Toluene Oxidation on $LaVO_3$ Perovskite Catalyst

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Abstract: ***The heterogeneous catalytic vapour phase oxidation of toluene gave benzaldehyde, benzoic acid, maleic acid and CO_2 as products over $LaVO_3$ catalyst. The $LaVO_3$ has been found to be the active and selective catalyst giving 60.8 selectivity for benzaldehyde at 450ºC with surface area 9.0 m^2/g. The Kinetic analysis indicates that the oxidation is first order. The activation energy (Ea) value for $LaVO_3$ is 26.14 KJ/mole.***

Keywords: Oxidation; Activation energy, Toluene, catalysis

1. Introduction

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

2. Literature Survey

A comparative study on Perovskite type mixed oxide catalysts $A^1XA1\text{-}XBO_3\text{-}\lambda(A^1$=Ca, Sr A=La, B=Mn, Fe, Co) for NH_3 oxidation was done[6]. Preparation characterization and catalytic properties of $LaMO_3$ oxides was done by JMD Tascon et al.

Toluene oxidation on $LaCoO_3$, $LaFeO_3$ and $LaCrO_3$ perovskite catalysts was done by D.D. Agrawal and H.S. Goswami. Oxidation of toluene on lanthanum cobaltite perovskite ($LaCoO_3$) was done by KL Madhok.

3. Methodology

The catalyst of $LaVO_3$ prepared by the citrate decomposition method [19, 20]. The surface area of catalyst was determined using ethylene glycol monoethylether (EGME) adsorption method [21, 22] at different temperature. 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 product such as Benzaldehydes, Benzoic acid, Maleic acid and Carbon dioxide were the same as described else were [25-28]. The I.R. spectra of the Perovskites was recorded in KBr using Perkin-Elmer 883 spectraphotometer.

4. Results and Discussion

The catalysts were characterized using techniques Viz; I.R., Surface area, packing density, surface acidity and surface basicity. The result of these studies has been incorporated in table 1 and 2. In $LaVO_3$ the peak at 1020cm^{-1} which has been assign to (V-O-V) band in the I.R. spectra of V_2O_5 was absent. A very strong and broad Band in 820-850 cm^{-1} region suggest the presence of stretching mode of the longer vanadium-oxygen bonds. This shows that vanadium is not present as Vanadium penta oxide and the spectral Pattern suggest the formation of $LaVO_3$.

The surface area measurements in the temperature range 350ºC to 600ºC (Table 2) shows that surface area of the catalyst increases with increase in temperature up to 450ºC but on further increase the surface area decreases. The surface acidity and basicity measures show that $LaVO_3$ have only acid sites on the surface of the catalyst.

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

Table 1: Characteristics of $LaVO_3$ perovskite catalysts

Catalyst	Decomposition (ºC)	Packing density (g/cc)	Acid strength n-butylamine titre, meq/q		Base strength nbutyla-mine titre, meq/q	I.R. frequ-ency
			PKa=6.8 (Natural red.)	PKa=4.8 (Methyl red.)	Bromo thymol blue PK_1=7.2	
$LaVO_3$	600	0.92	0.98	0.224	NIL	780-850, 420, 390, 360

The kinetics of the reaction was studied by studying the effect of contact time, W/F (where W is the mass of catalysts and F is the flow rate) on the overall conversion of toluene. The value of log (1/1-x) were calculated and plotted 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 plot (Fig.1) are presented in table 3. The rate parameters, determined from Arrhenius plot (Fig. 2) are the value of activation energy (Ea) = 26.14 KJ/mole; pre-exponential factor- log 0.29 for $LaVO_3$.

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

The formation of benzaldehyde as a function of temperature and aerial activity of $LaVO_3$ at 350ºC, 400ºC, 450ºC, 550ºC and 600ºC is given in the table 2. An initial increase in temperature from 350ºC to 450ºC shows an increase in the percentage conversion of BzH from 4.2 to 7.6 on $LaVO_3$ (specific surface area of $LaVO_3$ increases from 2.7 to 9.0m^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 contaminant 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 ºC may be due to a decrease in surface disorder due to the relatively high mobility of O^{2-} ions in the lanthanide susquioxides [31] and resulting in the formation of low surface area at 600 ºC

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
	log A	Activation energy of reaction (Ea) (KJ/mole)			
$LaVO_3$	-0.29	26.14			

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 oxide [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 26.14 KJ/mole. Thus the activity and selectivity of catalyst is co-related to surface area values and activation energy values.
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.

Legends to Figures

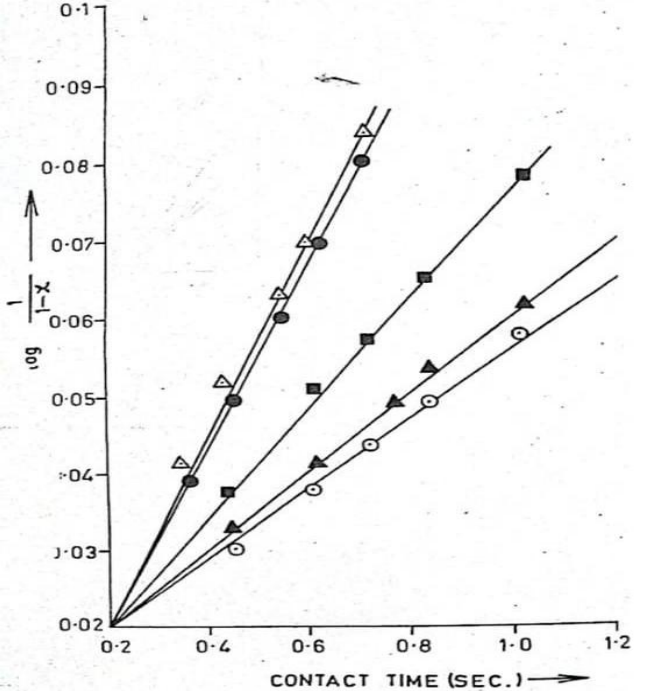

Figure 1: First order plots for the oxidation of toluene on $LaVO_3$

[⊙ – 350°C; ▲– 400°C; ■– 450°C; ●– 550°C; △– 600°C]

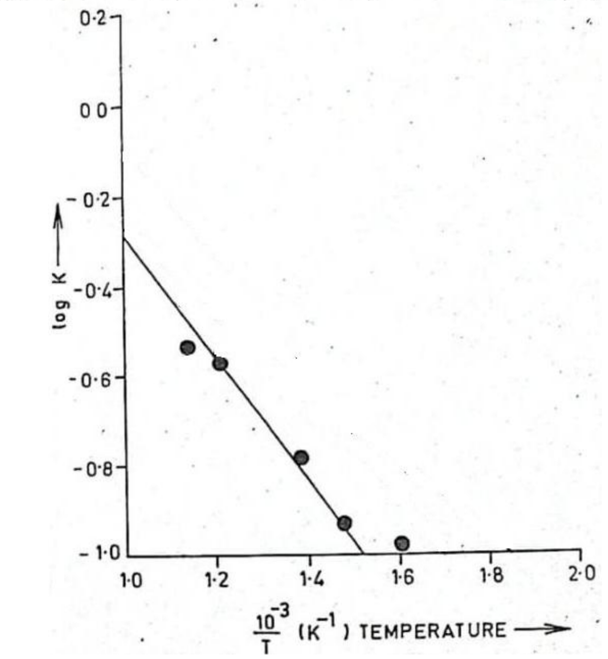

Figure 2: Arrhenius plots for the oxidation of toluene
- $LaVO_3$

5. Conclusion

1) A very strong and broad band in 820-850 cm^{-1} region suggest presence of stretching mode of the longer Vanadium oxygen bonds. This shows that Vanadium is not present as Vanadium pentaoxide and spectral pattern suggest the formation of $LaVO_3$.
2) $LaVO_3$ have only acid sites on the surface of the catalyst.
3) Oxidation of toluene follows the first order kinetics.
4) Activity & Selectivity of catalyst is co-related to surface area values and activation energy values.

6. Further Scope

The Perovskite materials can be used not only as light absorbing layer but also an election/Hole transport layer due to the advantages of its high extinction coefficient, high charge mobility, long carrier life time and long carrier diffusion distance.

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