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Short Communication

OXIDATION OF TOLUENE ON UNSUPPORTED $LaVO_3$ AND SUPPORTED $LaVO_3/Al_2O_3$ PEROVSKITES

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ABSTRACT

The heterogeneous catalytic vapour phase oxidation of toluene gave benzeldehyde, benzoic acid, maleic acid and CO_2 as products over $LaVO_3$ and $LaVO_3$ supported on Al_2O_3 as catalysts. The $LaVO_3/Al_2O_3$ has been found to be the most active and selective catalyst giving 72.8% selectivity for benzaldehyde at 450°C with surface area $45.6m^2/g$. The kinetic analysis indicates that the oxidation is first order. The order of catalytic reactivity is $LaVO_3/Al_2O_3 > LaVO_3$. The activation energy (Ea) values for $LaVO_3/Al_2O_3$ and $LaVO_3$ are 16.44 KJ/mole and 26.14 KJ/mole respectively.

Keywords: Oxidation; Activation energy, Toluene, Catalysis.

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 [1-4], CH_4 [5], NH_3 [6], Methanol [7], Olefins [8], Paraffin [9-11], Aromatic compounds [12-16], Hydrogenation [17] and oxygenate [18]. 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 literature survey reveal the oxidation of aromatic and aliphatic hydrocarbon over $LaMO_3$ (M=Al, Ni, Mn, Co, Fe, Cr etc.) Perovskites have been studied but work with $LaVO_3$ and $LaVO_3/Al_2O_3$ are very scanty. It was thought interesting to screen the catalytic activity of unsupported and supported $LaVO_3$ using Al_2O_3 as supports. Toluene oxidation has been carried out and results of $LaVO_3$ and $LaVO_3/Al_2O_3$ oxidation have been presented.

2. MATERIAL AND METHODS

The catalyst of $LaVO_3$ and $LaVO_3$ supported on Al_2O_3 were prepared by the citrate decomposition method [19, 20]. The surface area of catalyst was determined using ethylene glycol monoethyl ether (EGME) adsorption method [21, 22] at different temperatures. The surface acidity and surface basicity of perovskites catalyst were determined by n-butylamine titration [23] and phenol adsorption method [24] 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 [25-28]. The IR spectra of the perovskites were recorded in KBr using Perkin-Elmer 883 spectrophotometer.

3. RESULTS AND DISCUSSION

The catalyst was characterized using techniques *viz*; IR, surface area, packing density, surface acidity and surface basicity. The results of these studies have been incorporated in table 1 and 2.

The surface area measurements in the temperature range 350°C to 600°C (table 2) show that surface area of the catalyst increases with increase in temperature up to 450°C but on further increase, the surface area decreases. The specific surface area for different catalysts was found to follow the order $LaVO_3/Al_2O_3 > LaVO_3$. The surface acidity and basicity measurements show that $LaVO_3/Al_2O_3$ perovskite have both acid and basic sites but unsupported $LaVO_3$ have only acid sites on the surface of the catalyst. The order of packing density for catalyst is $LaVO_3/Al_2O_3 > LaVO_3$.

Unsupported and supported $LaVO_3$ were tested for toluene oxidation. The oxidation of toluene gave Benzaldehyde (BzH), Benzoic acid (BzA), Maleic acid (MA) and CO_2 as the products.

The kinetics of the reaction was studied by studying the effect of contact time, W/F (Where W is the mass of catalyst and F is the flow rate) on the overall conversion of toluene. The value of log (1/1-x) were calculated and ploted against contact time. The straight line plots (fig. 1) indicate that the oxidation of toluene follows a first order kinetics. The rate constants calculated from the slope (slope=K/2.303) of these plots (fig. 1) are presented in table 3. The rate parameters determined from Arrhenius plot (fig. 2) are the values of activation energy (Ea) =26.14 KJ/mole; Pre-exponential factor - log 0.29 for $LaVO_3$ and Ea=16.44 KJ/mole and pre-exponential factor -log 0.27 for $LaVO_3/Al_2O_3$ respectively.

Table 1: Characteristics of $LaVO_3$ and $LaVO_3/Al_2O_3$ perovskite catalysts

Catalyst	Decom-position (°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.)	Bromothymol blue PK_1=7.2	
$LaVO_3$	600	0.92	0.98	0.224	Nil	780-850, 420, 390, 360
$LaVO_3/Al_2O_3$	600	1.21	0.072	0.28	1.19	

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		
$LaVO_3$	2.7	350	4.2	2.0	2.6	1.9	10.7	39.2
	3.4	400	6.2	2.2	1.4	1.0	10.8	57.4
	9.0	450	7.6	1.6	2.0	1.3	12.5	60.8
	6.4	550	7.0	2.6	2.1	3.2	14.9	46.9
	4.5	600	5.7	2.4	3.0	3.6	14.7	38.7
$LaVO_3/Al_2O_3$	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

Table 3: Rate parameter from the slopes of the first order plots

Temperature (Kelvin)	623	673	723	823	873
Rate constant (K) $LaVO_3$	0.1043	0.1171	0.1638	0.2677	0.2821
Rate constant (K) $LaVO_3/Al_2O_3$	0.1403	0.2343	0.2568	0.3481	0.2648
	log A	Activation energy of reaction (Ea) (KJ/mole)			
LaVO3	-0.29	26.14			
$LaVO_3/Al_2O_3$	-0.27	16.44			

The formation of benzaldehyde as a function of temperature and aerial activity of $LaVO_3$ and $LaVO_3/Al_2O_3$ at 350°C, 400°C, 450°C, 550°C and 600°C is given in the table 2. An initial increase in temperature from 350°C to 450°C shows in an increase in the percentage conversion of BzH from 4.2 to 7.6 on unsupported $LaVO_3$ (specific surface area of $LaVO_3$ increases from 2.7 to 9.0 m^2/g) and on $LaVO_3/Al_2O_3$; 6.4 to 12.1% (specific surface area of $LaVO_3/Al_2O_3$ increase from 30.0 m^2/g to 45.6 m^2/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 contaminants such as adsorbed gases, hydroxy species of adsorbed water [28-29] and to the generation of stoichiometric or structural defects such as anion vacancies or disorders and exposed metal ions, which serves as catalytic sites [30]. The decrease in activity observed above 450°C may be due to a decrease in surface disorder due to the relatively high mobility of O^{2-} ions in the lanthanide sesquioxides [31] and resulting in the formation of low surface area at 600°C

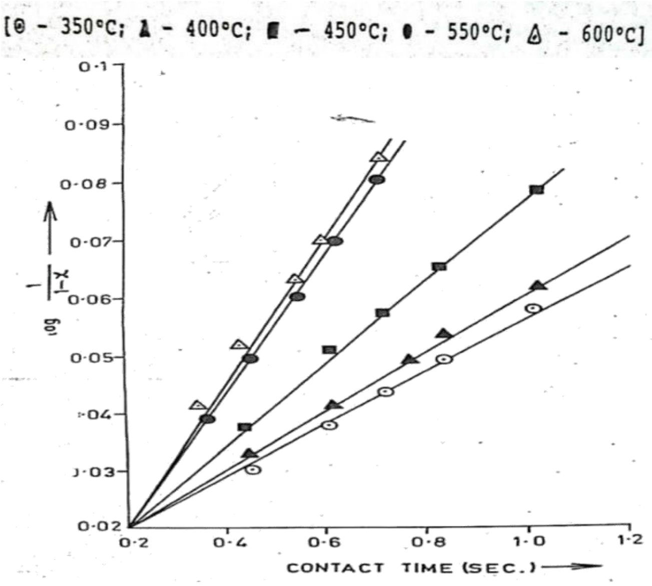

Fig. 1: First order plots for the oxidation of toluene on $LaVO_3$

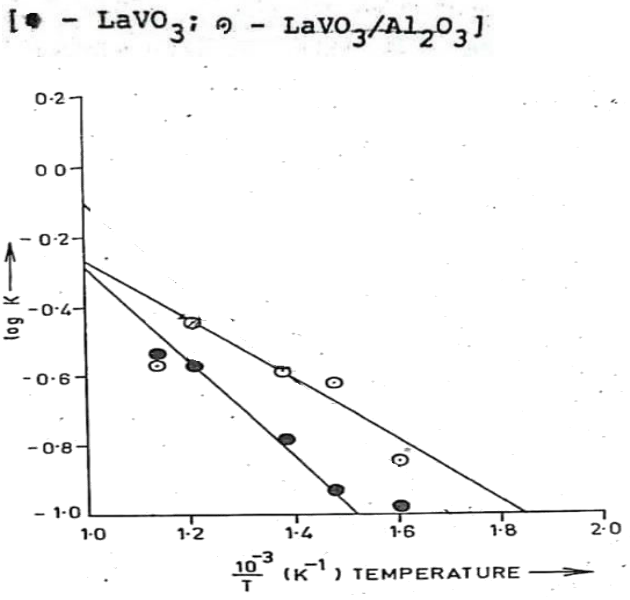

Fig. 2: Arrhenius plots for the oxidation of toluene

The difference in catalytic activity of these perovskites heated at different temperature can also be related to the different degrees of heterogenecity on the surface of these oxides [32, 33]. 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. The activation energy (Ea) (table 3) for toluene oxidation was found to follow the order $LaVO_3 > LaVO_3/Al_2O_3$. Thus the activity and selectivity of catalysts is co-related to surface area values and activation energy values.

The most active and selective catalyst is found to be $LaVO_3$ supported on Al_2O_3 as it has more surface area and less activation energy than $LaVO_3$.

As for the mechanism of toluene oxidation using $LaVO_3$ is concerned a mechanism similar to that proposed by Haber et al [34] can be suggested.

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