

Oxidation of Toluene over LaCoO₃/SiO₂ and LaVO₃/SiO₂ Perovskite catalysts. A comparative study

H.S.Goswami

Lecturer

Department of Chemistry, Government College, Karauli (Raj.) India

Abstract:

The vapour phase catalytic oxidation of toluene over perovskites Viz., LaCoO₃/SiO₂ and LaVO₃/SiO₂ has been studied. The characterization of the catalyst was carried out using technique Viz. Surface area, Packing density, Surface acidity, Surface basicity. The surface area measurements in the temperature range 350°C to 600°C. The maximum surface area & maximum activity was observed at 450°C.

The heterogeneous catalytic vapour phase oxidation of toluene give benzaldehyde, benzoic acid, maleic acid and CO₂ as products over LaCoO₃/SiO₂ and LaVO₃/SiO₂ as catalyst. The LaCoO₃ supported on SiO₂ has been found to be the most active and selective catalyst giving 79.4% selectivity for benzaldehyde at 450°C with surface area 61.1 m²/g. The overall Kinetic analysis indicate that the oxidation of Toluene to benzaldehyde is first order. The order of catalytic reactivity is LaCoO₃/SiO₂ > LaVO₃/SiO₂. The selectivity and activity of catalyst is correlated to surface area values.

Keywords: Catalysis, Oxidation, Toluene, Supported, Benzaldehyde, Surface area.

Introduction:

Perovskites type oxides are known to be catalyst for a number of reactions such as total partial Oxidation, Hydrocracking, hydrogenation, hydrogenolysis and reduction etc. Amongst the more important reactions in which these compounds have been used as catalyst are oxidation of CO^[1-4], NH₃^[5], Methanol^[6], Olefins^[7], Paraffin^[8-10], Aromatic compounds^[11-15], Hydrogenation^[16] and oxygenate^[17]. The oxidation of light Paraffin's as methane, propane and n-butane has been frequently taken as a test reaction for perovskites oxides. Effort has largely been directed towards synthesis of an unsupported and supported Perovskites, Oxides of moderates or high specific surface area, their bulk and surface properties and their role in heterogeneous catalysis. The vapour phase oxidation of toluene is of industrial importance. The partial oxidation of toluene over mix oxide has been studied but work with Perovskites is scanty. It was thought interesting to screen the catalytic activity of LaCoO₃/SiO₂ and LaVO₃/SiO₂ and compare their reactivity.

Materials and Methods:

The LaCoO₃/SiO₂ catalyst was prepared by the oxalate decomposition method^[18].

Preparation method:

LaCoO₃/SiO₂ were prepared. A general method for preparing 20% LaCoO₃ on Silica is follows-Aqueous solution of La(NO₃)₃.6H₂O(7.2gm), Co(NO₃)₂.6H₂O(4.73gm), Concentrate oxalic acid and Silica (20gm) were mixed in a beaker and then transferred to china dish. The contents were heated at 1000°C in a muffle furnace to get the desired catalyst. The catalyst LaVO₃/SiO₂ was prepared by amorphous precursors citrate decomposition method^[19].

Preparing LaVO₃ on SiO₂ are follows: Aqueous solution of La(NO₃)₃.6H₂O (7.27 gm), NH₄VO₃ (1.96 gm), Citric acid (3.45 gm) and Silica (20gm) were mixed in a beaker and then transfer china dish. The final mizture was heated on the sand bath for 10-12Hrs. Finally the catalyst powder so obtained was heated at 600 °C in a muffle furnace to get the desired catalyst.

The surface area of catalyst was determined using ethylene glycol monoethylether (EGME) adsorption method^[20,21] at different temperature. The surface acidity & surface basicity of perovskites catalyst were determined by n-butylamine titration^[22] and phenol adsorption method^[23] respectively. The experimental setup and the methods for the analysis of the products such as benzaldehyde, benzoic acid, maleic acid and carbon dioxide were the same as described elsewhere^[24-27].

Table 1- Characteristics of LaCoO₃/SiO₂ and LaVO₃/SiO₂ Perovskite catalysts.

Catalyst	Decomposition Temperature (°C)	Packing density (g/cc)	Acid strength n-butylamine titre, meq/g		Base strength n-butylamine titre, meq/g
			PKa=6.8 (Neutral red.)	PKa=4.8 (Methyl red.)	Bromo thymol blue PK _i =7.2
LaCoO ₃ /SiO ₂	1000 °C	1.11	0.091	0.241	2.9
LaVO ₃ /SiO ₂	600 °C	1.34	0.016	0.211	0.63

Table 2- Activity and Selectivity data.

Catalyst	Surface area m ² /g	Reaction Temp. °C	Conversion % to				Total Conversion	% selectivity to BzH
			BzH	BzA	MA	CO ₂		
LaCoO ₃ /SiO ₂	50.1	350	9.0	2.6	1.9	2.4	15.9	56.6
	54.2	400	10.6	2.4	1.9	2.0	16.9	62.7
	61.1	450	15.1	1.0	1.8	1.1	19.0	79.4
	56.4	550	9.8	2.1	1.7	3.2	16.8	58.3
	59.0	600	9.0	2.9	2.0	2.6	16.5	54.5
LaVO ₃ /SiO ₂	10.2	350	6.4	2.6	2.2	1.2	12.4	51.6
	10.6	400	8.7	2.1	2.9	2.3	16.0	54.3
	16.4	450	11.2	2.1	2.0	1.3	16.6	67.4
	10.4	550	7.4	1.3	3.8	2.6	15.1	49.0
	10.4	600	6.5	4.0	4.0	2.9	17.4	37.3

The oxidation was studied at space velocities (2998) temperature 350°C, 400°C, 450°C, 550°C and 600°C at air toluene ratio (121) respectively.

Results and Discussion

The catalyst was characterized using techniques Viz; Surface area, packing density, surface acidity and surface basicity. The result of these studies has been incorporated in table 1 and 2. The surface area measurements in the temperature range 350°C to 600°C (Table II) shows that surface area of the catalyst increases with increase in temperature up to 450°C but on further increase in temperature the surface area decreases. The specific surface area for different catalyst was found to follow the order LaCoO₃/SiO₂ > LaVO₃/SiO₂. The surface acidity and basicity measurements show that LaCoO₃/SiO₂ and LaVO₃/SiO₂ have both acidic and basic sites. The LaCoO₃/SiO₂ is more basic than LaVO₃/SiO₂. The order of packing density for catalyst is LaVO₃/SiO₂ > LaCoO₃/SiO₂.

LaCoO₃/SiO₂ and LaVO₃/SiO₂ were subjected to toluene oxidation. The oxidation of toluene gave benzaldehyde (BzH), benzoic acid (BzA), maleic acid (MA) and CO₂ as the products.

The formation of benzaldehyde as a function of temperature and aerial activity of LaCoO₃/SiO₂ and LaVO₃/SiO₂ at 350°C, 400°C, 450°C, 550°C and 600°C are presented in Table 2. The rate of formation of BzH in the beginning is higher on both catalysts. An initial increase in temperature from 350 °C to 450 °C shows an increase in the percentage conversion of BzH from 56.6% to 79.4% on LaCoO₃/SiO₂ (Specific surface area of LaCoO₃/SiO₂ increases from 50.1 m²/g to 61.1 m²/g). On LaVO₃/SiO₂ from 51.6% to 67.4% (Specific surface area of LaVO₃/SiO₂ increases from 10.2 m²/g to 16.4m²/g).

Further increase in temperature from 450 °C to 600 °C decreases the percent conversion of benzaldehyde (Table 2). Thus in the present investigation the catalyst have been found to be active as well as selective at 450 °C for the partial oxidation of toluene. The increase in activity up to 450 °C can be ascribed to increasing removal of trace surface contaminant such as adsorbed gases, hydroxy species of adsorbed water [27] and to the generation of stoichiometric or structural defects such as anion vacancies or disorders and exposed metal ions, which serves as catalytic sites [28]. The decrease in activity observed above 450 °C may be due to a decrease in surface disorder due to the relatively high mobility of O₂⁻ ions in the lanthanide sesquioxides [29] and resulting in the formation of low surface area at 600 °C.

From the result it has been seen that the catalyst is highly select in the oxidation of toluene. The selectivity and activity of catalyst is correlated to surface area values. The most selective and active catalyst is LaCoO₃/SiO₂ catalyst because it has more surface area value than LaVO₃/SiO₂ catalyst.

The difference in catalytic activity of these Perovskites heated at different temperature can also be related to the different degrees of heterogeneity of the surface of these oxide [30,31]. This is caused by terraces, steps, Kinks, Vacancies etc., having atoms with different degrees of unsaturated and with unusual oxidation states which may play an important role in catalysis.

Voorhoeve et al [32] have suggested that the catalytic activity of LaCoO₃ for CO Oxidation increases with increasing Co²⁺ content in the sample. Bhide et al. [33] have shown that in the temperature range employed in the present study LaCoO₃ contains Co²⁺ and Co⁴⁺ besides low and high spin Co³⁺ and their relative concentrations depend on the temperature.

Based on Haber et al [34]: It can be suggested that toluene activated by the abstraction of hydrogen atom is attacked by a nucleophilic O₂⁻ ion. It can further be suggested that benzaldehyde appears when O₂⁻ ion approaches the -CH₂ group from the direction perpendicular to the benzene ring. This is precisely the direction from which nucleophilic addition of a surface O₂⁻ ion of an oxide catalyst could be expected if the toluene molecule were adsorbed side on at an site of the surface through its π electron system. It can thus be concluded that oxidation of toluene to benzaldehyde at the surface of a catalyst is a nucleophilic oxidation.

Conclusion:

The most selective and active catalyst is LaCoO₃/SiO₂ catalyst at 450 °C for the partial oxidation of toluene. The selectivity and activity of catalyst is correlated to surface area value.

References:

1. H.R. Khan ,H.Frey, **J.Alloys compd**,190(2), 209(1993)
2. J.M.D.Tascon,L.Gonzalez Tejuca :**React,kinet, Catal.lett**, 15, 185 (1980)
3. G.Kremenic,J.M.Lopez Nieto,J.M.D. Tascon,L.Gonzalez tejuca: **J.chem. soc. faraday trans.**1,81,939(1985)
4. H.Faleen, M.J.Martiner-Lope, J.A.Alonso,**J.L.G.Fierro solid state Ionics-Elsevier**vol.131,issues3-4, page 237-24 (2000)
5. Yue Wu, Tao yu, Bo Sheng, Dou, Cheng-Xian Wang, Xiaofan Xie, Zuo-long yu, Shu-rong Fan, Zhi-Rong Fan, Lian Chi Wang; **J.catal**,120,88(1989)
6. B.lavasseur, S.Kalianguine-**Applied catalysis A; General Elsevier** vol.343 Issues 1-2 page 29-38 (2008)
7. G.Kremenic, J.M.L.Nieto, J.M.D.Tascon, L.G.Tejuca;**J.chem.soc.faraday Trans.**1,81,939(1985)
8. T.Hayakawa,H.orita,M.Shimizu,K.Takehira,A.G. Anderson, Nomura,Y.Ujihira;**Catal.lett**,16(4),359(1992)
9. H.Arai,T.Yamada,K.Equchi,T.Seiyama;**Appl.Catal.**26,265 (1986)

10. T.Nitadori,S.Kurihara,M.Misono;**J.catal**,(98) 221(1986)
11. Liu,Tuan Chi, Hsu Young Ming; **J.chin.inst.chem. Eng.**23(1) 67(1992)
12. S.Lars,T.Anderson;**J.chem.soc.faraday Trans.**88(1), 83 (1992)
13. K.L.Madhok;**React.kinet.catal.lett.**,30,185(1986).
14. S.Irusta,M.P.Pina,M.Menendez,J.Santa Maria; **Journal of catalysis, Elsevier** vol.179, issue 2(1998) page 400-412.
15. C.C.Alexandre, Rodrigues; **Catalysis Communication** Vol. 8 issue 8 (2007) pages 1221-1231.
16. S.Amrita Kulkarni, V.Radha Jayaram, **Journal of molecular catalysis A, Chemical Elsevier** pages 107-110 Volume 223, Issue 1-2 (2004).
17. T. Shimizu; **Appl. Catal**; 28,81 (1986).
18. J.M.D. Tascon, S.Mendiroz, L.G.Tejuca; **Z.Phys. Chem. Neue Folge**, 124, 109 (1981).
19. Scott K, Kang MP, Winnick J. **J.Electro. Chem. Soc.**, 1983; 130:523.
20. S.Bhagat, J.D.Ahuja; **Ind. J.Chem.** 9, 358 (1971).
21. M.Zawadzki, J.Trawczynski, **Catalysis today** Vol. 176 issue 1(2011) Pages 449-452.
22. O.Spalet, J.Balei, I. Paseka; **J.Chem.Soc. Faraday Trans.** 1,78,2349 (1982).
23. M.M.Dubin: **In Proc. Int. Symp. On Pre Structure and Properties of materials, Modrys (ed.) Praque**, 4, 27 (1973).
24. K.L.Madhok, K.P.Srivastava, S.Yadav: **Indian J. Technol** 21,184 (1982).
25. R. Pereniguez, J.L.Hueso, F.Gaillard, **Catalysis Letters, Springer**. 142,408-416 (2012).
26. G.Perchi, M.G.Jiliberto, E.J.Delgado, **J.Chem. Technol Biotechnology** 86 (8) 1067-73 (2011).
27. H.Hattori, K.Maruyama, K.Tanabe: **J.Catal**; 44,50 (1976).
28. M.P.Rosynek, J.S.Fox: **J.Catal**; 49,285 (1977).
29. L.Eyring : **In "Handbook of the physics and chemistry of rare earths**. Vol. 3, P.337. North Holland, Amsterdam, 1979.
30. G.A.Somorjai; **Science** 201, 489 (1978).
31. L.Wachowski, S.Zielinski, A.Burewicz; **Acta.Chim.Acad.Sci.Hung**; 106,217 (1981).
32. R.J.H. Voorhoeve, J.P.Remeika, L.E.Trimple: **Ann. N.Y.Acad.Sci.**, 272, 3(1976).
33. V.G.Bhide, D.S.Rajoria, G.R.Rao, C.N.R.Rao; **Phys.Rev.**, 86, 1021 (1972).
34. J.Haber, M.Witko, E.Broclawik: **J.Mol. Catal**; 45,183 (1980).