Oxidation of Toluene over $LaVO_3$, $LaVO_3/SiO_2$ and $LaVO_3/Al_2O_3$ Perovskite Catalysts. A Comparative Study

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1. ABSTRACT:

The heterogeneous catalytic vapour phase oxidation of toluene gave benzeldehyde, benzoic acid, Maleic acid and CO_2 as products over $LaVO_3$, $LaVO_3$/ SiO_2 and $LaVO_3$ /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 ºC with surface area 45.6 m^2/g . The kinetic analysis indicates that the oxidation is first order. The order of catalytic reactivity is $LaVO_3/Al_2O_3$> $LaVO_3/SiO_2$> $LaVO_3$.

Keyword: Oxidation, Toluene, Catalysts, Surface area and Benzaldehyde.

2. INTRODUCTION

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 that 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 $LaVO_3/Al_2O_3$, $LaVO_3/SiO_2$ and $LaVO_3$ are very scanty. It was thought interesting to screen the catalytic activity of unsupported and supported $LaVO_3$ using SiO_2 and Al_2O_3 as supports. Perovskite type oxides are known to be catalysts for a number of reactions such as total and partial oxidation, hydrocracking, hydrogeneous, hydrogenolysis and reduction etc. Amongst the more important reactions in which these compound have been used as catalyst are oxidation of CO[1-4], CH4[5], NH3[6], Methanol[7], Olefins[8], Paraffin[9-11], Aromatic compounds[12-16], Hydrogenation[17] and oxygenate[18]. Toluene oxidation has been carried out and results of $LaVO_3$, $LaVO_3$/ SiO_2 and $LaVO_3/Al_2O_3$ oxidation have been presented.

3. EXPERIMENTAL

The catalyst of $LaVO_3$, $LaVO_3$/ SiO_2 and $LaVO_3/Al_2O_3$ were prepared by the citrate decomposition method [19,20] . The surface area of catalyst was determined using ethylene glycol monoethyle ether (EGME) adsorption method [21,22] at different temperature. The surface acidity & 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 I.R. spectra of the perovskites was recorded in KBr using Perkin-Elmer 883 spectrophotometer.

4. RELATED WORK

A comparative study on Perovskites type mixed oxide catalyst A'xA^1-XBO_3-λ(A'=Ca,Sr A=La, B=Mn, Fe, Co) for NH_3 oxidation was done[6]. Preparation characterization and catalysis properties of $LaMO_3$ oxide was done by JMD Tascom et al. Toluene oxidation on $LaCoO_3$, $LaFeO_3$ and $LaCrO_3$ Perovskite Catalysts was done by K.L.Madhok, D.D. Agarwal and H.S.Goswami.

5. RESULTS AND DISCUSSION

The catalyst were characterized using techniques Viz; I.R., Surface area, Packing density, Surface acidity and surface basicity. The result of these studies have been incorporated in Table 1 and 2.

The surface area measurements in the temperature range 350ºC to 600ºC (Table 2) show that surface area of the catalyst increases with increase in temperature up to 450ºC but on further increase the surface area decreases. The specific surface area for different catalysts was found to follow the order $LaVO_3/Al_2O_3$ >LaVO3/ SiO2 >$LaVO_3$. The surface acidity and basicity measurements show that $LaVO_3/Al_2O_3$ and $LaVO_3/SiO_2$ perovskites have both acid and basic sites but unsupported $LaVO_3$ have only acid sites on the surface of the catalyst. The $LaVO_3/Al_2O_3$ is more basic than LaVO3/ SiO_2. The order of packing density for catalyst is $LaVO_3$/ SiO2> $LaVO_3/Al_2O_3$ >LaVO3.

$LaVO_3$, $LaVO_3/Al_2O_3$ and $LaVO_3$/ SiO2 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 $LaVO_3$ and $LaVO_3$/ SiO_2 perovskite catalysts.

Catalyst	Decomposition (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.)	Bromothymol blue PK1=7.2	
$LaVO_3$	600	0.92	0.98	0.224	Nil	780-850, 420, 390, 360
$LaVO_3$/ SiO_2	600	1.34	0.016	0.211	0.63	
$LaVO_3/Al_2O_3$	600	1.21	0.072	0.28	1.19	

Table 2- Activity and Selectivity data.

Catalyst	Surface area m2/g	Reaction Temp. ºC	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
$LaVO_3$/ 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
	10.2	600	6.5	4.0	4.0	2.9	17.4	37.3
$LaVO_3/Al_2O_3$	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

The formation of benzaldehyde as a function of temperature and aerial activity of $LaVO_3$, LaVO3/ SiO_2 and $LaVO_3/Al_2O_3$ at 350ºC, 400ºC, 450ºC, 550ºC and 600ºC is given in 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 unsupported $LaVO_3$ (Specific surface area of $LaVO_3$ increases from 2.7 to 9.0 m2/g), on $LaVO_3/SiO_2$: 6.42 to 11.2 % (Specific surface area of $LaVO_3/SiO_2$ increase from 10.2 to 16.4 m^2/g) and $LaVO_3/Al_2O_3$: 6.42 to 12.1 % (Specific surface area of $LaVO_3/Al_2O_3$ increase from 30.0 to 45.6 m^2/g)

Further increase in temperature from 450ºC to 600ºC decreases the percentage conversion of benzaldehyde (Table 2). Thus in the present investigation the catalyst have been found to be active as well as selective at 450 for the partial oxidation of toluene. The increase in activity upto 450 can be ascribed in 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 decreases in activity observed above 450ºC 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 600ºC

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 activity and selectivity of the catalyst is correlated to surface area values. The most active and selective catalyst is found to be $LaVO_3/Al_2O_3$ catalyst. It has more surface area than others.

As for the mechanism of toluene oxidation using $LaVO_3$, LaVO3/ SiO_2 and $LaVO_3/Al_2O_3$ are concerned a mechanism similar to that proposed by Haber et al [34] can be suggested.

6. CONCLUSION

The most selective and active catalyst is $LaVO_3/Al2O_3$ catalyst at 450ºC for the partial oxidations of toluene. The selectivity and activity of the catalyst is correlated to surface area value.

7. REFERENCE

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