TOLUENE OXIDATION USING $LaCoO_3/Sio_2$ AND $LaVO_3/SiO_2$ PEROVSKITE CATALYSTS: A COMPARATIVE STUDY

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Abstract:

This study examines the vapour phase catalytic oxidation of toluene over perovskites, namely $LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$. The catalyst was characterized using the Viz method. The surface area Packing density. Surface area measurements at temperatures ranging from 350°C to 600°C. At 450°C, both surface area and activity were at their peak. Toluene undergoes heterogeneous catalytic vapour phase oxidation, producing benzaldehyde, benzoic acid, maleic acid, and Co_2 using catalysts $LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$. $LaCoO_3$ supported on SiO_2 was determined to be the most active and selective catalyst, achieving 79.4% selectivity for benzaldehyde at 450^0C with a surface area of 61.1 m_2/g. The kinetic study shows that the oxidation of toluene to benzaldehyde is first order. The catalytic reactivity is $LaCoO_3/SiO_2 > LaVO_3/SiO_2$. Surface area values correspond with catalytic selectivity and activity.

Keywords: Benzaldehyde, Oxidation, Toluene, Supported, Surface area, Catalysis

Introduction:

Perovskites oxides operate as catalysts in several processes, including partial oxidation, hydrocracking, hydrogenation, hydrogenolysis, and reduction. These compounds have been utilized as catalysts for a variety of processes, including the oxidation of CO, NH_3, Methanol, Olefins, Paraffin, Aromatic compounds, Hydrogenation, and Oxidation. The oxidation of light paraffins, such as methane, propane, and n-butane, is often used to evaluate perovskites oxides. The focus has been on synthesizing unsupported and supported perovskites oxides with moderate or high specific surface area, as well as understanding their bulk and surface characteristics and involvement in heterogeneous catalysis. Toluene vapour phase oxidation is a significant industrial process. The partial oxidation of toluene on mixed oxide has been investigated, although research using Perovskites is limited. It was believed intriguing to evaluate the catalytic activity of $LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$.

Materials and methods:

The $LaCoO_3/SiO_2$ catalyst was produced using the oxalate decomposition technique.

Preparation Method:

$LaCoO_3/SiO_2$ was produced. The typical approach for preparing 20% $LaCoO_3$ on Silica is as follows: An aqueous solution of $La(NO_3)3.6H_2O$ (7.2gm), $Co(NO_3)2.6H_2O$ (4.73gm), concentrated oxalic acid, and silica (20gm) was combined in a beaker and transferred to a china dish. To get the necessary catalyst, the components were heated in a muffle furnace to 1000^0C. The catalyst $LaVO_3/SiO_2$ was created using amorphous precursor citrate breakdown.

Preparing $LaVO_3$ on SiO_2 involves the following steps: An aqueous solution of La $(NO_3)3.6H_2O$ (7.27 gm), NH_4VO_3 (1.96 gm), Citric acid (3.45 gm), and Silica (20gm) was combined in a beaker and transferred to a china dish. The resulting mixture was heated in a sand bath for 10 to 12 hours. After obtaining the catalyst powder, it was heated in a muffle furnace at 600°C to produce the necessary catalyst.

The catalyst's surface area was measured using the EGME adsorption technique at various temperatures. Surface acidity and basicity of perovskites catalysts were evaluated using n-butylamine titration and phenol adsorption respectively. The experimental setup and procedures for analyzing compounds such as benzaldehyde, benzoic acid, maleic acid, and carbon dioxide were the same as previously reported.

Table 1- Characteristics of $LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$ Perovskite catalysts

Catalyst	Decomposition Temperature (°C)	Packing density (g/cc)	Acid strength n-butylamine titre, meq/q		Base strength n-butylamine titre, meq/q
			PKa=6.8 (Neutral red.)	PKa=4.8 (Methyl red.)	Bromo thymol blue PK_1=7.2
$LaCoO_3/SiO_2$	1000 °C	1.11	0.091	0.241	2.9
$LaVO_3/SiO_2$	600 °C	1.34	0.016	0.211	0.63

Table 2- Activity and Selectivity data.

Catalyst	Surface area m2/g	Reaction Temp. °C	Conversion % to				Total Conversion	% selectivity to BzH
			BzH	BzA	MA	CO_2		
$LaCoO_3/SiO_2$	50.1	350	9.0	2.6	1.9	2.4	15.9	56.6
	54.2	400	10.6	2.4	1.9	2.0	16.9	62.7
	61.1	450	15.1	1.0	1.8	1.1	19.0	79.4
	56.4	550	9.8	2.1	1.7	3.2	16.8	58.3
	59.0	600	9.0	2.9	2.0	2.6	16.5	54.5
$LaVO_3/SiO_2$	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
	10.4	600	6.5	4.0	4.0	2.9	17.4	37.3

Oxidation was tested at various temperatures and air-toluene ratios.

Results and Discussion

The catalyst was characterized using several methodologies, including surface area, packing density, surface acidity, and surface basicity. Tables 1 and 2 provide the results of these research. Surface area measurements at temperatures ranging from 350°C to 600°C (Table II) reveal that the catalyst's surface area rises up to 450°C, but declines beyond that. The specific surface area of several catalysts was found to be in the sequence $LaCoO_3/SiO_2 > LaVO_3/SiO_2$.

Surface acidity and basicity measurements indicate that $LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$ include both acidic and basic sites. $LaCO_3/SiO_2$ is more basic than $LaVO_3/SiO_2$. The packing density for catalysts is $LaVO_3/SiO_2>LaCoO_3/SiO_2$.

$LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$ were reacted with toluene. Toluene was oxidized to produce benzaldehyde (BzH), benzoic acid (BzA), maleic acid (MA), and Co_2.

Table 2 shows the generation of benzaldehyde at various temperatures and aerial activity levels for $LaCoO_3/SiO_2$ and $LaVO_3/SiO_2$ at 350°C, 400°C, 450°C, 550°C, and 600°C. Both catalysts have a greater initial rate of BzH formation. Increasing the temperature from 350°C to 450°C enhances BzH conversion from 56.6% to 79.4% on $LaCoO_3/SiO_2$. The specific surface area of $LaCoO_3/SiO_2$ rises from 50.1 m_2/g to 61.1 m_2/g. $LaVO_3/SiO_2$ increased from 51.6% to 67.4%, with a specific surface area of 10.2 m_2/g to 16.4 m_2/g.

Increasing the temperature from 450°C to 600°C reduces the % conversion of benzaldehyde (Table 2). The catalyst demonstrated activity and selectivity for partial oxidation of toluene at 450°C in this study. The increase in activity up to 450°C can be attributed to the removal of trace surface contaminants like adsorbed gases and hydroxy water. Additionally, stoichiometric or structural defects like anion vacancies and exposed metal ions serve as catalytic sites. The drop-in activity reported at 450°C may be owing to a decrease in surface disorder caused by the strong mobility of O_2 ions in lanthanide sesquioxides, resulting in decreased surface area above 600°C.

The results show that the catalyst is very selective in the oxidation of toluene. Surface area correlates with catalytic selectivity and activity. $LaCoO_3/SiO_2$ catalyst is more selective and active due to its larger surface area compared to $LaVO_3/SiO_2$.

Perovskites' catalytic activity varies with temperature due to surface heterogeneity. Terraces, steps, kinks, and vacancies may lead to atoms with varying degrees of unsaturation and unique oxidation states, potentially impacting catalysis.

According to Voorhoeve, raising the Co^{+2} level in a sample enhances the catalytic activity of $LaCoO_3$ for CO oxidation. According to Bhide, the relative concentrations of Co^{2+}, Co^{4+}, and low and high spin Co^{3+} in $LaCoO_3$ vary with temperature.

According to Haber, the removal of hydrogen atoms activates toluene, which is then attacked by a nucleophilic O_2-ion. Benzaldehyde may form when an O_2 ion approaches the $-CH_2$ group perpendicular to the benzene ring. Nucleophilic addition of a surface O_2-ion of an oxide catalyst is predicted if the toluene molecule adsorbed side on at a surface site via its π electron system. The oxidation of toluene to benzaldehyde on a catalyst surface is nucleophilic.

Conclusion

At 450°C, the $LaCoO_3/SiO_2$ catalyst is the most selective and active for partial oxidation of toluene. Surface area values correspond with catalyst selectivity and activity.

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