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Oxidation of Toluene by Ozone over Surface-Modified γ-Al₂O₃: Effect of Ag Addition

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Abstract: In this study, the ability of ozone to oxidise toluene present in low levels into CO and CO₂ was studied. The catalytic ozonation of toluene was carried out in a micro-fixed bed reactor. The oxidation was done in two steps: toluene adsorption on the catalyst followed by sequential ozone desorption. Toluene breakdown by ozone at low temperature and atmospheric pressure was achieved using γ-Al₂O₃ supported transition metal oxides impregnated with a reduced noble metal. The catalyst Ag–CoOₓ/γ-Al₂O₃ efficiently oxidised and transformed toluene into products (52.4% COₓ yield). This catalyst has a high surface area, more acidic sites, and lattice oxygens for better toluene oxidation. The addition of Ag to the CoOₓ/γ-Al₂O₃ catalyst surface improved toluene adsorption on the catalyst surface, resulting in improved product yield, selectivity, and carbon balance.

Keywords: VOC; transition metal oxides; catalytic ozonation

1. Introduction

The volatile organic compounds from paints, furnishings and sprays are the leading causes of indoor air pollutants. Industrial and vehicular exhausts and other human activities lead to outdoor air pollution [1]. Nowadays, people spend a long time indoors for work and family. Hence, indoor air purification technologies are gaining importance [2]. Several methods, such as sorption techniques [3], biofiltration [4], photocatalytic oxidation [5] and non-thermal plasma [6–8], are used to remove indoor air pollutants [9–11]. Thermal incineration is helpful in many applications, but heterogeneous catalysis can improve efficiency [12,13]. Catalytic oxidation drastically reduces the reaction temperature of VOCs from ~1000 °C in thermal oxidation to around ~250 °C [14].

Catalytic oxidation technology is generally used for industrial applications due to its wide adaptability to a significant number of VOCs. Liu and co-workers obtained a conversion of ~94% benzene using birnessite-type MnO₂ synthesised via the green synthesis method [15]. The ability of MnOₓ/TiO₂ composite nanofibers for the complete oxidation of acetone was demonstrated by Zhu et al. [16]. A few groups, such as Shi et al. [17] and Wang et al. [18], have studied the role of different morphologies of MnOₓ in the catalytic combustion of toluene. Catalytic oxidation is highly exothermic and works for high input VOC concentrations. However, when the reactant concentration is low, it is not economical to carry out these reactions. Combining catalytic oxidation technology with proper combustion technology will reduce the reaction temperature and completely degrade VOCs [14]. In this regard, catalytic oxidation using ozone is an alternative and effective method to destroy VOCs. There are numerous studies on the oxidation of various VOCs with ozone. Zhao et al. studied the effect of water vapour on catalytic ozonation of formaldehyde over MnOₓ. They demonstrated that humid air reduces the accumulation of...
carbonate species over the catalyst [19]. Lin and co-workers studied the degradation of mixed Cl-VOCs by catalytic ozonation over MnOx impregnated on different supports [20].

Many studies have also focused on using either noble metals or transition metal oxides unsupported or supported on materials with a high specific surface area such as Al2O3, TiO2, SiO2, etc. Tian and co-workers studied the degradation of gaseous methanol at normal temperature using Pt/FeOx [21]. He et al. used wet scrubbing along with catalytic ozonation for the first time to eliminate CH3SH using Ag/MnO2 [22]. Though noble metals are efficient for VOC degradation, their high cost limits their usage. Transition metal oxides such as Cu, Fe, Co, Mn, and Ni have been widely studied for VOC degradation under ozone flow. Furthermore, the type of material used as support plays a crucial part in aiding the catalyst activity. Al2O3 is the most used support material for its large surface area, moderate chemical activity, and low cost [23,24]. Hence, modifying the support system with different metal oxides (mono or bimetallic) may greatly enrich the catalytic activity. Even though numerous studies have focused on the role of Mn oxides in VOC degradation, there are few reports on Co-based oxides.

The current work looks at transition metal-based heterogeneous catalysts (γ-Al2O3 supported Mn, Co, and Ag catalysts) in the ozone-assisted toluene degradation process. Furthermore, the oxidation products, CO and CO2, are quantified, and the limitations of catalytic ozonation of toluene are analysed. The plausible reasons for the improved activity of the catalytic systems are evaluated.

2. Results and Discussion
2.1. XRD

Figure 1 depicts the synthesised catalysts’ X-ray diffraction (XRD) patterns. All the catalysts display three major diffraction peaks at 2θ = 37.5°, 46.2° and 66.8°, corresponding to (311), (400) and (440) planes of crystalline γ-Al2O3 (Joint Committee on Powder Diffraction Standards (JCPDS)-290063), respectively. Peaks with 2θ at 37.3°, 42.9° and 56.9° corresponding to (110), (101), and (102) planes, respectively, can be assigned to MnO2 in MnOx/γ-Al2O3 and Ag–MnOx/γ-Al2O3 (JCPDS 72-1982). Low intense peaks observed at 2θ = 36.8° and 65.2° (merged with γ-Al2O3 peak) match the (311) and (440) planes of Co3O4 in CoOx/γ-Al2O3 and Ag–CoOx/γ-Al2O3 (JCPDS 78-1970), suggesting that Co is highly dispersed on the support. XRD patterns of Ag in Ag/γ-Al2O3, Ag–MnOx/γ-Al2O3 and Ag–CoOx/γ-Al2O3 were not distinct amid the other metal oxide peaks, possibly due to the high distribution of Ag particles on the support.

![Figure 1. XRD patterns of the bare and metal oxide modified γ-Al2O3; * γ-Al2O3, # MnOx, * CoOx.](image-url)
2.2. Physisorption

Brunauer-Emmett-Teller (BET) surface area, average pore diameter and total pore volume of the synthesised catalysts are summarised in Table 1. The induction of Mn and Co on $\gamma$-Al₂O₃ leads to blocked pore diameter, and consequently, the BET surface area is less than bare $\gamma$-Al₂O₃. The introduction of silver on $\gamma$-Al₂O₃ and the other two catalysts ($\text{MnO}_x/\gamma$-Al₂O₃ and $\text{CoO}_x/\gamma$-Al₂O₃) positively increased the surface area. Figure 2a and b show the N₂ adsorption and desorption isotherms and the pore size distribution curves of the fresh catalysts. All catalysts exhibited Type-V isotherm with H3 type hysteresis loop in the range of 0.4 to 0.95 $P/P_0$, indicating the catalysts’ mesoporous nature.

Table 1. Physio-chemical properties of the catalysts.

| Catalysts          | Surface Area (m²/g) | Total Pore Volume (cc/g) | Average Pore Diameter (nm) | $O_{\text{lat}}/O_{\text{surf}}$ |
|--------------------|---------------------|--------------------------|---------------------------|---------------------------------|
| $\gamma$-Al₂O₃     | 293                 | 0.83                     | 11.36                     | 0.85                            |
| $\text{MnO}_x/\gamma$-Al₂O₃ | 256             | 0.7                      | 10.94                     | 0                               |
| $\text{CoO}_x/\gamma$-Al₂O₃ | 253             | 0.72                     | 11.34                     | 0                               |
| Ag/$\gamma$-Al₂O₃  | 272                 | 0.78                     | 11.44                     | 0                               |
| Ag–MnOₓ/$\gamma$-Al₂O₃ | 265             | 0.77                     | 11.62                     | 0.80                            |
| Ag–CoOₓ/$\gamma$-Al₂O₃ | 267             | 0.76                     | 11.35                     | 1.1                             |

Figure 2. (a) N₂ adsorption-desorption isotherms. (b) Pore size distribution of fresh catalysts.

2.3. CO₂ TPD Analysis and NH₃ TPD Analysis

CO₂ TPD (Temperature programmed desorption) was conducted to account for the basic sites in the catalysts. Figure 3a depicts the corresponding TPD profiles of the as-synthesised catalysts. Except for $\gamma$-alumina, all other catalysts showed three desorption peaks in the temperature range of 110–300 °C, 350–475 °C and 500–700 °C, related to weak, moderate, and strong basic sites, respectively. From Table 2, $\text{MnO}_x/\gamma$-Al₂O₃ and $\gamma$-Al₂O₃ had similar basic strengths. The addition of Ag reduced the number of basic sites. For evaluating acidic sites in the catalysts, NH₃ TPD was done, and the TPD profiles of the catalysts are presented in Figure 3b. Broad peaks were observed for all the catalysts in the temperature range of 110–450 °C, while a comparatively sharp peak was observed in the higher temperature range of 500–750 °C, suggesting the presence of strong acidic sites in this region. The overall concentration of acidic sites increased with Ag addition to Mn and Co catalysts. This could be due to the acidic sites originating from the dispersion and interaction of Ag with Mn and Co [25]. Additionally, the ratio of acidic sites to basic sites ($S_a/S_b$) was determined to account for the catalysts’ activity. The order is as follows: Ag–CoOₓ/$\gamma$-Al₂O₃ > CoOₓ/$\gamma$-Al₂O₃ > Ag–MnOₓ/$\gamma$-Al₂O₃ > Ag/$\gamma$-Al₂O₃ > $\gamma$-Al₂O₃ > MnOₓ/$\gamma$-Al₂O₃. A comparison of the acidic and basic sites in various temperature ranges is shown in Table 2. The results indicate that the acidic sites are more abundant in Ag–CoOₓ/$\gamma$-Al₂O₃, which is beneficial for the toluene adsorption, activation, and oxidation.
Figure 3. (a) CO$_2$-TPD profiles, (b) NH$_3$-TPD profiles of the fresh catalysts.

Table 2. A comparison table of acidic and basic sites of freshly prepared catalysts.

| Catalysts                  | Acidic Sites (mmol/g) | Basic Sites (mmol/g) | S$_a$/S$_b$ |
|----------------------------|-----------------------|----------------------|-------------|
|                            | Weak  | Medium | Strong | Total (S$_a$) | Weak  | Medium | Strong | Total (S$_b$) |         |
| γ-Al$_2$O$_3$              | 0.209 | 0.077  | 0.064  | 0.35         | 0.183 | 0.346  | 0.182  | 0.711         | 0.492   |
| MnO$_x$/γ-Al$_2$O$_3$      | 0.122 | 0.098  | 0.072  | 0.292        | 0.128 | 0.256  | 0.32   | 0.704         | 0.414   |
| CoO$_x$/γ-Al$_2$O$_3$      | 0.176 | 0.142  | 0.087  | 0.405        | 0.125 | 0.186  | 0.141  | 0.452         | 0.896   |
| Ag/γ-Al$_2$O$_3$           | 0.045 | 0.105  | 0.08   | 0.23         | 0.083 | 0.24   | 0.121  | 0.444         | 0.518   |
| Ag–MnO$_x$/γ-Al$_2$O$_3$   | 0.127 | 0.115  | 0.087  | 0.329        | 0.122 | 0.174  | 0.163  | 0.459         | 0.716   |
| Ag–CoO$_x$/γ-Al$_2$O$_3$   | 0.156 | 0.179  | 0.102  | 0.437        | 0.109 | 0.279  | 0.087  | 0.475         | 0.920   |

2.4. XPS

X-ray photoelectron spectroscopy (XPS) analysis confirmed Mn, Co, and Ag’s elemental state on the γ-Al$_2$O$_3$ surface. Figure 4 illustrates all the characteristic spectra of the synthesised catalysts. The XPS spectra of Mn2p for all the catalysts are shown in Figure 4a. Mn$^{3+}$ and Mn$^{4+}$ are the dominant oxidation states found in the prepared catalysts. The binding energies were divided between Mn$^{3+}$ and Mn$^{4+}$. The peaks at binding energies 640.5 eV and 640.09 eV corresponding to Mn2p$_{3/2}$ could be assigned to Mn$^{3+}$, and peaks at 644.3 eV corresponding to Mn2p$_{3/2}$ could be designated Mn$^{4+}$ [26,27]. Co2p spectrum for the synthesised catalysts can be disintegrated into two distinctive peaks (Figure 4b). Two spin doublets ascribed to CoO$_x$ between 780–781.5 eV and 796–796.6 eV are related to Co2p$_{3/2}$ and Co2p$_{1/2}$. The spin-orbit doublet of Co2p$_{3/2}$ between 780–781 eV can be deconvoluted into Co$^{3+}$ and Co$^{2+}$. Satellite peaks near the spin-orbit doublets imply cobalt oxides [28]. The two peaks in the Ag-loaded catalysts depicted in Figure 4c can be assigned to Ag3d$_{5/2}$ at 368.0 eV and Ag3d$_{3/2}$ at 374.0 eV. A slight shift of the binding energies from 368 eV to 367.2 eV on the Ag–MnO$_x$/γ-Al$_2$O$_3$ catalyst indicates an oxidised form of silver species [29]. The O1s spectra are represented in Figure 4d around 531 eV. Peak deconvolution suggested two types of oxygen molecules. The peak at the lower binding energy of 529.6 eV relates to lattice oxygen (O$_{\text{latt}}$). In comparison, the peak near the binding energy of 530.7–531 eV corresponds to the surface-adsorbed oxygen (O$_{\text{surf}}$) [29]. The ratios of O$_{\text{latt}}$ to O$_{\text{surf}}$ for the synthesised catalysts are listed in Table 1. Al2p showed a single peak near 74.1 eV for γ-Al$_2$O$_3$ modified by metal oxides. Bare γ-Al$_2$O$_3$ displayed a peak at 73.3 eV (Figure 4e) [30].
2.5. Catalytic Activity

For adsorption and catalytic ozonation, the catalysts must possess higher adsorption capacities to make them economically viable on an industrial scale. According to a previous study, lower metal loading promotes toluene oxidation up to 80 °C [29]. As a result, the metal oxide loading in the current investigation was maintained at 5% by weight. In this regard, it is essential to understand different catalysts’ performance for adsorption capacity and catalytic activity in ozone under various conditions [31]. Thus, 200 ppm of toluene was sent into the reactor with air at a total flow rate of 1000 lph. Adsorption was performed up to the breakthrough of toluene at the reactor outlet. The breakthrough curves of six catalysts and the corresponding toluene lost during the experiment are displayed in Figure 5. Once the toluene breakthrough was attained, the reactor was flushed with air to remove loosely bonded (physisorbed) toluene from the catalyst surface. A strongly or irreversibly bonded amount of toluene (chemisorbed) was obtained by subtracting the amount of toluene desorbed during flushing from the total amount of toluene adsorbed in the adsorption step.
Figure 5. (a) Breakthrough curves of toluene; (b) amount of toluene desorbed as a function of time during ozone treatment of the catalysts.

In comparison to other catalysts, Ag/\(\gamma\)-Al\(_2\)O\(_3\) has the longest breakthrough time, as shown in Figure 5a. It should be observed that metal oxide catalysts containing Ag had significantly greater toluene absorption. Except for \(\gamma\)-Al\(_2\)O\(_3\), all the catalysts had similar surface areas, implying that the increased toluene adsorption is not solely physical. The addition of Mn and Co alone does not have nearly the same impact as the addition of Ag. The number of active sites accessible for toluene adsorption increases because of Ag addition. Because of \(\pi\)-complexation, the d orbital of Ag\(^+\) can bond with unsaturated hydrocarbons [31–33].

The chemisorbed toluene on the catalysts was desorbed using the strong oxidising agent ozone. The catalysts did not show any significant activity in removing toluene at room temperature. However, their activity was enhanced upon maintaining the desorption temperature at 75 °C. Furthermore, reports suggest that at temperatures higher than 80 °C, ozone decomposes and hence loses the ability to degrade the VOC [1,11]. Another reason can also be that there can be catalyst deactivation at room temperature due to the accumulation of carbonates on the surface of the catalysts. CO and CO\(_2\) were the two main products of catalytic ozonation of toluene for the catalysts. Figure 6a,b show the amount of CO\(_2\) and CO generated during the catalytic ozonation of the catalysts with respect to time. CO and CO\(_2\) evolution peaked in the early stages of ozonation and then gradually declined. CO\(_x\) concentrations rise to a maximum before falling as the amount of toluene left on the catalyst diminishes as the reaction progresses. Among all the catalysts, Ag–CoO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) displayed the highest CO\(_2\) concentration. The CO\(_2\) evolution trend of the catalysts is as follows: Ag–CoO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) > Ag/\(\gamma\)-Al\(_2\)O\(_3\) > Ag–MnO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) > MnO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) > CoO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) ~ \(\gamma\)-Al\(_2\)O\(_3\).

Figure 6c,d show the CO\(_2\) and CO selectivity of all the catalysts. Except for bare \(\gamma\)-Al\(_2\)O\(_3\), the CO\(_2\) selectivity decreased to a minimum before increasing and reaching a constant value. Kim et al. reported that the selectivity of CO\(_2\) in gas-phase toluene decomposition is less than that of toluene adsorbed on the catalysts [34]. The trend in CO\(_2\) selectivity may be attributed to the desorption of toluene during ozonation. Figure 7 shows that the amount of toluene desorbed during ozonation is less with Ag–CoO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\), implying that a considerable portion of the adsorbed toluene undergoes oxidation rather than desorption. Figure 7 demonstrates the carbon balance of the synthesised catalysts after catalytic ozonation. Ag–CoO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) displayed the highest total carbon balance of 99.7%, of which 39.6% was lost during the flushing step while 52.4% was CO\(_x\) yield and 7.7% was recovered from toluene desorbed during ozonation.
A comparison was made between Ag-impregnated metal oxides and pure metal oxides supported on γ-Al₂O₃. Metal oxides supported on γ-Al₂O₃ have higher activity than bare γ-Al₂O₃. However, toluene adsorption has been shown to impact active site mobility over Mn and Co based catalysts [35,36]. However, with the impregnation of Ag, the toluene adsorption increases due to the strong intermolecular force between Ag and toluene, thus creating the active site for reactions on the oxide surface [37]. In addition, the ratio of lattice oxygen to surface oxygen could be improved with Ag addition, boosting the catalytic
activity of Ag–CoO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} [38]. The presence of lattice oxygens in Ag–CoO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} facilitates the initial partial oxidation of toluene, which is then oxidised to CO and CO\textsubscript{2} due to the presence of O\textsubscript{3} [39].

Furthermore, literature studies show that the surface acidity of catalysts impacts catalytic activity for VOC degradation [39]. Because toluene adsorption occurs more readily on acidic surfaces, it may be harder to desorb it at low temperatures. The increased density of weakly acidic sites in Ag–CoO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} compared to other catalysts contributes to the catalyst’s better activity. This quickly aids in surface adsorption and re-desorption of toluene at ambient temperature [40]. Table 3 provides a comparison between previous studies and the present work.

Table 3. A comparison of literature studies and the present study for catalytic ozonation of toluene.

| Catalyst | Carrier Flow Rate | Toluene Concentration | Ozone Concentration | Reaction Temperature (°C) | Toluene Removal Efficiency (%) | CO\textsubscript{2} Selectivity (%) | Reference |
|----------|-------------------|-----------------------|---------------------|---------------------------|-------------------------------|-------------------------------|-----------|
| Zeolite and MCM-41 | 0.12–0.39 m\textsuperscript{3}/h | 0.3–4.5 ppmv | 0–80 ppmv | 25 | 96% | CO\textsubscript{2} 95% | [41] |
| MnO\textsubscript{2}-graphene | 0.15 L/min | 200 ppm | 400 ppm | 22 | 33.6% | 100% (Pd) | 90% | [42] |
| MnO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} | 400 mL/min | 120 ppm | 1050 ppm | 22–100 | >91% | >88% | [1] |
| MnO\textsubscript{2}/CoO | 200 mL/min | 100 ppm | 1000 ppm | 120 | >91% | >88% | [43] |
| (M: Fe, Cu, Ru, Ag) | 1 L/min | 100 ppm | 1000 ppm | 25 | 36% (RuMnZ) | -95% | [44] |
| Meso Mn/Al\textsubscript{2}O\textsubscript{3} | 1 L/min | 50 ppm | 1000 ppm | 25 | 100% | >80% | [26] |
| Pt-γ-Al\textsubscript{2}O\textsubscript{3} | 100 mL/min | 35 ppm | 350 ppm | 25 | 100% | 70–100% | [45] |
| MnO\textsubscript{2} on γ-Al\textsubscript{2}O\textsubscript{3} or MCM-41 | 400 mL/min | 120 ppm | 1050 ppm | 22–100 | >91% | >88% | [10] |
| Ag–MOx/γ-Al\textsubscript{2}O\textsubscript{3} (M = Mn/Co) | 1000 L/h | 200 ppm | 500 ppm | 75 | >91% | >88% | Present work |

3. Materials and Methods

3.1. Material Synthesis and Characterisation

Manganese and cobalt oxide supported on γ-Al\textsubscript{2}O\textsubscript{3} were synthesised by the wet impregnation of γ-Al\textsubscript{2}O\textsubscript{3} with the corresponding metal nitrate solution. Manganese (II) nitrate tetrahydrate, cobalt (II) nitrate hexahydrate and γ-Al\textsubscript{2}O\textsubscript{3} (1/8-inch pellets) were obtained from Alfa Aesar (Haverhills, MA, USA). The γ-Al\textsubscript{2}O\textsubscript{3} support was first calcined at 500 °C for four hours to remove the adsorbed impurities. The appropriate metal precursor solutions were added to γ-Al\textsubscript{2}O\textsubscript{3} while stirring constantly and then dried overnight at 110 °C. Later, the dried samples were calcined at 500 °C for four hours in an air atmosphere. The precursor’s amount was calculated such that the final metal loading was 5% by weight. Then, 2 wt% silver metal-supported manganese and cobalt oxides on γ-Al\textsubscript{2}O\textsubscript{3} were prepared by depositing silver nitrate (Fisher Scientific, Waltham, MA, USA) on the synthesised MnO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} and CoO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} using a similar procedure. The obtained AgO\textsubscript{x}-based catalysts were reduced by an H\textsubscript{2} flow of 30 mL/min at 200 °C for two hours.

Panalytical X’Pert PRO diffractometer (Malvern Panalytical Ltd., United Kingdom) with a CuKα radiation source (= 1.5418) was used to examine the catalysts’ powder X-ray diffraction (XRD) patterns. Scans were collected in the range of 2θ between 10 and 90° with a scan rate of 0.01670° s\textsuperscript{-1}. The synthesised catalysts’ specific surface area was determined using N\textsubscript{2} physisorption at −196 °C using Quantachrome, U.S.A., NOVA2200e surface area analyser (Boynton Beach, FL, United States). The surface area was measured between N\textsubscript{2} partial pressure ratio (P/P\textsubscript{0}) of 0.05 to 0.3. Temperature-programmed desorption (TPD) tests were conducted using MicrotracBEL Corp. chemisorption apparatus (BEL Microtrac Co., Ltd., Tokyo, Japan) with a thermal conductivity detector. NH\textsubscript{3}-TPD experiments were conducted to examine the acidic properties of the catalysts. After pre-treatment of the catalysts for one hour at 500 °C under He flow, they were cooled down to 100 °C, subsequently followed by adsorption of NH\textsubscript{3} from a flow of 5 vol.% NH\textsubscript{3}/He at 100 °C. The flow was switched to pure He flow at the same temperature to remove any physisorbed
NH₃. The TPD profile was then calculated by heating the samples linearly to 500 °C at a rate of 10 °C min⁻¹ with a flow rate of 30 mL min⁻¹ He. CO₂-TPD experiments were conducted to investigate the basic nature of the catalysts. After pre-treatment of the catalysts for one hour at 300 °C under He flow followed by cooling down to 100 °C, CO₂ adsorption was carried out in a flow of 10 vol.% CO₂/He at the same temperature. The flow was switched to pure He flow at the same temperature to remove any physisorbed CO₂. Later, the TPD profile was recorded by heating the samples linearly to 900 °C at 10 °C min⁻¹ under 30 mL min⁻¹ He flow. The amount of NH₃/CO₂ desorbed from catalysts is represented by the area under the curve of the respective TPD profiles, which correlates to catalysts’ acid/basic site density (mmol/g). The prepared catalysts’ chemical state and surface composition were determined using X-ray photoelectron spectroscopy. Krato axis Ultra Spectrometer (Shimadzu Corp., Kyoto, Japan) with AlKα monochromatic excited radiation of 1489.5 eV with an emission current of 10 mA and applied voltage of 15 kV was used for the same procedure.

3.2. Experimental Setup

Catalytic activity was evaluated using a micro-fixed bed. Figure 8 depicts the experimental setup. A total of 10 g of the synthesised catalyst was filled between glass wool packing in a stainless-steel reactor with an internal diameter of 40 mm. The reactor was positioned inside an oven to control the reaction temperatures. Oxidation of toluene in the presence of ozone was used to determine the activity of the calcined catalysts. Before carrying out the reactions, the catalysts were not subjected to any pre-treatment and were used at room temperature and atmospheric pressure to mimic the industrial process. A toluene feed of 200 ppm was injected into the air stream (for balance) by a syringe pump (Ravel syringe infusion pump, RH-SY10 by Ravelhrteks Pvt. Ltd., Chennai, Tamil Nadu). Airstream was supplied through a compressor at a rate of 1000 lph. Ozone was provided through a droplet ozone generator (output = 500 ppm of ozone per hour as analysed using Ozone monitor, API-450 Nema (Advanced Pollution Instrumentation, Inc., 2530 Patra Drive, El Sobrante, CA, USA)). Experiments were carried out in the following steps: The first step is the catalysts’ saturation with toluene vapour until the toluene’s outlet concentration matches the inlet concentration. After the breakthrough was achieved, the reactor was flushed with pure air (toluene feed was halted) to remove physisorbed toluene. Immediately, the oven temperature was increased to 75 °C and ozone generator was turned on (airflow was discontinued) to measure the catalytic activity under different catalyst packing.

Figure 8. Experimental setup 1. Air compressor; 2. Syringe pump; 3. Rotameter; 4. Control unit; 5. Vaporiser; 6. Mixing chamber; 7. Heating coil (oven); 8. Stainless steel reactor; 9. Collector.
The toluene lost during flushing, CO\textsubscript{x} yield obtained by the conversion of toluene to CO and CO\textsubscript{2}, selectivity to CO\textsubscript{2}, and the carbon balance were determined to assess the catalytic activity of the catalysts as given below:

\[
\text{CO}\textsubscript{x} \text{ yield (\%)} = \frac{n\text{ produced}^{\text{CO}_2} + n\text{ produced}^{\text{CO}}} {n\text{ adsorbed}^{\text{C}_7\text{H}_8}} \times 7
\]

\[
\text{S}_{\text{CO}_2} (\%) = \frac{C_{\text{CO}_2}^{44}} {C_{\text{CO}}^{28} + C_{\text{CO}_2}^{44}} \times 100
\]

\[
B_c (\%) = \frac{n\text{ produced}^{\text{CO}} + n\text{ produced}^{\text{CO}_2} + n\text{ flushed}^{\text{C}_7\text{H}_8} + n\text{ desorbed}^{\text{C}_7\text{H}_8} \times 7} {n\text{ adsorbed}^{\text{C}_7\text{H}_8}} \times 100
\]

\[
n_{\text{C}_7\text{H}_8}^{\text{adsorbed}} = \int_{t_0}^{t_a} F_a C_{\text{C}_7\text{H}_8}^a \text{d}t, \quad n_{\text{C}_7\text{H}_8}^{\text{flushed}} = \int_{t_0}^{t_f} F_f C_{\text{C}_7\text{H}_8}^f \text{d}t, \quad n_{\text{C}_7\text{H}_8}^{\text{desorbed}} = \int_{t_0}^{t_d} F_d C_{\text{C}_7\text{H}_8}^d \text{d}t
\]

\[
n_{\text{CO}}^{\text{produced}} = \int_{t_0}^{t_a} F_d C_{\text{CO}} \text{d}t, \quad n_{\text{CO}_2}^{\text{produced}} = \int_{t_0}^{t_d} F_d C_{\text{CO}_2} \text{d}t
\]

where \(C_{\text{C}_7\text{H}_8}^a\) and \(C_{\text{C}_7\text{H}_8}^d\) are the concentrations of toluene in the adsorption step and desorption step (mg m\textsuperscript{-3}). \(F_a, F_f\) and \(F_d\) are the flow rates of the airstream throughout the adsorption, flushing and desorption step. \(t_a, t_f\) and \(t_d\) are the adsorption time, flushing time, and desorption time (min). \(C_{\text{CO}}\) and \(C_{\text{CO}_2}\) are the concentrations of CO and CO\textsubscript{2} produced during the desorption step (mg m\textsuperscript{-3}). \(B_c\) is the carbon balance.

### 3.3. Analysis

A Fourier-transform infrared spectrometer (FTIR) (Bruker Tensor II, Billerica, MA, USA) equipped with a liquid N\textsubscript{2} cooled Mercury-Cadmium-Telluride detector and gas cell with a path length of 8 m was used to monitor toluene concentration near the outlet. Spectra were collected using OPUS software with 16 scans per spectrum and a spectral resolution of 0.5 cm\textsuperscript{-1}. Siemens Ultramat 23 (Siemens AG, Munich, Germany) was used to analyse CO\textsubscript{x} products formed during ozonation.

### 4. Conclusions

Based on the catalytic ozonation of toluene using the synthesised catalysts, the toluene decomposition efficiencies varied with modifying the support surface with different transition metal oxides. The addition of Ag to the transition metal oxides significantly improved the activity of the catalyst. Ag–CoO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} had the highest ratio of surface acidic to basic sites, which improved toluene adsorption capacity on the catalyst. The formation of ample lattice oxygens and correspondingly having the highest O\textsubscript{latt}/O\textsubscript{surf} ratio facilitated better toluene oxidation in the presence of the oxidising agent ozone. Hence, the CO\textsubscript{x} selectivity and the carbon balance improved for Ag–CoO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3}.

### Author Contributions:

Conceptualisation, K.B., T.S. and C.S.; Formal analysis, K.B., D.R. and P.C.; Funding acquisition, T.S. and C.S.; Investigation, K.B., D.R. and P.C.; Methodology, K.B., D.R. and P.C.; Investigation, S.M.; Resources, S.M.; Project administration, C.S.; Supervision, C.S.; Writing—original draft, K.B.; Writing—review and editing, C.S. All authors have read and agreed to the published version of the manuscript.

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### Data Availability Statement:

The data presented in this study are available on request from the corresponding author.

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