Oxidation of Toluene over $LaFeO_3$/ Al_2O_3 and $LaVO_3$/ Al_2O_3 Perovskite catalysts. A comparative study.

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ABSTRACT

The vapour phase catalytic oxidation of toluene over perovskite viz. $LaFeO_3/Al_2O_3$ and $LaVO_3/Al_2O_3$ has been studied. The heterogeneous catalytic vapour phase oxidation of toluene give benzaldehyde, benzoic acid, maleic acid and CO_2 as products. $LaFeO_3/Al_2O_3$ has been found to be the most active and selective catalyst giving 80.2% selectivity of benzaldehyde at 450 ºC with surface area 53 m^2/g. The overall kinetic analysis indicates that the oxidation of toluene to benzaldehyde is first order. The order of catalytic reactivity is $LaFeO_3/Al_2O_3$> $LaVO_3/Al_2O_3$. The selectivity and activity of catalyst is correlated to surface area value.

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

1. 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], NH_3[4], Methanol[5], Olefins[6], Paraffin[7-9], Aromatic compounds[10-14] , Hydrogenation[15] and oxygenate[16].

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 $LaFeO_3/Al_2O_3$ and $LaVO_3/Al_2O_3$ in the oxidation of toluene and compare their reactivity.

2. EXPERIMENTAL

The $LaFeO_3/Al_2O_3$ and LaVO3/Al_2O_3 catalyst were prepared by amorphous precursor's citrate decomposition method [17, 18]. Preparation method:

Catalyst $LaFeO_3/Al_2O_3$: An aqueous solution of La $(NO_3)_3.6H_2O$ (2.49 gm), Fe $(NO_3)_3.9H_2O$ (2.32 gm), Citric acid (1.2 gm) and Alumina (20gm) were mixed in a beaker and then transferred to china dish. The contents were heated at 650ºC in a muffle furnace to get the desired catalyst.

Catalyst $LaVO_3/Al_2O_3$: A general method for preparing $LaVO_3$ on Alumina is as follows-Aqueous solution of $La(NO_3)_3.6H_2O$ (7.27 gm), NH_4VO_3(1.96 gm), Citric acid (3.45 gm) and Alumina (20gm) were mixed in a beaker and then transferred to china dish. The contents were heated at 600ºC in a muffle furnace to get the desired catalyst.

The surface area of catalyst was determined using ethylene glycol monoethylether (EGME) adsorption method [19,20]. The surface acidity & surface basicity of perovskites catalyst were determined by n-butylamine titration [21] and phenol adsorption method [22] 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[23] . 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[24-25] .

The oxidation was studied at space velocities (2998 lit $hr^{-1}lit^{-1}$) temperature (350ºC, 400ºC, 450ºC, 550ºC and 600ºC) at air toluene ratio (121) respectively.

3. RESULT AND DISCUSSION

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 350ºC to 600ºC (Table II) shows that surface area of the catalyst increases with increase in temperature up to 450ºC but on further increase in temperature the surface area decreases. The specific surface area for different catalyst was found to follow the order $LaFeO_3/Al_2O_3$> $LaVO_3/Al_2O_3$. The surface acidity and basicity measurements show that $LaFeO_3/Al_2O_3$ and $LaVO_3/Al_2O_3$ perovskite have acidic and basic sites. The $LaFeO_3/Al_2O_3$ is more basic than $LaVO_3/Al_2O_3$.

The order of packing density for catalyst is $LaFeO_3/Al_2O_3$> $LaVO_3/Al_2O_3$.

$LaVO_3/Al_2O_3$ and $LaFeO_3/Al_2O_3$ were subjected to toluene oxidation. The oxidation of toluene gave benzaldehyde (BzH), benzoic acid (BzA), maleic acid (MA) and CO_2 as the products.

The formation of benzaldehyde as a function of temperature and aerial activity of $LaFeO_3/Al_2O_3$ and $LaVO_3/Al_2O_3$ at 350ºC, 400ºC, 450ºC, 550ºC and 600ºC are presented in Table II. The rate of formation of BzH in the beginning is higher on both catalysts. An initial increase in temperature from 350 ºC to 450 ºC shows an increase in the percentage conversion of BzH from 7.6% to 13.0% on $LaFeO_3/Al_2O_3$ (Specific surface area of $LaFeO_3/Al_2O_3$ increases from 40.1 m^2/g to 53.0 m^2/g); On $LaVO_3/Al_2O_3$ from 6.4% to 12.1% (Specific surface area of $LaVO_3/Al_2O_3$ increases from 30.0 m^2/g to 45.6 m^2/g).

Further increase in temperature from 450 ºC to 600 ºC 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 ºC for the partial oxidation of toluene. The increase in activity up to 450 ºC can be ascribed to increasing removal of trace surface contaminants such as adsorbed gases, hydroxy species of adsorbed water [26] and to the generation of stoichiometric or structural defects such as catalytic site[27] . The decrease in activity observed above 450 ºC may be due to a decrease in surface disorder, due to the relatively high mobility of O_2^- ions in the lanthanide susquioxides [28] and resulting in the formation of low surface area at 600 ºC.

From the result it has been seen that the catalyst is highly select in the oxidation of toluene. This suggests that the lanthanum iron oxide ($LaFeO_3$) exhibit oxidative non-stoichiometry. Similar behavior has been observed in $LaFeO_3$ perovskites by Tascon et al.[29] and by Wachowski et al. [30] with $Fe^{4+}$to balance the oxygen excess in $LaFeO_{3.18}$

The selectivity and activity of catalyst is correlated to surface area values. The most selective and active catalyst is $LaFeO_3/Al_2O_3$ catalyst because it has more surface area value than $LaVO_3/Al_2O_3$ catalyst.

The difference in catalytic activity of these Perovskites heated at different temperature can also be related to the different degrees of heterogenecity 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 at [31]: It can be suggested that toluene activated by the abstraction of hydrogen atom is attacked by a nucleophilic O_2^- ion. It can further be suggested that benzaldehyde appears when O_2^- ion approaches the – CH_2 group from the direction perpendicular to the benzene ring. This is precisely the direction from which nucleophilic addition of a surface O_2^- 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.

Table 1- Characteristics of $LaFeO_3/Al_2O_3$ and $LaVO_3/Al_2O_3$ Perovskite catalysts.

Catalyst	Decomposition Temperature (ºC)	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.)	Bromo thymol blue PK_1=7.2	
$LaFeO_3/Al_2O_3$	650 ºC	1.22	0.072	0.216	2.02	1410, 560
$LaVO_3/Al_2O_3$	600 ºC	1.21	0.072	0.28	1.19	

Table 2- Activity and Selectivity data.

Catalyst	Surface area m^2/g	Reaction Temp. ºC	Conversion % to				Total Conversion	% selectivity to BzH
			BzH	BzA	MA	CO_2		
$LaFeO_3/Al_2O_3$	40.1	350	7.6	2.0	1.7	1.9	13.2	57.5
	45.1	400	8.0	2.1	1.9	2.0	14.0	57.1
	53.0	450	13.0	1.0	1.0	1.2	16.2	80.2
	49.0	550	9.2	2.9	2.1	1.8	16.0	57.5
	47.4	600	8.1	3.1	2.4	2.1	15.7	51.5
$LaVO_3/Al_2O_3$	30.0	350	6.4	3.4	2.0	1.0	12.8	50.0
	35.0	400	9.9	3.1	1.6	1.9	16.5	60.0
	45.6	450	12.1	2.3	1.2	1.0	16.6	72.8
	39.0	550	9.0	2.9	3.0	2.9	17.8	50.5
	38.2	600	6.9	2.0	1.4	3.1	14.2	48.5

4. CONCLUSION

The most selective and active catalyst is $LaFeO_3/Al_2O_3$ catalyst at 450 ºC for the partial oxidation of toluene. The selectivity and activity of catalyst is correlated to surface area value.

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