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Oxidation of Toluene on Supported & Unsupported LaCrO₃ Perovskite catalyst

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ABSTRACT: The heterogeneous catalytic vapour phase oxidation of toluene give benzaldehyde, benzoic acid, maleic acid and CO₂ as products over LaCrO₃ and LaCrO₃ supported on Al₂O₃ and SiO₂ as catalysts. LaCrO₃ supported on Al₂O₃ has been found to be the most active and selective catalyst giving 75.1% selectivity of benzaldehyde at 450 °C with surface area 52.0 m²/g. The overall kinetic analysis indicates that the oxidation of toluene to benzaldehyde is first order. The order of catalytic reactivity is LaCrO₃/Al₂O₃ > LaCrO₃/SiO₂ > LaCrO₃.

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

I. INTRODUCTION

Perovskite type oxides are known to be catalysts for a number of reactions such as total and partial oxidation, hydrocracking, hydrogenation, hydrogenolysis and reduction etc. Amongst the more important reactions in which these compound have been used as catalyst are oxidation of CO^[1-3], CH₄^[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. Efforts has largely been directed towards synthesis of 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 over mixed oxide has been studied but work with perovskites is scanty. In this note we report the results of a systematic study of LaCrO₃ and LaCrO₃ supported on Al₂O₃ and SiO₂ in the oxidation of toluene.

II. RELATED WORK

A comparative study on perovskite type mixed oxide catalyst A¹XA₁-XBO₃-λ (A¹=Ca, Sr, A=La, B=Mn, Fe, Co) for NH₃ oxidation was done [5]. Preparation, characterization and catalytic properties of LaMO₃ oxides was done by JMD Tascon et al. Toluene oxidation on LaCoO₃, LaFeO₃ and LaCrO₃ perovskite catalysts was done by K.L.Madhok, D.D. Agarwal and H.S. Goswami.

III. METHODOLOGY

The LaCrO₃ catalyst was prepared by amorphous precursor's citrate decomposition method^[18, 19]. Preparation method: A concentration solution of citric acid was added to concentration solution of La(NO₃)₃.6H₂O and Cr(NO₃)₃.9H₂O. The amorphous precursor was obtained by slow drying and finally heated in muffle furnace at 750°C for 10-12 hours to get LaCrO₃.

Supported LaCrO₃ on Alumina and Silica. A general method for preparing 20% LaCrO₃ on Alumina is as follows- Aqueous solution of La (NO₃)₃.6H₂O (7.25 gm), Cr (NO₃)₃.6H₂O (6.7 gm), Citric acid (3.5 gm) and Alumina (20gm)/Silica (20 gm) were mixed in a beaker and then transferred to china dish. The contents were heated at 750°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]. The surface acidity & surface basicity of perovskites catalyst were determined by n-butylamine titration^[22] and phenol adsorption method^[23] respectively. The I.R. spectra of the perovskites was recorded in KBr using Perkin-Elmer 883 spectrophotometer. The reactor assembly was set up as reported elsewhere^[24]. Toluene was taken in a bubbler. The catalyst pellets were heated for 2 hour in a tube furnace at 300 in the stream of air-toluene mixture. Activated catalyst (20 c.c.) was weighed and packed loosely in the reactor. The toluene bubbler preheater zone and furnace zone (catalyst



zone) were heated till the required temperature was achieved. The compressed air was allowed to pass through the system.

The air was bubbled through the toluene bubbler and air toluene vapours were passed over the catalyst bed. It was passed through a water condenser. The products were condensed in different containers. Carbon dioxide was estimated from strength of KOH solution. The other products Viz; benzaldehyde, benzoic acid and maleic acid were analysed using literature procedure^[25-27].

The oxidation was studied at space velocities (2998 lit hr⁻¹lit⁻¹) temperature (350°C, 400°C, 450°C, 550°C and 600°C) at air toluene ratio (121) respectively.

IV. EXPERIMENTAL RESULTS

The characterization of the catalyst was carried out using techniques Viz; I.R., Surface area, packing density, surface acidity and surface basicity. The result of these studies has been incorporated in table I and II. 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 LaCrO₃/Al₂O₃>LaCrO₃/SiO₂>LaCrO₃. The surface acidity and basicity measurements show that LaCrO₃/Al₂O₃ and LaCrO₃/SiO₂ perovskite have acidic and basic sites but unsupported LaCrO₃ have only acid sites on the surface of the catalyst. The LaCrO₃/Al₂O₃ is more basic than LaCrO₃/SiO₂.

The LaCrO₃ perovskite catalyst (Unsupported) shows absorption band at 660-590 cm⁻¹ as a sharp broad band. This band weakened and further broadened and appeared as a shoulder when IR spectra of Silica Supported catalyst was recorded. This band was observed at 1410cm⁻¹ as a sharp band when catalyst was supported on alumina. The order of packing density for catalyst is LaCrO₃/SiO₂>LaCrO₃/Al₂O₃>LaCrO₃.

Unsupported LaCrO₃ and Supported LaCrO₃ Viz. LaCrO₃/Al₂O₃ and LaCrO₃/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 LaCrO₃, LaCrO₃/SiO₂ and LaCrO₃/Al₂O₃ at 350°C, 400°C, 450°C, 550°C and 600°C are presented in Table II. The rate of formation of BzH in the beginning is higher on all catalysts. An initial increase in temperature from 350 °C to 450 °C shows an increase in the percentage conversion of BzH from 5.8% to 7.9% on unsupported LaCrO₃ (Specific surface area of LaCrO₃ increases from 8.0 m²/g to 14.0 m²/g). On LaCrO₃/SiO₂ from 8.2% to 12.6% (Specific surface area of LaCrO₃/SiO₂ increases from 7.9 m²/g to 17.1 m²/g). On LaCrO₃/Al₂O₃ from 10.4% to 15.4% (Specific surface area of LaCrO₃/Al₂O₃ increases from 31.0 m²/g to 52.0 m²/g)

Further increase in temperature from 450 °C to 600 °C decreases the percent conversion of benzaldehyde (Table II). 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 contaminants such as adsorbed gases, hydroxy species of adsorbed water^[28] and to the generation of stoichiometric or structural defects such as catalytic site^[29]. 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^[30] 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 LaCrO₃ supported on Al₂O₃ catalyst because it has more surface area value than unsupported LaCrO₃ and LaCrO₃/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^[31]. This is caused by terraces, steps, Kinks, Vacancies etc.; having atoms with different degrees of unsaturation and with unusual oxidation states which may play an important role in catalysis.

Based on Haber et al^[32]: 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.



V. TABLE

Table 1- Characteristics of LaCrO₃, LaCrO₃/ SiO₂ and LaCrO₃/Al₂O₃ Perovskite catalysts.

Catalyst	Decomposition Temperature (°C)	Packing density (g/cc)	Acid strength n-butylamine titre, meq/q		Base strength n-butylamine titre, meq/q	I.R. frequency
			PKa=6.8 (Neutral red.)	PKa=4.8 (Methyl red.)		
LaCrO ₃	750 °C	0.65	0.096	0.216	NIL	660-590, 410, 380, 330, 250
20% LaCrO ₃ / SiO ₂	750 °C	1.24	0.072	0.216	0.65	1080, 800, 780, 695, 600, 460
20% LaCrO ₃ /Al ₂ O ₃	750 °C	1.10	0.072	0.18	2.28	1410, 600

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		
LaCrO ₃	8.0	350	5.8	2.0	1.1	1.4	10.3	56.3
	10.2	400	6.2	1.4	1.9	1.1	10.6	58.4
	14.0	450	7.9	1.0	2.0	1.0	11.9	66.3
	9.6	550	7.2	3.8	2.4	1.2	14.6	49.3
	8.4	600	6.8	2.0	2.6	2.4	13.8	49.2
LaCrO ₃ /SiO ₂ (20% LaCrO ₃)	7.9	350	8.2	2.1	1.9	1.9	14.1	58.1
	10.9	400	9.6	3.2	1.7	1.7	16.2	59.2
	17.1	450	12.6	2.1	1.9	1.7	18.6	69.3
	13.1	550	10.4	3.0	2.0	1.9	17.3	60.1
	12.0	600	9.2	3.1	2.2	2.0	16.5	55.7
LaCrO ₃ /Al ₂ O ₃ (20% LaCrO ₃)	31.0	350	10.4	2.9	2.1	1.8	17.2	60.4
	45.0	400	12.4	2.4	2.1	2.0	18.9	65.6
	52.0	450	15.4	2.3	1.6	1.2	20.5	75.1
	46.0	550	12.6	3.4	2.6	1.2	19.8	63.6
	48.0	600	11.1	3.1	2.5	1.3	18.0	61.6



VI. CONCLUSION

The most selective and active catalyst is LaCrO_3 supported on Al_2O_3 catalyst at 450°C for the partial oxidation of toluene. The selectivity and activity of catalyst is correlated to surface area value.

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