy radical (**II**), which is further transformed to a peroxy acid (**III**) [35] with subsequent formation of a oxo-chromium(V) (**IV**). This oxo-chromium(V) reacts with tetralin to furnish products through path A. In addition to path A, the reaction may concurrently furnish the radical $C_{10}H_{11}^{\bullet}$ [36] by transferring hydrogen atoms to **II** (Scheme 2, path B) to

produce the respective products. Using *t*-BuOOH as oxidant, the reaction mechanism may involve the formation of a peroxo-compound through the interaction of catalyst and oxidant, which subsequently reacts with tetralin to produce an unstable intermediate product *tert*-butylperoxytetralin [37,38] followed by its decomposition to the corresponding products. No change of metal oxidation state occurs in this pathway [39].

CONCLUSION

Tetralin oxidation over a chromium-containing molecular sieve, CrAPO-5, was investigated using either aldehyde and O_2 or *t*-BuOOH as an oxidant. The *in-situ* generated acylperoxy radicals in the pivalaldehyde/O_2 oxidant system resulted in superior activity and selectivity to 1-tetralone compared to *t*-BuOOH. Again, CrAPO-5 showed high activity and selectivity to 1-tetralone using pivalaldehyde/O_2 oxidant system at room temperature. The catalytic performance also showed a strong dependence on the nature of aldehyde used in the aldehyde and O_2 system. The influence of reaction time on product yields suggested that tetralin oxidation proceeds through simultaneous formation of 1-tetralone and 1-tetralol from the reaction intermediate, followed by further conversion of 1-tetralol to 1-tetralone. A reaction mechanism of tetralin oxidation involving highly active acylperoxy radicals generating an oxo-chromium(V) species over CrAPO-5 catalyst was proposed for the aldehyde/O_2 oxidant system.

ACKNOWLEDGEMENTS

This work was supported by University of Dhaka (CARS) internal fund for a fine chemicals preparation project (2016), and in part by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant number: NRF-2015R1A4A1042434).

REFERENCES

1. J. Muzart, *Bull. Soc. Chim.*, 65 (1986).
2. H. G. Franck and J. W. Stadelhofer, Industrial Aromatic Chemistry, Springer-Verlag, Berlin, **313** (1988).
3. G. A. Wachter, R. W. Hartman, T. Sergejew, G. L. Grun and D. Ledergerber, *J. Med. Chem.*, **39**, 834 (1996).
4. R. G. Tailleur, G. A. Salva and G. Garcia, *Fuel*, **88**, 744 (2009).
5. J. Muzart, *Tetrahedron Lett.*, **28**, 2131 (1987).
6. J. Muzart, *J. Chem. Rev.*, **92**, 113 (1992).
7. J. Muzart and A. A. Nait, *J. Mol. Catal.*, **92**, 277 (1994).
8. S. L. H. Rebelo, M. M. Q. Simoes, M. P. M. S. Neves, A. M. S. Silva, P. Tagliatesta and J. A. S. Cavaleiro, *J. Mol. Catal. A: Chem.*, **232**, 135 (2005).
9. L. J. Csanyi, K. Jaky, Z. Kota and T. Pali, *J. Mol. Catal. A: Chem.*, **209**, 59 (2004).
10. Y. M. Chung, W. S. Ahn and P. K. Lim, *J. Catal.*, **173**, 210 (1998).
11. S. H. Cho, M. S. Cheong, K. D. Jung, C. S. Kim and S. H. Han, *Appl. Catal. A: Gen.*, **267**, 241 (2004).
12. S. Sithambaram, E. K. Nyutu and S. L. Suib, *Appl. Catal. A: Gen.*, **348**, 214 (2008).
13. X. F. X. Llabres, O. Casanova, R. G. Tailleur, H. Garcia and A. Corma, *J. Catal.*, **255**, 220 (2008).
14. J. Kim, S. Bhattacharjee, K. E. Jeong, S. Y. Jeong and W. S. Ahn, *Chem. Commun.*, 3904 (2009).
15. S. Bhattacharjee, K. E. Jeong, S. Y. Jeong and W. S. Ahn, *New J. Chem.*, **34**, 156 (2010).
16. J. D. Chen and R. A. Sheldon., *J. Catal.*, **153**, 1 (1995).
17. H. E. B. Lempers and R. A. Sheldon, *Appl. Catal. A: Gen.*, **143**, 137 (1996).
18. P. Tian, Z. Liu, Z. Wu, L. Xu and Y. He, *Catal. Today*, **93**, 735 (2004).
19. R. A. Shaikh, G. Chandrasekar, K. Biswas, J. S. Choi, W. J. Son, S. Y. Jeong and W. S. Ahn, *Catal. Today*, **132**, 52 (2008).
20. O. B. Ryan, D. E. Akporiaya, R. H. Holm and M. Stocker, *Stud. Surf. Sci. Catal.*, **108**, 369 (1997).
21. S. E. Dapurkar, H. Kawanami, T. Yokoyama and Y. Ikushima, *New J. Chem.*, **33**, 538 (2009).
22. S. E. Dapurkar, H. Kawanami, T. Yokoyama and Y. Ikushima, *Catal. Commun.*, **10**, 1025 (2009).
23. S. K. Mohapatra, F. Hussain and P. Selvam, *Catal. Lett.*, **85**, 217 (2009).
24. A. Sakthivel, S. K. Badamali and P. Selvam, *J. Catal.*, **80**, 73 (2002).
25. Z. Lounis, A. Riahi, F. Djafri and J. Muzart, *Appl. Catal. A: Gen.*, **309**, 270 (2006).
26. B. M. Choudary, A. D. Prasad, V. Bhuma and V. Swapna, *J. Org. Chem.*, **57**, 5841 (1992).
27. S. K. Mohapatra and P. Selvam, *J. Catal.*, **249**, 394 (2007).
28. C. Mahendiran, P. Sangeetha, P. Vijayan, S. J. Sardhar and K. Shanthi, *J. Mol. Catal. A: Chem.*, **275**, 84 (2007).
29. R. A. Sheldon, *J. Mol. Catal. A: Chem.*, **107**, 75 (1996).
30. K. B. Sharpless and T. R. Verhoeven, *Aldrichim. Acta.*, **12**, 63 (1979).
31. J. Kim, S. Bhattacharjee, K. E. Jeong, S. Y. Jeong, M. Choi, R. Ryoo and W. S. Ahn, *New J. Chem.*, **34**, 2971 (2010).
32. A. Sakthivel, S. E. Dapurkar and P. Selvam, *Catal. Lett.*, **77**, 155 (2001).
33. P. Karandikar, M. A. Gashe, K. Vijayamohanan and A. Chandwadkar, *J. Appl. Catal. A: Gen.*, **257**, 133 (2004).
34. P. Aguirre, S. Zolezzi, J. Parada, E. Bunel, S. A. Moya and R. Sariego, *Appl. Organometal. Chem.*, **20**, 260 (2006).
35. S. I. Murahashi, T. Naota and N. Komiya, *Tetrahedron Lett.*, **36**, 8059 (1995).
36. M. M. Dell'Anna, P. Mastrorilli and C. F. Nobile, *J. Mol. Catal. A: Chem.*, **130**, 65 (1998).
37. T. Yamauchi and H. Nabu, US Patent, 4,283,352 (1981).
38. M. Martan, J. Manassen and D. Vofsi, *Tetrahedron*, **26**, 3815 (1970).
39. Y. O. Moro, *Catal. Today*, **45**, 3 (1998).