AU(III) AND CU(II) CATALYST FOR OXIDATION OF AROMATIC AND CYCLIC HYDROCARBON BY CERIUM (IV) IN ACIDIC MEDIUM UNDER MICROWAVE IRRADIATION

Manish Srivastava,[*] Ashu Goyal, Anamika Srivastava, Aakanksha Mishra and Preeti Tomar
[*]Department of Chemistry, Banasthali Vidyapith, Banasthali, Rajasthan, 304022, India.
Corresponding author email id: sagermanish1@gmail.com

Abstract

The addition of traces of Au(III) chloride with Ce(IV) sulphate (catalyst: substrate ratio (1: 80 to 1: 300)) and in case of Cu(II) sulphate with Ce(IV) sulphate(catalyst: substrate ratio (1: 60 to 1: 250)) in solution phase under microwave irradiation resulted in good to excellent yields of corresponding to phenol, quinone and carbonyl compounds. In case of oxidation of anthracene, phenanthrene, naphthalene, cyclohexane and toluene dissolved in acetic acid to give 95.02 %, 85.25%, 34.68%, 40.94%, and 56.54% yields in case of gold catalyst and 93.5%, 83.4%, 24.68%, 38.25% and 47.11% yields in case of copper as a catalyst. Phenanthrene was oxidized in 9-Fluorenone instead of phenanthraquinone to get the benzylic rearrangement.

Keywords: Aromatic hydrocarbons, Oxidation, Cerium(IV) sulphate, Ce(IV)-Au(III), Ce(IV)-Cu(II) system, Characterization, Microwave Synthesizer.

INTRODUCTION

Research field of gold catalysis has emerged to become one of fastest growing fields in catalysis at the moment[1]. Gold is understood to be the noblest of all the metals with well-established that the nobility of gold as catalyst [3] although, since the work performed within the group of Haruta[2]. Gold had long been regarded to be being catalytically methods less active than several transition metals. However, since the pioneering work of haruta, it has been found that gold can exhibit astonishingly high catalytic reactivity once it is extremely dispersed on reducible metal oxides (e.g., TiO_2). [4-6] Use of gold can be more selective than platinum and palladium for the catalyzed oxidation of alcolol[7] in further, focus is on the use of gold nanoparticle as an catalyst for oxidation of alcohols[8]. Cyclohexane can be oxidized to cyclohexanol and cyclohexanone over a gold catalyst[9]. High activity for an oxidation reaction was unprecedented and this has led to an explosion of interest in catalysis by gold[10-13]. Catalysts derived from copper and its oxides are commonly used in many chemical reactions, including the oxidation of organosulfur compounds. The common use of copper catalysts in various chemical reactions is attributed to their high activity related to facile electron transfers between copper in various oxidation states (Cu^0,Cu^{1+},Cu2+). We should also expect dimensional effects in the use of highly-dispersed copper catalysts in the low-temperature oxidation of CO and organic compounds. Oxidation of aromatic hydrocarbons, aldehydes and cyclic alcohol by sodium ferrate in presence of copper nano particle has been reported[14-15].

Chemistry of cerium is a very broad area which has received considerable attention through the years, resulting in substantial advance both in the synthetic[16-17] and mechanistic categories. Cerium (IV) oxidation of aromatic compounds in the presence and absence of metal ions has been frequently reported from the synthetic point of view[18]. Cerium (IV) is a well known oxidant in acidic media[19-21] having reduction potential[22-23] of the couple Ce (IV)/Ce(III)1.70V and is stable only in high acid concentration. The metal ion oxidants have been widely employed in the synthetic chemistry[24-26] including carbohydrates chemistry[27-28]. These are stable, in expensive and can readily be stored and handled.

Thabaj et al., reported the reaction of Ce (IV) oxidation of L-serine catalyzed by a small amount of Ag^+ in aqueous sulfuric acid medium. In sulfuric acid and sulfate media, several sulfate complexes of Ce(IV) form exist such as $Ce(SO)_4^{2+}$,$Ce(SO_4)_2$, $Ce(SO_4)_2HSO^{4-}$, and $H_3Ce(SO_4)^-_4$, but their role has not received much attention so far, because of the increase in the rate of reaction with increasing sulfuric acid concentration. The mechanism may be quite complicated due to the formation of different Ce(IV) complexes in the form of active species.

Cerium(IV) is a strong one electron oxidant used as associated analytical chemical reagent particularly in acid media (Richardson, 1965)[29] . Ceric ammonium nitrate a versatile oxidant for synthetic organic chemistry has been used as a catalyst also in a number of synthetic reactions[30] Liquid phase oxidation of cyclohexane was carried out over mesoporous Ce-MCM-41 catalysts using aqueous hydrogen peroxide as oxidant and acetic acid as solvent without adding any initiator[31]. CAN catalyzed oxidation of alkyl aromatics giving rise to aldehydes, ketones, acids or alcohols with potassium bromate has been reported[32]. It has been shown that oxidation of aromatic hydrocarbons with cerium (IV) results in their conversion to quinones. Naphthalene is converted to 1, 4-Napthaquinone (90%). In case of hydrogen peroxide[33] naphthalene is converted to α-naphthol.

EXPERIMENTAL SECTION

Copper (II) sulphate, cerium (IV) sulphate, naphthalene, cyclohexane, toluene, and phenanthrene, anthracene, were used as such without further purification.

Gold solution was prepared by dissolving the sample [Hydrochloroauric acid trihydrate(III)] in deionized water. The final strength of gold catalyst is 1.90×10^{-3} and prepared the 1.0 mmol copper (II) sulphate solution dissolving the sample $CuSO_4.5H_2O$ in deionized water.

A CEM Discover Microwave synthesizer was used for studying the reactions under microwave irradiation, in which control of temperature, time and power was possible. In order to achieve the maximum yield, five to seven sets were performed by changing the concentration, time temperature and other conditions of each component, which can affect the yield, for example in the synthesis of cyclohexanone from cyclohexane for performing the reactions in the solution phase, 0.15 mmol of copper(II) sulphate with 2.5mmol cerium(IV) sulphate were added to 3.4 mmol of acetic acid solution containing 1.0 mmol of 2.0 mmol of cyclohexane and the mixture was heated under microwave irradiation for 3.0 min taken in a microwave vessel. The microwave vessel was kept under microwave synthesizer at a fixed temperature for the 3.0 min. Contents were cooled and extracted with appropriate solvents. The extract was dried over anhydrous MgSO4. Solvent was removed under reduced pressure; again replacing the 0.20 mmol gold (III) chloride solution was heated under microwave irradiation for 3.0 min. Contents were cooled and extracted with di ethyl ether. The extract was dried over anhydrous MgSO4. Solvent was removed under reduced pressure, and prepared the hydrazone derivative of the product and noted the achieved yield. IR (Bruker 8201 IR spectrophotometer) and 1H NMR (Bruker 400MHz) spectra were recorded, and reactions were monitored with thin-layer chromatography, TLC (Merck GF254 silica-gel-coated plates). TLC, IR, NMR spectra and melting points of the derivative confirmed the purity and identification of products.

RESULTS AND DISCUSSION

In all the cases, running TLC plates with hydrazone of the authentic sample showed only one spot, reaction conditions in which various experiments were performed are summarized in Table-2, and the general procedures for performing the reactions in solution phase and under microwave irradiation are given in the experimental section. 2, 4-Dinitrophenyl hydrazone derivatives of the products were prepared by the standard method[34], hydrazone of cyclohexanone from cyclohexane was recrystallized with ethyl alcohol.

Yield of cyclohexanone (A') from cyclohexane was found in the case of copper catalytic system (38.25%) is comparatively lower than that of found in gold catalytic system (40.94%). On conducting the reaction in a microwave irradiation (100 %power, 5.0 min with both catalyst). Hydrazone mp was 160°C (reported as 162°C).

IR: ν_{max} = 2938.1 cm^{-1} (ν_{C-H}, str), 1711.4 cm^{-1} ($\nu_{C=O}$), 1450 cm^{-1} (ν_{C-H}, bend).

NMR: 2.25-2.46 (2H, d),   1.97-1.216 (3H, m).

Yield of benzaldehyde (B') from toluene (B) was found in case of copper catalytic system (47.11%) is comparatively lower than that of found in gold catalytic system (56.54%). On conducting the reaction in a microwave irradiation (100 %power, 5.0 min with both catalyst). Hydrazone mp was 230 ° C (reported as 241° C).

IR peaks: $_{max}$ = 2816.74 cm^{-1} ($_{C-H - CHO \, str}$), 1696 cm^{-1} ($_{c=o}$), 1592.37 cm^{-1} ($_{benzene \, ring \, str.}$), 824-922 cm^{-1} ($_{c-c \, str}$).

NMR Signals: 9.97 (1H, s),   6.9-7.71 (5H, m).

Yield of   -naphthol (C') from naphthalene was found in copper catalytic system (24.68%) is comparatively lower than that of found in gold catalytic system (34.68%). On conducting the reaction in a microwave irradiation (80% power, 3.0 m in with both catalysts)   -naphthol   mp was 90ºC (reported as 94ºC).

IR Peaks: ν_{max} =3226.28 cm^{-1}(€ $_{OH}$), 1591 cm^{-1}(€ c = c), 1384 cm^{-1} ($_{C-O \ phenolic \ strs}$), 821-874 cm^{-1}($_{benzene \ ring \ str}$)

 NMR signals: 6.929-7.7029 (7H, m),   5.5678 (1H, s).

Yield of anthraquinone (D') from anthracene (D) was found in copper catalytic system (93.5%) is comparatively lower than that of found in gold catalytic system (95.02%). On conducting the reaction in a microwave irradiation (80% power, 3.0 min). Anthraquinone mp was 280ºC (reported as 286 ºC).

IR peaks: ν_{max} = 1694.92 cm^{-1} ($\nu_{C=O \ quinone}$), 1540.16 cm^{-1} ($_{C=C}$), 3072 cm^{-1} ($_{Ar-H}$), 935–809 cm^{-1} (ν $_{benzene \ ring}$).

NMR: 7.6095 - 7.9726 (8Hm).

Yield of 9-fluorenone (E) from phenanthrene (E') was found in copper catalytic system (83.4%) is comparatively lower than that of found in gold catalytic system (85.25%). On conducting the reaction in a microwave irradiation (80% power, 3.0 min with both catalyst), 9-fluorenone mp was 83ºC (reported as 82-85ºC).

IR€ $_{max}$: 1690.31 cm^{-1} (c=o), 2960 cm^{-1} (ν_{C-H}, str .aromatic$^.$), 756-866 cm^{-1} (ν_{C-H} bend aromatic), 1540.24 cm^{-1}($V_{C=C \ Str. \ atm.}$).
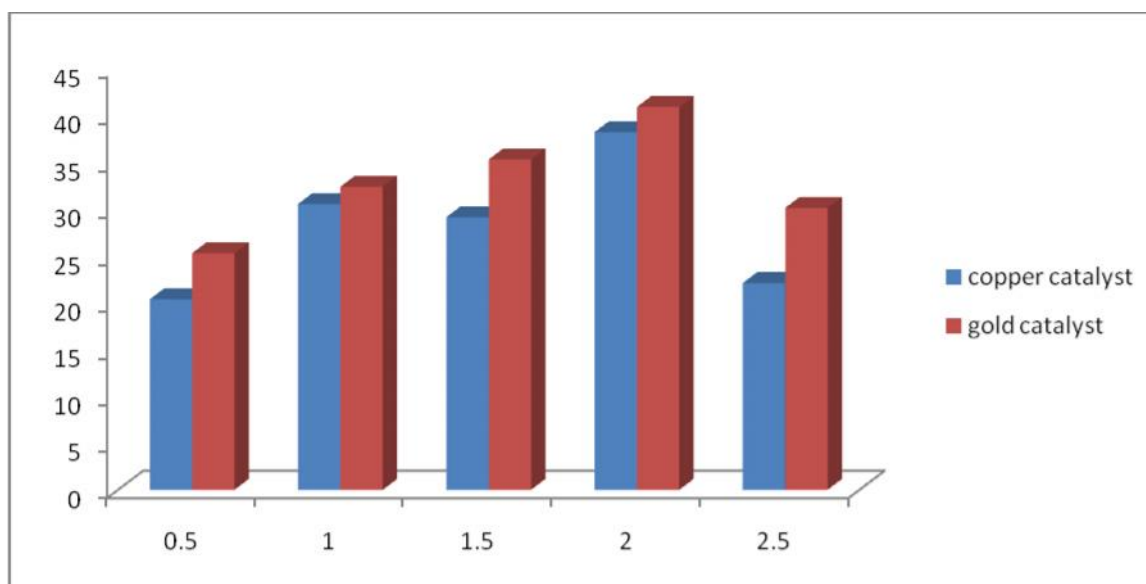
NMR: 7.124-7.719 (8H, m).

Oxidation of phenanthrene generally results in the formation of 9, 10- phenanthraquinone which undergoes benzylic rearrangement and finally gives 9-fluorenone in heating conditions through the formation of 9-hydroxyfluorene-9-carboxylic acid.

The study was performed mainly to determine the efficiency and economy of the novel, simple one-pot cerium (IV)-gold (III) and cerium (IV)-copper (II) system for the oxidation of aromatic and aliphatic cyclic hydrocarbons. Four to six set performed to obtained the maximum yield by changing the experimental condition of each component and change in the concentration of acetic acid did not change the yield of product , indicating that it act as a solvent to dissolved the hydrocarbons. In the case of oxidant variation increase the concentration of cerium (IV) sulphate decrease the yield of the product because at high concentration dimeric species is formed so the rate of reaction is decrease, yield is decrease (Table-1, entry 4 and 5) and in case of catalyst variation increase the concentration of catalyst decrease the yield of the product because at high concentration un- reactive species is formed so the yield of product is decrease (Table-1, entry 4 and 5). In the absence of catalyst the yield of product is zero (Table-1, entry 6) ie, the reaction is not occurs. This indicating that catalyst is responsible for the oxidation of cyclohexane in fig 1 the bar diagram show that increase the concentration of Au(III) and Cu(II) catalyst increase the percentage yield of cyclohexanone but at high concentration yield is decrease. UV-Visible spectral study we get the complex formed between the organic substrate and oxidant. During the kinetics study of oxidation of cyclic alcohols, aromatic aldehydes and aromatic hydrocarbons we observed[35-37] that the complex formed cerium(IV) with organic substrate in the first step. Ce(IV), Mn(III), Co(III) and V(V) in one – equivalent oxidant that remove one electron at a time from the substrate it undergo generate anionic, cation radicals or free radicals[38] neutral or anionic organic species, cation radicals or free radicals are generated. Normally, these intermediates undergo C-H, C-C bond cleavage or hydrogen transfer depends on their structure. In the oxidation of aromatic hydrocarbons, phenol, alcohols and aromatic aldehydes17   with cerium (IV) sulphate in liquid phase and solvent fewer conditions has been reported. In fig-2 the bar diagram show that in case of gold(III) catalyst give the higher yield as compare to copper(II) catalyst because the electronic configuration of Au(III) is $4f^{14}5d^8$ and Cu(II) is $3d^9$. The electrode potential of the Au(III) is +1.42 and Cu(II) is +0.34.The electrode potential of gold(III) is higher than compare to copper(II) electrode potential so Au3+ oxidation state is more stable and more reactive than Cu2+. Known that AuCl3 in aqueous medium gives Au(OH)2(H2O)2+, Au(OH)3(H2O)0 species. It has also been reported that Au3+ and Au2+ ions are the stable species of gold Further, the acid medium of Au(III) gives Au(OH)2(H2O)SO4-, Au(OH)2(H2O)2SO40and Au(OH)(H2O)(SO4)22- species.39 In the present case, the concentration of acetic acid did not affect the yield, indicating that acetic acid probably does not change the species of catalyst in the medium. The reported novel one-pot system is highly efficient, easy, and also can be used to oxidize a variety of

other functional groups, for which studies are being done. Above all, it oxidizes cyclohexane, toluene and naphthalene, which are otherwise difficult to oxidize. High yield of the carbonyl group makes the system very attractive from a synthetic point of view. The least minimum amount of solvent used in the synthesis under microwave irradiation is also important from an environmental point of view.

Table 1: Effect of diverse factors on the yield of Cyclohexanone from cyclohexane (2.0 mmol) by gold(III)-cerium(IV) sulphate and copper(II) sulphate-cerium (IV) sulphate catalytic system in aqueous acetic acid medium in solution phase under microwave irradiation.
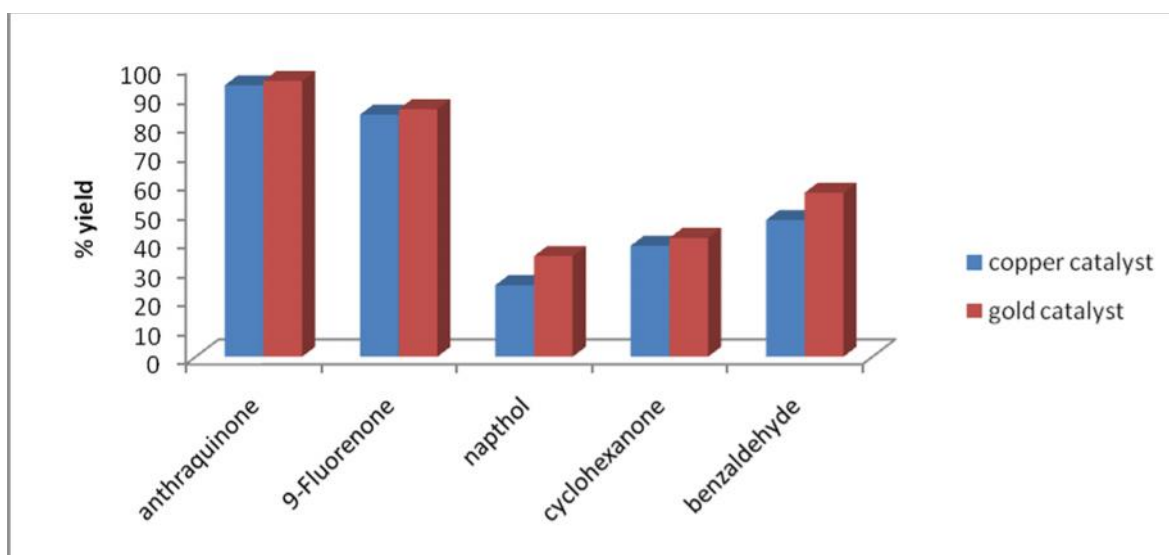
AS.No.	Acetic acid (mmol)	Ce(IV) sulphate (mmol)	$Cu(II) \times 10^3$ catalyst[a] (mmol)	$Au(III) \times 10^3$ catalyst[b] (mmol)	Time (min.)	Temp. (°C)	MW power (W)	% yield With Cu(II) catalyst[a]	% yield With Au(III) catalyst[b]
1.	3.4	2.5^a 2.5^b	0.05	0.05	3.0^a 3.0^b	60^a 60^b	80^a 80^b	20.37	25.30
2.	3.4	2.5^a 2.5^b	0.10	0.10	5.0^a 5.0^b	100^a 100^b	80^a 80^b	30.56	32.41
3.	3.4	2.5^a 2.5^b	0.15	0.15	5.0^a 5.0^b	100^a 100^b	80^a 80^b	29.15	35.32
4.	3.4	2.5^a 2.5^b	0.20	0.20	5.0^a 5.0^b	100^a 100^b	80^a 80^b	38.25	40.94
5.	3.4	2.5^a 2.5^b	0.25	0.25	7.0^a 7.0^b	140^a 140^b	80^a 80^b	22.12	30.15

Figure 1: Effect of variant of copper and gold catalyst on the yield of cyclohexanone.

Table 2: Comparative study of gold (III) chloride and copper (II) sulphate as catalyst in solution phase for oxidation of hydrocarbons by cerium (IV) sulphate dissolve in acetic acid under microwave irradiation

S.No.	Acetic acid (mmol)	Ce(IV) sulphate (mmol)	Cu(II)x10^3 catalyst[a] (mmol)	Au(III)x10^3 catalyst[b] (mmol)	Time (min.)	Temp. (^{o}C)	MW power (W)	% yield With Cu(II) catalyst[a]	% yield With Au(III) catalyst[b]
1.	3.4	2.5[a] 2.5[b]	0.05	0.05	3.0[a] 3.0[b]	60[a] 60[b]	80[a] 80[b]	20.37	25.30
2.	3.4	2.5[a] 2.5[b]	0.10	0.10	5.0[a] 5.0[b]	100[a] 100[b]	80[a] 80[b]	30.56	32.41
3.	3.4	2.5[a] 2.5[b]	0.15	0.15	5.0[a] 5.0[b]	100[a] 100[b]	80[a] 80[b]	29.15	35.32
4.	3.4	2.5[a] 2.5[b]	0.20	0.20	5.0[a] 5.0[b]	100[a] 100[b]	80[a] 80[b]	38.25	40.94
5.	3.4	2.5[a] 2.5[b]	0.25	0.25	7.0[a] 7.0[b]	140[a] 140[b]	80[a] 80[b]	22.12	30.15

Fig 2: Effect of variant of copper and gold catalyst on the yield of compounds.

CONCLUSIONS

This study was principally mostly to determine the effectiveness and economy of the narrative, straightforward, one-pot novel gold(III)-cerium(IV) sulphate and copper(II) sulphate-cerium (IV) sulphate catalyzed system on to oxidize numerous organic compounds. Yields in all the cases reached outmost and then ongoing to decrease with advance increase in catalyst and oxidant concentrations signifying that most favorable conditions are required to get the uppermost yield. In conclusion, we have developed a rapid and efficient microwave assisted procedure for the synthesis of various organic compounds using new catalytic system and also mentioned the yield comparison on using cerium (IV) sulphate as oxidants. The reported novel one-pot system is highly competent, effortless, and also can be used to oxidize a multiplicity of other functional groups, for which studies are being done. High yield of the

carbonyl group makes the system very attractive from a synthetic point of view. Microwave reactions are also important from the environmental point of view because using very less amount of solvent and not use the hazarded chemical in reaction.

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REFERENCES

1. Bond, G. C.; Louis, C. Catalysis by Gold, Imperial College Press, London (2006). (b) Hashmi, A.S.K.; Hutchings, G.J. Angew. Chem. Int. Ed. 45, p. 7896, (2006). (c) Thompson, D.T. Topics in Catalysis. 38, p. 231, (2006). (d) Hashmi, A.S.K. Gold nanoparticle catalyzed oxidation of alcohols From biomass to commodity chemicals. Chem. Rev. 107, p. 3180, (2007).
2. Hammer, B.; Norskov, J.K. CO oxidation on gold nanoparticles: Theoretical studies. Nature 376 238. (1995).
3. Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M.J.; Delmon, B. CO oxidation on gold nanoparticlest theoretical studies. J. Catal. 144, 175, (1993).
4. Haruta, M. Catalytic Role of gold in gold based catalysts: A density functional theory study on the co oxidation on gold. M. Appl. Catal. A. Gen. 222, 427, (2001).
5. Hammer, B.; Norskov, J. K. Catalytic role of gold in gold based catalysts: A density functional theory study on the co oxidation on gold. Nature. 376, 238, (1995).
6. Valden, M.; Lai. X.; Goodman, D. W. Catalytic role of gold in gold based catalysts: A density functional theory study on the co oxidation on gold. Science. 281, 1637, (1998).
7. Rossi, L. M. Gold nanoparticle catalyzed oxidation of alcohols from biomass to commodity chemicals. Journal of Catalysis. 176, p. 552, (1998).
8. Abad, A.; Concepción, P. Gold nanoparticle catalyzed oxidation of alcohols from biomass to commodity chemicals. Angew. Chem. Int. Ed. 44, p. 4066.9 (2005) (b) Edwards, D.I.; Gold nanoparticle catalyzed oxidation of alcohols from biomass to commodity chemicals Science. 311, p. 362, (2006).
9. (a) Zhao, R. ; Chem. Commun, p. 904 (2004), (b) Xu, Y. Catal. Lett. 101, p. 175, (2005).
10. Hashmi, A.S.K. Nanocrystalline gold and gold–palladium alloy oxidation catalysts: a persona reflection on the nature of the active sites. Gold Bull. 37, 51, (2004).
11. Bond,G.C.; Thompson, D.T. Nanocrystalline gold and gold–palladium alloy oxidation catalysts: a personal reflection on the nature of the active sites. Gold Bull. 33, 41, (2000).
12. Meyer,R.C.; Lemaire, S.K.; Freund, H.J. Nanocrystalline gold and gold–palladium alloy oxidation catalysts a personal reflection on the nature of the active sites. Gold Bull. 37, 72, (2004).
13. Hashmi,A.S.K.; Hutchings, G.J.Angew. Chem, Int. Ed. Nanocrystalline gold and gold–palladium alloy oxidation catalysts: a personal reflection on the nature of the active sites. 45, 7896, (2006).
14. Tandon, P.K.; Singh, S.B.; Srivastava, M. Synthesis of some aromatic aldehyedes and acid by sodium ferrate in the Presence of copper-nano particles absorbed on K10 Mont Morillonite using microwave irradiation. Appl. Organometal. Chem. 21: 264-267, (2007).
15. Tandon, P.K.; Singh, S.B.; Singh, S.; Kesarwani, B. Oxidation of hydrocarbons, Cyclic alcohols and aldehydes by in situ prepared sodium ferrate. J. Indian Chem. Soc. 89, 1363-1367, (2012).
16. Tandon, P.K.; Purwar, M.; Dwivedi, P. B.; Srivastava, M. Kinetics of iridium(III) catalyzed oxidation of benzaldehyde and p-nitro benzaldehyde by Cerium(IV) in aqueous acidic medium. Transition Metal Chemistry. 33, 791– 795, (2008).
17. Tandon, P.K.; Purwar, M.; Singh, S.; Srivastava N.; Srivastava, M. Graphical separation of uncatalyzed reaction in iridium(III) catalyzed oxidation of cinnamaldehyde by cerium(IV) in aqueous acid medium. J. Mol. Catalyst A: Chemical, 293, 39 – 44, (2008).
18. Tandon, P.K.; Srivastava, M.; Singh, S. B.; Singh, S. Liquid phase and microwave assisted oxidation of some hydrocarbons, aromatic aldehydes and phenols by cerium(IV) catalyzed by iridium(III) in acidic medium. Synthetic communications. 38: 13, 2125 – 2137, (2008).
19. Tandon, P.K.; Srivastava, M.; Singh, S. B.; Srivastava, N. Liquid phase and solvent less oxidation of cyclohexane, benzene and other hydrocarbons by cerium(IV) catalyzed by iridium(III) in acidic medium. Synthetic communication, 38: 18, 3183-3192, (2008).

20.   Tandon, P.K.; Purwar, M.; Dwivedi, P.B.; Srivastava, M. Kinetics of iridium(III) catalyzed oxidation of benzaldehyde and p-nitro benzaldehyde by Cerium(IV) in aqueous acidic medium. Transition Metal Chemistry, 33, 791 – 795, (2008).

21.   Tandon, P.K.; Srivastava, M.; Kumar, S.; Singh, S. Iridium(III) catalyzed oxidation of toluene and ethyl benzene by cerium(IV) in aqueous acidic medium, J. Mol. Catal A. Chemical, 304, 101-106, (2009).

22.   Day, M. C.; Selbin, J.J. Theoretical Inorganic chemistry (Reinhold Publishing Corporation, New York, p. 226 (1964).

23.   Vogel, AI. A text Book of quantitative inorganic analysis. 3rd Ed. Longmans: London; (1961).

24.   Chinn, L.J. Selection of oxidants in synthesis, oxidation at carbon atoms. Marcel Dekker, New York; (1971).

25.   Belew, J. S. In Oxidation techniques and applications in organic synthesis. Augustine, R. L., Ed. New York, Vol. 1, p 294,(1969).

26.   Evans, WL. Oxidation of carbohydrate with alkaline permanganatc silver oxide and copper acetate. Chem.Rev.; 6: 281-284,(1929).

27.   Butterworth, R. F.; Haneesian, S. Selected method of oxidation in carbohydrate chemistry Sythesis. 7-78, (1971).

28.   Heyns, K.; Paulsen, H. The mechanism of carbohydrate oxidation. Adv. Carbohydr. Chem. 17, 169-176, (1962).

29.   Seema, S. B.; Suresh M. Tuwar Oxidation of clindamycin phosphate by cerium(IV) in perchloric acid medium. A kinetic and mechanistic approach. Arabian Journal of Chemistry, (2013).

30.   Dakshinamoorthy, A. Cerium(IV) Ammonium Nitrate: A Versatile Oxidant in synthetic organic chemistry, Syn lett. 19, 3014–3015, (2005).

31.   Yao, W.; Chen, Y.; Min, L.; Fang, H.; Yan Z.; Wang, J. Liquid oxidation of cyclohexane to cyclohexanol over cerium-doped MCM-41. J. Mol. Catal. A: Chemical, 246, 162-166, (2006).

32.   Ganin , E.; Amer, I. Cerium- catalyzed selective oxidation of alkylbenzenes with bromate salts. Synth. Commun. 25, 3149 – 3154,(1995).

33.   Tandon, P.K.; Baboo, R.; Singh, A.K.; Purwar, M. Appl. Organometal. Chem. Volume 19, Issue 10, 1979 (2005).

34.   Shriner, R.L.; Hermann, C.K.F.; Morrill, T.C.; Curtin D.Y.; Fuson, R.C. The systematic identification of organic compounds. John Wiley and Sons: New York,pp. 321-322,(1998).

35.   Tandon, P. K.; Sahgal, S.; Singh, A. K.; Purwar, M. Oxidation of ketones by ceric perchlorate catalyzed by iridium(III). J. Mol. Catal. A: Chem. 232, 83–88.5, (2005),

36.   Tandon, P. K.; Sahgal, S.; Purwar, M.; Dhusia, M. Oxidation of ketones by cerium(IV) in presence of iridium(III) chloride. J. Mol. Catal, A: Chem., 250, 203–209.6, (2006).

37.   Tandon, P. K.; Sahgal, S.; Singh, A. K.; Kumar, S.; Dhusia, M. Oxidation of cyclic ketones by cerium(IV) in presence of iridium(III) chloride. J. Mol. Catal, A: Chem, 258, 320–326, (2006).

38.   Tse, L. H. Organic synthesis by oxidation with metal compounds, Plenum Publishing Corporation, p. 570,(1986).

39.   Mironov, I.V; and Makotchenko, E.V.; On the existence of gold (III) complex species in acid sulphate solution. Russian journal of inorganic chemistry,Vol 50, no 5, pp 799-804, (2005).