

Toluene Oxidation: CO₂ vs Benzaldehyde: Current Status and Future Perspectives

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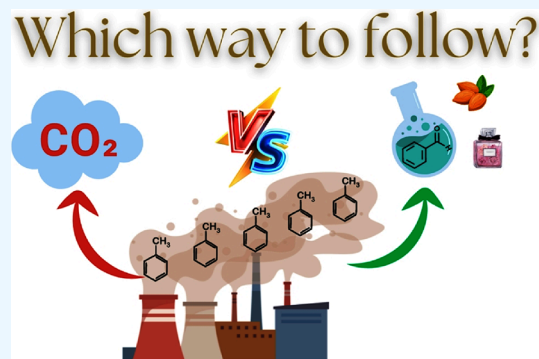
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ABSTRACT: Toluene is a common and significant volatile organic compound (VOC). Although it finds extensive application in various industrial processes (chemical manufacturing, paint and adhesive production, and as a solvent), it creates a huge environmental impact when emitted freely into the atmosphere. Two solutions were found to mitigate the emission of this pollutant: the total oxidation to CO₂ and H₂O and the selective oxidation into benzaldehyde. This review discusses the two main alternatives for tackling this problem: converting the toluene into carbon dioxide by total oxidation or into benzaldehyde by selective oxidation. It presents new catalytic advances, new trends, and the advantages and disadvantages of both methods.



INTRODUCTION

Volatile organic compounds (VOCs) are organic chemical compounds (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate), whose composition allows them to evaporate under normal atmospheric conditions of temperature and pressure, and participate in atmospheric photochemical reactions.^{1,2}

The emission of these compounds leads to a negative impact on air quality (formation of ground-level ozone, a key constituent of smog) and public health (ozone can detrimentally affect respiratory health and damage the liver, kidneys, and central nervous system). Moreover, certain VOCs are classified as carcinogens, elevating the risk of cancer development among those exposed and in the overall environment (harming vegetation and ecosystems). Additionally, these compounds can participate in chemical reactions with other atmospheric components, yielding secondary pollutants that further degrade air quality and impact the environment.

Toluene is a common and significant VOC. Although it finds extensive applications in various industrial processes (chemical manufacturing, paint and adhesive production, and as a solvent), it creates a huge environmental impact when emitted freely into the atmosphere. In 2015, 11 kt of toluene was emitted into the atmosphere by US industries, while worldwide it reached 10 Mt. In 2019/20 Australia reported emissions of 2.5 kt of toluene and an average from 2015 to 2020 of almost 3.0 kt per year. More recently, the US estimated a VOC emission of 12 kt/year since 2020, a value constant up to 2022.

The UK reported an emission of 781 kt on all non-methane volatile organic compounds where toluene is included.^{3–7}

Therefore, a solution must be found to mitigate the emanation of this pollutant into the atmosphere. Adsorption, thermal incineration, and catalytic oxidation are some of the techniques that could be applied, but with some issues. Thermal incineration is considered to be very expensive due to the amount of energy input necessary to achieve the high temperatures required. On the other hand, adsorption comes with the main problem of constant replacement and regeneration due to limited adsorption capacity. Catalytic oxidation (or total oxidation) is presented to be a better alternative due to its reusability of the catalysts, low energy, and high efficiency with the only products produced being CO₂ and H₂O.⁸ Although this eliminates the problem of VOC release, the emission of CO₂ is not sustainable in the current climate crisis we are living in, since no permanent solution for the capture, application, or storage of CO₂ is fully developed and operational to be used as a counterbalance to those emissions. This topic is very well explored in Gabrielli et al.'s review of net-zero emission in the chemical industry.⁹

Another alternative is the transformation of toluene into a product with a higher market value. Benzaldehyde (Bz) is a

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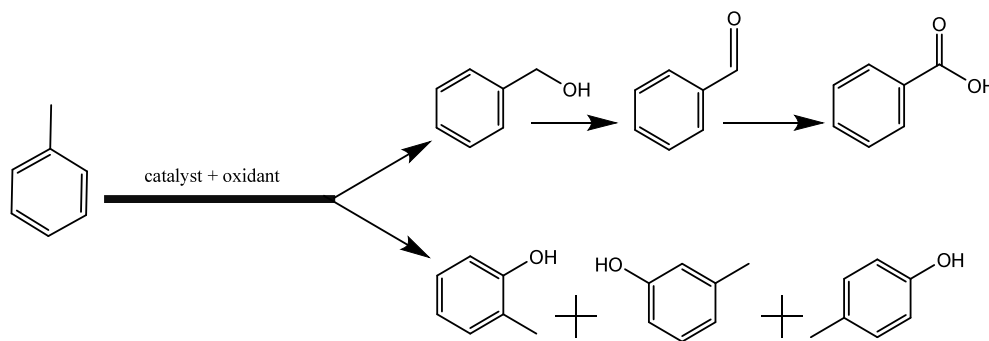
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Scheme 1. Schematic Representation of the Selective Oxidation of Toluene



product of the oxidation of toluene, with numerous uses such as dyes, perfumes (representing 30% of the market),¹⁰ pharmaceuticals, or as an intermediate to form for example benzoates.¹¹

Currently, benzaldehyde is obtained under very harsh conditions, by partial oxidizing toluene. The gas phase reaction occurs at a temperature between 250 and 650 °C in the presence of oxygen and an unreactive gas (water vapor, nitrogen, or CO₂, to avoid the overoxidation of the benzaldehyde), and a catalyst from groups V and VI of the periodic table. The application of high pressures inside the reactor and the introduction of potassium sulfate help the system to become more stable and selective, avoiding total oxidation and, in the end, the decomposition of benzaldehyde, thus ensuring a higher production. Currently, the conversion obtained is shallow 10–20% with various side products such as cresol, benzoic acid, and carbon dioxide among others.¹¹

The liquid oxidation of toluene occurs at a lower temperature of 80–250 °C in the presence of a cobalt, iron, manganese, or chromium catalyst and corrosive promoters such as bromides and hypochlorites, among others. The liquid oxidation tends to achieve a slightly higher yield (with longer reaction times) between 20 and 40% depending on the catalyst, promoter, and temperature with a selectivity of ca. 40–80%.¹¹

The approximate gross annual demand for benzaldehyde, in 2015, exceeded 90 kt worldwide,¹² and a market valued at ca. 210 million USD with the prospect of growing (compound annual growth rate of 4.4%, reaching a value of 300 million USD by 2030)^{13–15} selective oxidation of toluene into benzaldehyde by applying a greener process could be a solution for the emissions and creates an offer for a high-demand product with less impact on the environment.

This review will focus on both processes, showcasing their advantages and disadvantages and the current advances and trends. For selective oxidation, since it is a less explored topic, a longer scope was considered to showcase the evolution of the systems going back over the last 10 years, exploring different catalysts and operating conditions. In the case of total oxidation, there are thousands of reports, including several reviews, and therefore a more general approach was taken to highlight the last 5 years' discoveries, aggregated into sections of catalyst and conditions, and discussing their most interesting aspects.

SELECTIVE OXIDATION TO BENZALDEHYDE

The selective oxidation of toluene is a relatively less explored topic when compared with total oxidation. This is because of

not only the difficulty of finding the right conditions to oxidize toluene but also being selective to an aldehyde, Scheme 1, which is known to be very reactive to oxidation. This section will be divided into two subsections. The first section will discuss the systems in which conventional heating or some other alternative energy source methods were applied. The second will focus on photocatalytic systems since there is extended research on that topic, and the comparison between activities is presented in the form of the production of benzaldehyde ($\mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$) instead of the typical yield%.

In 2013 Cai and co-workers¹⁶ reported the solvent-free selective oxidation of toluene into benzaldehyde using zeolite doped with different metals. The best result obtained was when the pair Fe₂O₃/HZSM-5 was tested, achieving a conversion of 17.3%. Although it has the highest conversion it is the least selective catalyst with only 51.4% toward benzaldehyde. The other catalysts like Fe₂O₃/MCM-22, V/HZSM-5, and Co/HZSM-5 achieved a higher selectivity of over 70–80% but with a low conversion, below 10%. In this case, even after the optimization (90 °C for 4 h with 0.4 g of catalyst and H₂O₂ (30% aq.):toluene ratio of 3), it was not possible to increase the selectivity for the benzaldehyde without compromising the conversion of toluene. The recycling test showed the stability of the system being able to maintain its activity and selectivity for up to 3 cycles not showing signs of leaching of the iron species.

In 2014 Acharyya et al.¹⁷ published the preparation of CuCr₂O₄ spinel nanoparticles and studied their catalytic activity on the selective oxidation of toluene to benzaldehyde. The catalyst was tested under the following conditions: toluene:H₂O₂ (50% aq.) 1:3, 75 mg of catalyst, acetonitrile as the solvent, and 75 °C for 10 h, and it was able to convert 57.5% of toluene with a high selectivity toward benzaldehyde 84.4%, having as high secondary product benzyl alcohol. One of the most important parameters in the study found by the authors was the effect of the temperature. At lower temperatures like room temperature, the reaction was not able to be performed, but with the increase of the temperature, the conversion of toluene increased exponentially as well as the selectivity toward benzaldehyde. This effect is very visible in the decrease in the formation of benzyl alcohol. But when the temperature was increased over 75 °C several byproducts started to be formed such as benzoic acid (a sign of overoxidation of benzaldehyde) and *p*- and *o*-cresol. The nanoparticles were reused up to 5 cycles, maintaining the same conversion and selectivity during all cycles.

In the same year, Ghosh et al.¹⁸ reported the synthesis of a silver–tungsten nanostructure (AgW-N) and its catalytic activity on the oxidation of toluene to benzaldehyde. The

reaction was performed in acetonitrile with 0.1 g of catalyst, a molar ratio of 3:1 H_2O_2 (50% aq.):toluene at 90 °C for 16 h. The two catalyst nanostructures screened with 4.6, 7.3, and 11.2 wt % of silver converted respectively 42, 55, and 64% of toluene showing that the increase of silver loading would not significantly increase the conversion of the substrate. Adding that to the fact that higher loads tend to lose selectivity to the main product which started at 93% with the 4.6% load and finished at 82% with the 11.2% load. The reusability of the catalyst demonstrated the stability of the nanostructure, being able to maintain the same activity after 4 cycles and without any sign indicating silver leaching.

In 2015 Zhou et al.¹⁹ reported the application of cobalt aluminum oxides prepared through calcination of CoAl layered double hydroxides with different Co/Al ratios (2, 3, and 4). These catalysts were then applied to the selective oxidation of toluene using *tert*-butyl hydrogen peroxide (*t*-BuOOH) as an oxidant. The first test showed that the oxides are active under the conditions of the study (oxidant/substrate ratio of 4, acetonitrile as the solvent, 100 mg of catalyst, 70 °C and 9 h reaction time) achieving a relatively high selectivity toward benzaldehyde of over 78%. Although having a high selectivity, the conversion of toluene is relatively low achieving a maximum of 8.2% when the Co_4Al oxide is applied. From the test, it is possible to observe that the increase of the Co content on the catalyst increases the conversion of toluene and decreases the formation of benzyl alcohol in favor of increasing the formation of benzoic acid. The recycling tests for Co_4Al oxide showed the stability of the catalyst maintaining its activity and selectivity up to 5 catalytic cycles.

Gao and co-workers²⁰ explored the activity of a mixed-node MOF composed of copper, silver, and 1,3,5-benzene tricarboxylic acid (BTC). The catalytic tests were conducted in an autoclave where 1 MPa of oxygen was introduced to the catalyst and toluene, heated to 160 °C, and left to react for 4 h. This type of catalyst was synthesized using the postsynthetic exchange method, which results in an isomorphous replacement, in this case, of the copper ion by a silver ion. This allowed the creation of MOFs with different silver contents which were tested in this reaction. The Cu-BTC was able to convert only 6.5% of toluene but with excellent selectivity to benzaldehyde (99.5%). The introduction of the silver ion into the framework increased the conversion of toluene up to 12.7% when the silver content was 2.76 wt %. The increase of silver content up to 4.15 wt % did not influence the conversion, achieving only 13%. A comparison between the activity of Ag-Cu-BTC and silver nitrate was performed. Although the metallic salt can convert 20.5% of toluene in 4 h, it comes with a great cost of selectivity to benzaldehyde, which is only 41.4%. The Ag-Cu-BTC (4.15) can reach the same conversion capacity if the reaction is performed for 8 h and still has a selectivity of benzaldehyde over 90% (with the main secondary product being benzoic acid). The recyclability of the MOF was evaluated, and after 4 cycles, the conversion and selectivity values were maintained constant, and the ICP did not reveal the presence of any silver or copper in the solution demonstrating the stability of the new framework.

Also in 2015, Han and co-workers²¹ reported a highly selective system for the oxidation of toluene involving a carbon nitride ($\text{g-C}_3\text{N}_4$) doped with copper and boron. The newly produced catalysts were tested under mild conditions with acetonitrile as the solvent, and *t*-BuOOH (in a 2.5 or 4 molar ratio to toluene) as the oxidant at 70 °C for 10 h. The first

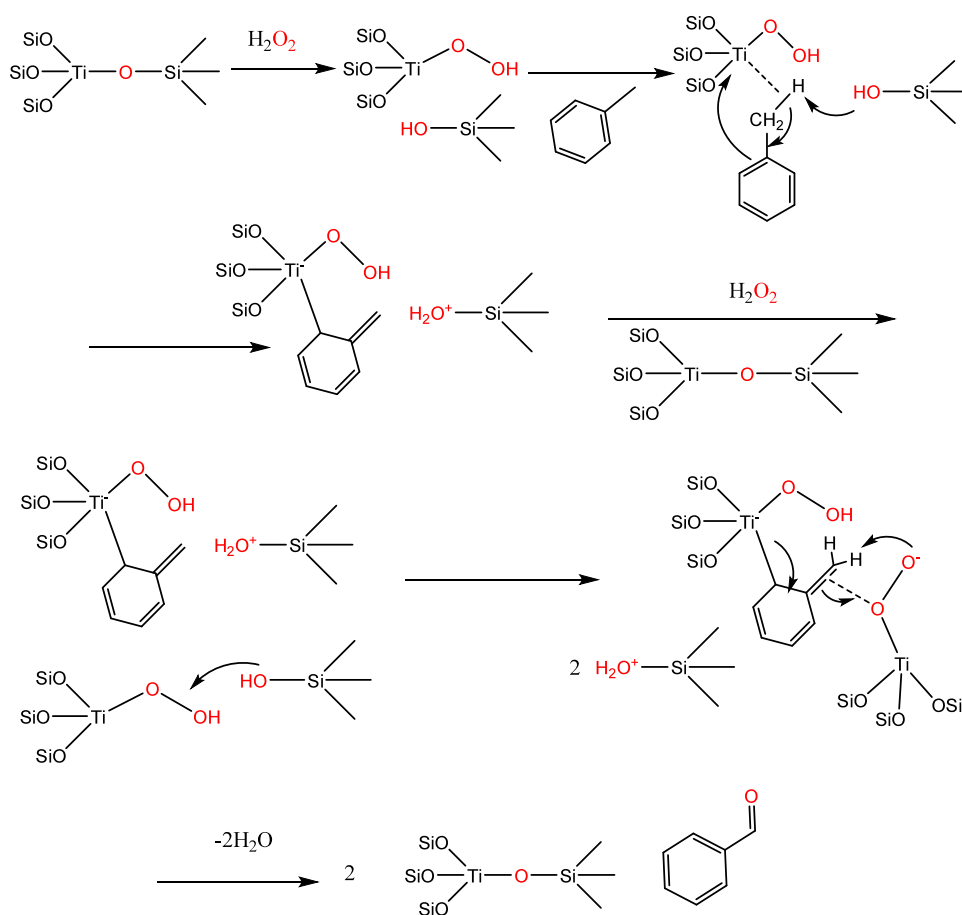
results showed a mild conversion of toluene but with a full selectivity toward the benzaldehyde. The catalyst composed solely of copper and the $\text{g-C}_3\text{N}_4$ achieved a conversion of 1.59%, but when boron was introduced in the catalyst, the conversion of toluene rose to 4.3%, maintaining the high selectivity. The conversion can be further increased by introducing more *t*-BuOOH into the reaction medium having a final conversion of 6.3% with the same selectivity obtained during the study. The introduction of the boron into the surface is believed to lead to an increase in the conversion since it may act as a Lewis acid site complementing the basic nitrogen sites already present. The last important test was the reusability of the catalyst, which showed it was able to catalyze the reaction up to 5 cycles without a major drop in the conversion.

Guajardo, Carlesi, and Aracena²² studied the possibility of performing this reaction using deep eutectic solvents (DESs). For this study choline chloride (ChCl) was used in combination with a hydrogen-bond donor such as urea (URA), glycerol (GLY), and ethylene glycol (ETA) creating the DESs that with the metal catalysts (sodium tungstate, iron(III) chloride, phosphotungstic acid, and phosphomolybdic acid) would be tested as catalysts. Under the set of conditions presented (60 °C, 6 h of reaction, 3:5 (v/v) DES/substrate, 0.3 g of the metal catalyst, and oxidant/substrate (v/v) ratio of 3), the two best catalysts were ETA- FeCl_3 with a conversion of 18% and a benzaldehyde selectivity of 73.5% and GLY- FeCl_3 with 14.3% toluene conversion and 61.2% benzaldehyde selectivity. When comparing the results obtained by FeCl_3 alone (8.4% conversion and 69% selectivity), it is evident the positive influence of DES in the catalytic system. The catalyst chosen by the authors to optimize was ETA- FeCl_3 which achieved only by increasing the temperature to 80 °C, 37.9% conversion, with a 63.6% selectivity toward benzaldehyde.

In 2017 Dabbagh and co-workers²³ tested the catalytic activity of VOHPO_4 supported in a mesoporous silica KIT-6. Three different catalysts were prepared by changing the quantity of mesoporous material introduced into the vanadium phosphate solution ($x = 0.4, 0.6, \text{ and } 0.8 \text{ g}$) and (x)KIT-6-VPO. The oxidation of toluene was performed at 75 °C with 0.1 g of catalyst, acetonitrile as the solvent, and H_2O_2 (35% aq solution) in a molar ratio of 1:1.4 toluene:oxidant. The catalysts were shown to be active under these conditions with (0.4)KIT-6-VPO having the highest conversion of 17.76%, after 10 h, while the others converted ca. 10% of toluene. Besides having the higher conversion, it is also the least selective toward benzaldehyde having only 69%, while the other two can reach up to 85%. Recycle tests showed a leaching of the vanadium compound with content decreasing from 17% to 10% after 5 cycles. This decrease led to a decrease in the conversion of toluene and the selectivity toward benzaldehyde with an increase of the cresols byproducts.

Asefa and co-workers²⁴ reported the synthesis of titanium silicate materials and their activity in the selective oxidation of toluene. Three different titanosilicate materials (TS-Bis, TS-Iso, and TS-But) were produced utilizing different precursors: titanium diisopropoxide bis(acetylacetonate), titanium(IV) isopropoxide, and titanium *n*-butoxide, respectively. TS-But presented the highest conversion capacity with almost full conversion (98%) and an outstanding selectivity of almost 100% to benzaldehyde (reaction performed at 80 °C, in acetonitrile, for 4 h, and H_2O_2 (50% aq. solution) as the

Scheme 2. Proposed Mechanism by the Authors for the Oxidation of Toluene to Benzaldehyde in the Presence of H₂O₂ and TS-But^a



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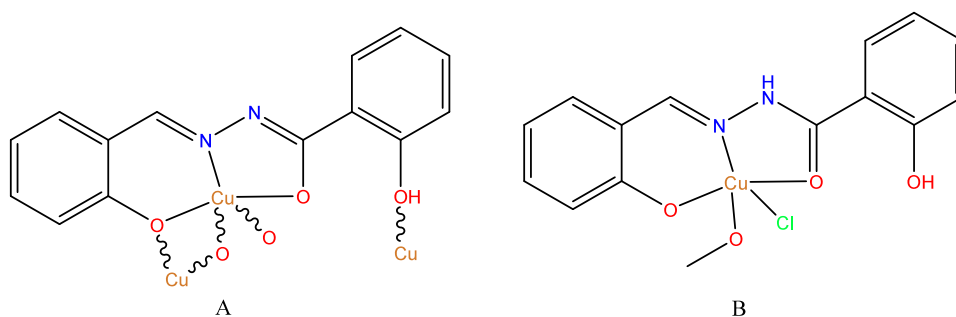


Figure 1. Representation of the keto-form monomer (A) and a polymeric enol (B) arylhydrazone copper(II) complex. Adapted with permission from ref 25. Copyright 2017 Elsevier.

oxidant in a (v/v) ratio to the substrate of 2.6). This result explained by the authors could be related to the number of acid-active sites available since when it was investigated the TON (in this case moles of toluene per moles of acid sites) is comparably low, 39 when compared to the other two catalysts, which achieved 70 (TS-Bis) and 147 (TS-Iso) demonstrating that the increase in the acid sites leads to an increase in the conversion of toluene. The catalyst TS-Iso also achieved an interesting result with a conversion of 68% and a selectivity toward the benzaldehyde of 88% besides having a lower acid-sites availability when compared to TS-But. The catalysts were also shown to remain stable and active after 5 reaction cycles

with the same reactivity as in the first one. The proposed mechanism by the authors involves the existence of strong and weak acid sites and is presented in Scheme 2.

In 2017 Sutradhar et al.²⁵ reported the use of a keto-form monomer (A) and a polymeric enol (B) arylhydrazone copper(II) complex, Figure 1, under microwave irradiation at low power (5 W). Complex A showed very low activity, having only 12.7% conversion of toluene, but is extremely selective to benzaldehyde (98.4%). This result was possible by adding HNO₃ as a cocatalyst which has been proven in several instances to be a good promoter for the oxidation of alkanes.^{26–28} The best result occurred in the presence of

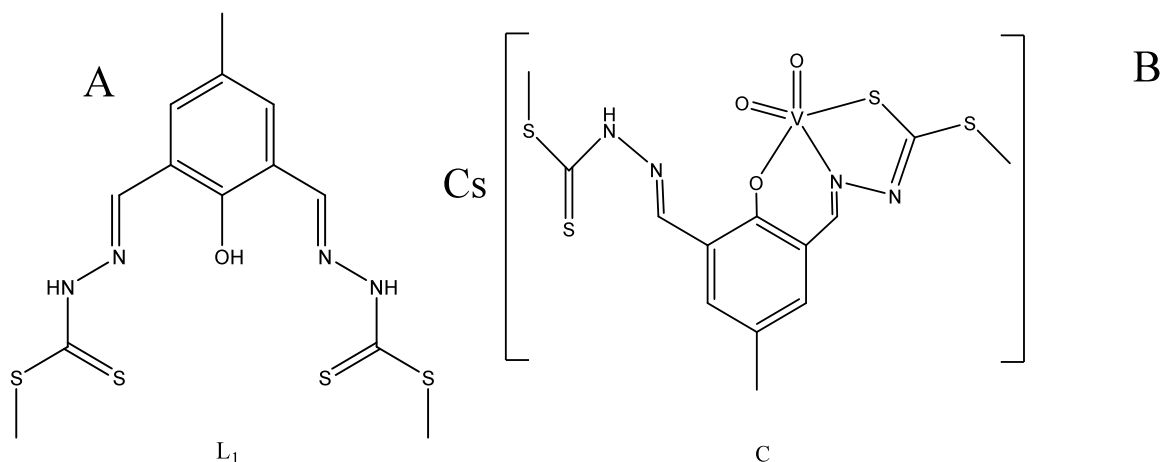


Figure 2. Representation of (A) the pro-ligand (L₁) and (B) the vanadium complex formed with cesium and L₁. Adapted with permission from ref 32. Copyright 2019 Royal Society of Chemistry.

complex B which was shown to be very active in this reaction. Only after 1 h of irradiation, at 50 °C using *t*-BuOOH 70% aq. as oxidant a total yield of benzaldehyde + benzyl alcohol of 38.7% with 98.5% selectivity to the benzaldehyde was achieved. With this catalyst, the addition of the promoter did not have a positive influence on the reaction, which stopped completely achieving only a 2% conversion. The solvent-free reaction was also attempted, resulting in a lower conversion of 29.8% but still with a high selectivity of 98%. Finally, the comparison with a conventional heating system was made, and the catalyst performed poorly, achieving only a total conversion of 11% with a benzaldehyde selectivity of 67% after 24 h.

In 2018 Song et al.²⁹ tested the catalytic activity of copper nanoparticles supported on graphene for the liquid oxidation of toluene in the presence of molecular oxygen. The copper nanoparticles were produced directly into the surface of the graphene by reduction in the presence of KOH and hydrazine hydrate (80 wt %) and applying hexadecyltrimethylammonium bromide (CTAB) as a capping agent avoiding the agglomeration. The new catalyst showed a toluene conversion of 11.5% after 8 h of reaction (2.0 MPa of O₂, 0.6 g of catalyst for 12 g of toluene at 65 °C in methanol) with a benzaldehyde selectivity of 66.5% with the second highest product being the benzoic acid. The copper nanoparticles could only achieve a conversion of 4.1% with a lower selectivity of only 52.4%. The authors explain this discrepancy due to the existence of a better distribution of the nanoparticles over the graphene support over the use of the free particles in solution. The reaction in this system achieves its maximum selectivity to benzaldehyde within the first hour of the reaction, followed by a continued decrease caused by the formation of benzoic acid. Ultimately the recycling tests revealed the reusability of the catalyst until the third cycle (without major activity loss) in which afterward it loses most of its activity achieving on the fourth cycle only 3.7% of conversion.

In the same year, Mal et al.³⁰ reported an efficient and selective oxidation of toluene by application of manganese tungstate nanobars (NB). In this system, the best result was obtained with 5 wt % of the catalyst being utilized with 3 equiv of H₂O₂ (30% aq.) with acetonitrile as the solvent. The reaction was heated at 80 °C and then left to react for up to 18 h. The MnWO₄NB was able to convert 33.7% of toluene

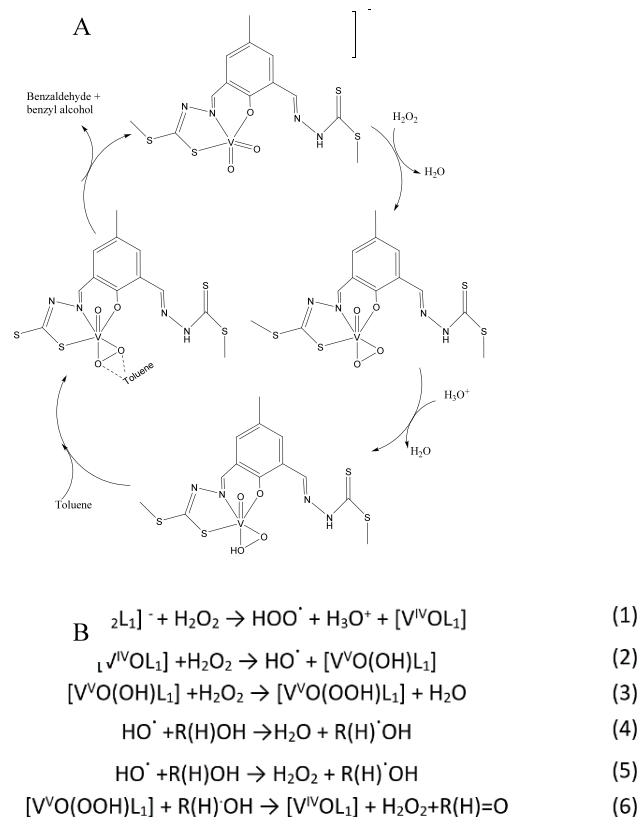
within the first 2 h of reaction with a selectivity to benzaldehyde of 66.1% and a secondary product the benzyl alcohol. The conversion of toluene continues to increase until the 18th hour of reaction achieving a high value of 59.5%. The most important result is the selectivity toward the benzaldehyde also increases with time reaching at the end at 90%. The reusability of the MnWO₄ NB was also investigated, and it was observed that for 5 cycles the catalyst was able to maintain its activity having the same conversion and benzaldehyde selectivity between the first and fifth cycle.

In 2019, Xu et al.³¹ investigated the synergetic effect of the bimetallic copper and chromium oxides supported on g-C₃N₄. The liquid oxidation of toluene occurs in the presence of 20 mg of catalyst in acetonitrile, 4:1 molar H₂O₂ (30% aq.):toluene at 75 °C for 5 h. Besides g-C₃N₄ other supports were tested such as Al₂O₃, MgO, and SiO₂. The CuCr₂@g-C₃N₄ achieved a high benzaldehyde yield of 42.9%, which represents 8.6 times and 5 times more than what is achieved by Cu@g-C₃N₄ and Cr@g-C₃N₄ alone, respectively. When the bimetallic catalyst was supported in other types of materials, only CuCr₂@SiO₂ was able to achieve a similar result as previously with a benzaldehyde yield of 42.0%. The CuCr₂@g-C₃N₄ exhibits a higher selectivity toward the benzaldehyde formation (92.3%) when compared to the SiO₂ counterpart (86.8%). The possible recyclability of the catalyst was also tested, and it was found at the end that CuCr₂@g-C₃N₄ remained active and stable for up to 6 catalytic cycles without losing the ability to convert and maintain its high selectivity toward the benzaldehyde. This report also presents the kinetic study of the reaction where it was calculated the activation energy for the reaction was 24.3 kJ/mol, and the reaction follows a first-order reaction between the 333.15 and 363.15 K.

Pessoa and co-workers³² synthesized and studied the application of new thiosemicarbazide and dithiocarbamate based oxidovanadium(IV) and dioxidovanadium(V) as pre-catalysts for the oxidation of alcohols and alkanes. For the oxidation of toluene, only one complex Cs[VVO₂L₁] (C), Figure 2A,B, was tested. In the reaction conditions applied (80 °C, 30% H₂O₂ as the oxidant in a molar ratio oxidant/substrate of 2 and 0.07 mol % of catalyst) after 20 h a conversion of toluene of 65% was achieved resulting in a very outstanding result. The selectivity toward the benzaldehyde was 78% with a TOF of 65. The authors proposed an outline for nonradical

pathways for the oxidation of alkanes in the presence of the precatalyst $Cs[V^V O_2 L_1]$ as presented in Scheme 3A and the more traditional radical approach in Scheme 3B.

Scheme 3. Proposed Mechanisms by the Authors for the Oxidation of Toluene by (A) a Coordinative and (B) a Radical Pathway in the Presence of Complex C^a



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Martins and co-workers³³ reported the activity of dinuclear aroylhydrazone copper(II) complex (Figure 3) as active catalysts under microwave irradiation for the oxidation of toluene. The reaction occurred solvent-free in the presence of

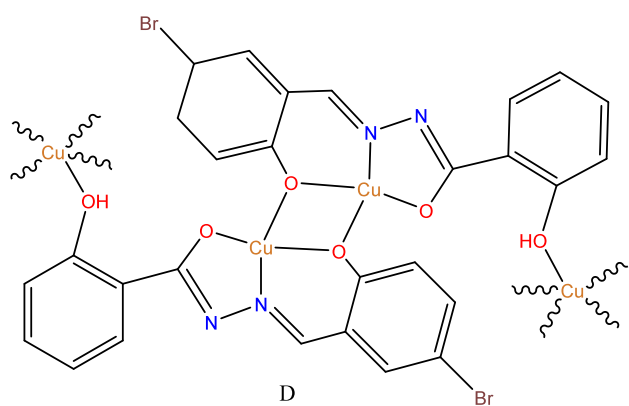


Figure 3. Representation of the dinuclear aroylhydrazone copper(II) complex (D). Adapted with permission from ref 33. Copyright 2019 MDPI.

2 equiv of *t*-BuOOH (70% aq.) and 50 °C. Catalyst D was in the study the most active, achieving a yield of 44% to benzaldehyde (without major byproducts selectivity over 99%) after 2.5 h of microwave irradiation at low power (5 W). The other two catalysts achieved respectively 30 and 37% of yield.

In 2020, Cd(II) aroylhydrazone Schiff bases coordination compounds were studied as heterogeneous catalysts by Pombeiro and co-workers.³⁴ In the study, complex E in Figure 4 was screened for the peroxidative oxidation of toluene and 1-

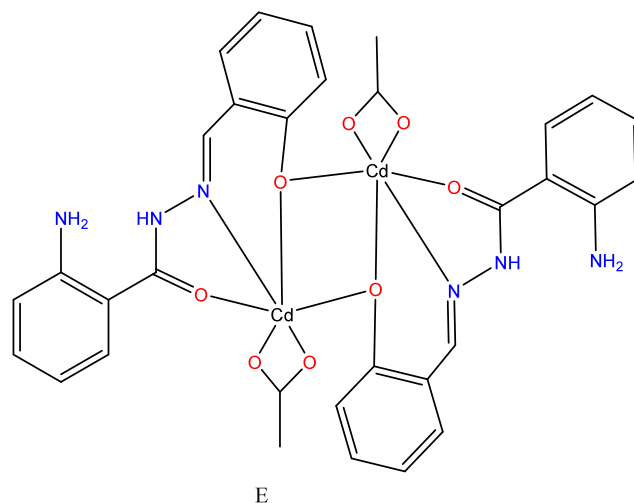


Figure 4. Representation of the Cd(II) aroylhydrazone Schiff base complex (E). Adapted with permission from ref 34. Copyright 2020 Royal Society of Chemistry.

phenyl ethanol using microwave irradiation. It was observed that the high activity of the polymer Cd(II) complex, in the following conditions (1.67 M of substrate, 3.3×10^{-3} M of catalyst, 3.3 M of *t*-BuOOH 70%, acetonitrile as solvent, and MW irradiation of 5 W for a temperature of 50 °C) was able to achieve a high product yield (benzaldehyde + benzyl alcohol) of 39.5% after only 1 h of irradiation with high selectivity to benzaldehyde of 92%. When the reaction was left for longer periods (3 h) the total yield did not increase exponentially reaching only a value of 49.1%. An interesting study was the effect of the solvent, since in the same conditions the solvent-free reaction could only achieve 21.8% yield. When compared to the use of conventional heating to microwave irradiation, the first was able to achieve a total yield of 68% but with a longer reaction time of 24 h resulting in a TOF significantly lower than what was obtained using the microwave. The recycling test of the catalyst was also conducted, and it was observed that after 5 cycles the activity of the catalysts decreased for ca. 30% of the total yield, which occurred until the third cycle stabilized afterward.

The same authors³⁵ reported the study of the same class of ligands, aroylhydrazone Schiff bases, applied this time with vanadium(V) as the metal center (Figure 5). When the complexes were applied in this reaction, they achieved a maximum yield of 19 and 23%, respectively, with the main product this time being benzoic acid. The condition of this study differs from the previous report with Cd(II) since no microwave irradiation was tested, and the overall conditions were a bit harsher (20 μmol of complex, 4:1 oxidant:toluene, 80 °C and 6 h reaction). This change of the reactions could lead to an overoxidation of benzaldehyde to benzoic acid since

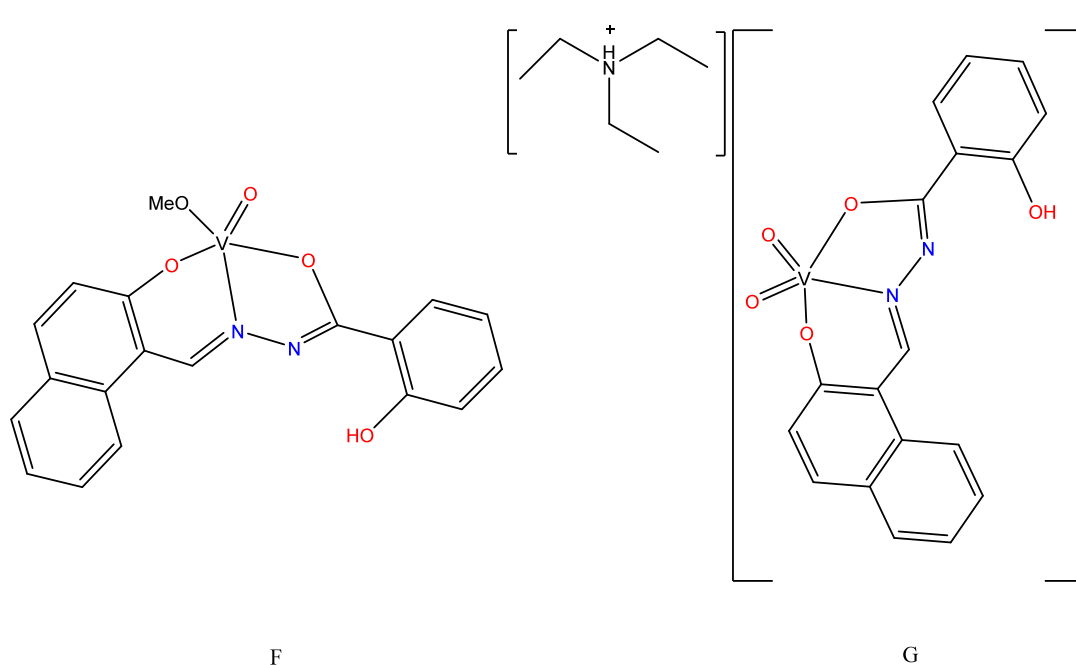


Figure 5. Representation of the vanadium aroylhydrazone Schiff bases complexes F and G. Adapted with permission from ref 35. Copyright 2022 Elsevier.

from the information in the report the peak of selectivity to benzaldehyde ($\pm 62\%$) for complex F occurred between the 30 and 60 min of reaction. Unfortunately, at that short reaction time, less than 5% conversion would have been obtained. The complexes were also heterogenized on MIL-100(Fe) and compared to the homogeneous results. It is possible to observe a decrease in the conversion of toluene (ca. 50%) but a slight increase in the selectivity toward benzaldehyde (of 3 and 12%). The stability of the heterogeneous catalysts was also tested; interestingly, F@MIL-100(Fe) showed a higher activity loss (74%) than G@MIL-100(Fe) (39%) over 3 cycles. This loss of activity was explained by leaching of the vanadium active species during the reactions.

In 2020 Lapa et al.³⁶ reported the use of gold C-scorpionate complexes as precatalysts for the oxidation of toluene. This system, like previous homogeneous systems, benefits from acidic conditions having reported as best conditions the following: catalyst precursor (Figure 6, H) (10 μmol), H_2O_2 (30% aq):toluene ratio of 2, acetonitrile as the solvent, 80 $^\circ\text{C}$, $n_{\text{acid}}/n_{\text{cat}} = 70$ (HNO_3 cc.). By applying these conditions with catalyst 1 it was able to achieve in the best conditions a total

yield of 8.1% with 82% of selectivity to the benzaldehyde after 6 h.

In the same year Xiao et al.³⁷ prepared several ZIF-67 with different morphologies and applied them to the oxidation of toluene using molecular oxygen. The system used a known cocatalyst for this reaction, *N*-hydroxyphthalimide (NHPI), and a solvent already used in some studies reported here, hexafluoropropan-2-ol (HFIP). The catalyst with the best performance was ZIF-67-24, which was able to convert 87.9% of toluene in 4 h of reaction at 40 $^\circ\text{C}$. The selectivity to the benzaldehyde is relatively lower 66.9%. The reaction could be performed under air, instead of pure oxygen, which leads to a decrease in the conversion of toluene (63%) but an increase in selectivity to benzaldehyde, 70.7%, and a change in the byproduct produced. Under the production of air, the main product is the benzyl alcohol, while under oxygen the main product is the overoxidized product of the reaction, the benzoic acid. The reusability of the catalyst showed a loss of activity decreasing the conversion to 72.4% and in the third cycle even more to a total of 54.1%. This loss of activity the authors believe may be caused by the formation of benzoic acid, since the catalyst also is destroyed in the presence of other acids like acetic acid.

In 2021 Sutradhar et al.³⁸ used a cubane-derived form of (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide copper complex in the liquid oxidation of toluene. This study reported two very interesting results and insight into the copper catalytic system of this reaction. The first result was a total yield of 11% which was obtained after 3 h at 80 $^\circ\text{C}$ when the reaction was performed with 20 μmol of catalyst using H_2O_2 30%, as oxidant, and HNO_3 ($n_{\text{acid}}/n_{\text{cat}} = 25$) as cocatalyst. In this case, the main product was the cresol (67% selectivity), the result of the oxidation on the aromatic ring. When the same conditions were utilized but the catalytic load was decreased to 2.5 μmol a shift in the reaction selectivity occurs. A total yield of 6.5% was obtained, but the main product this time, with a selectivity higher than 90%, was the benzaldehyde. This shows an

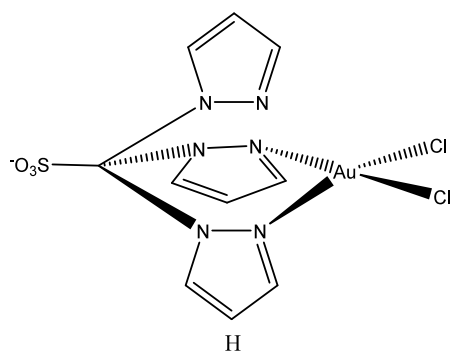
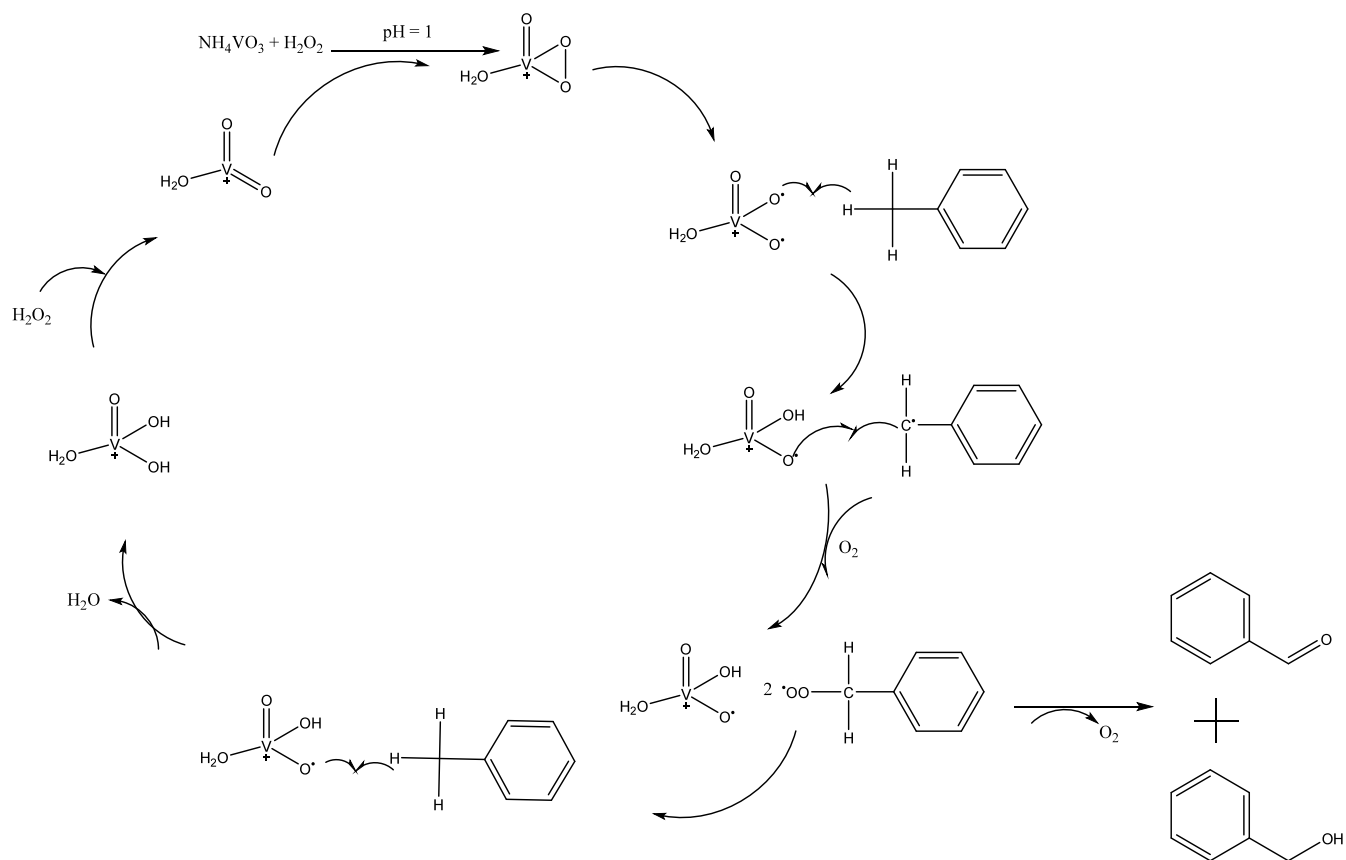


Figure 6. Representation of the gold C-scorpionate complex H. Adapted with permission from ref 36. Copyright 2020 Elsevier.

Scheme 4. Proposed Radical Mechanism by the Authors for the Oxidation of Toluene⁴

⁴Adapted with permission from ref 39. Copyright 2021 MDPI.

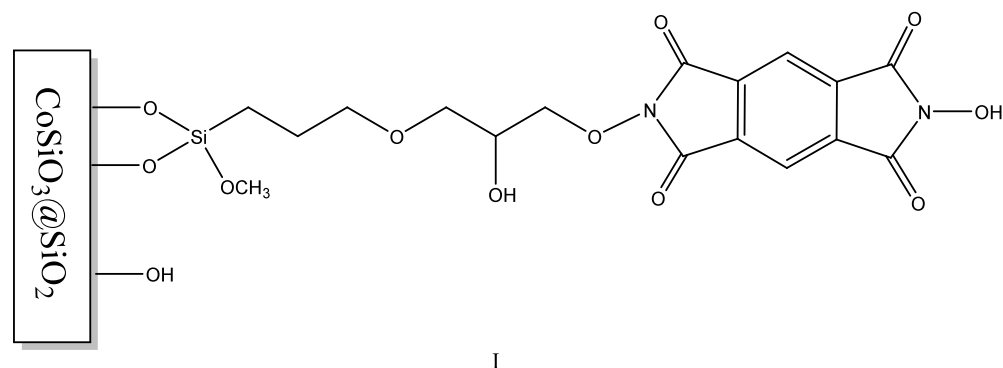


Figure 7. Representation of catalyst I. Adapted with permission from ref 41. Copyright 2021 Elsevier.

interesting aspect of the catalyst's ability to tune its selectivity with the increment or decrease of the load in the reaction.

In the same year Valentini et al.³⁹ studied the efficiency of this reaction when performed in water forming a biphasic system. This system was comprised of the toluene which worked as substrate and cosolvent and the application of the metal salt NH_4VO_3 in conjunction with KF. The oxidation was tested using H_2O_2 as an oxidant and under an oxygen atmosphere. Several conditions during optimization were tested such as the amount of catalyst, temperature of the reaction, air atmosphere, and other salts, among others. In the end, for a 20 mL volume reaction with a ratio toluene:water of 1 v/v, the reaction could be either performed at 25 or 60 °C in the presence of 50 or 20% of catalyst (molar base to the

oxidant), respectively, and it could achieve a benzaldehyde yield of 30% in 24 h. This result is considered very interesting since the authors claimed that either benzoic acid or benzyl alcohol was not detected during the process. The mechanism proposed by the authors, like many others, is radical and it is presented in Scheme 4. The process starts with the formation of the vanadium(V) peroxide complex (1) which is known to occur when the catalyst is dissolved in acidic water. After the formation of the new species, the homolytic cleavage of the O–O bond from the oxidant occurs leading to the formation of 2. This new species can abstract the H from toluene forming the benzyl radical and the new vanadium complex (3). The formation of the benzyl peroxy radical occurs afterward, through the reaction of the O_2 dissolved in the solution with

the newly formed benzyl radical. The coupling of two benzyl peroxy radical leads to the formation of benzaldehyde, benzyl alcohol, and O_2 through a previously established mechanism.⁴⁰ The formed benzyl alcohol is then immediately oxidized to benzaldehyde through a similar radical pathway, passing through H-abstraction from the OH group.

Shi et al.⁴¹ presented the possibility of aerobic oxidation of toluene to benzaldehyde by the cobaltous ions and NHPI supported over a silicate material **Figure 7**. The new catalyst (**I**) was tested for the oxidation of toluene as well as the constitution parts of the catalyst to evaluate the synergy between them. The reaction was performed using HFIP as the solvent and 2 MPa of oxygen and kept for 5 h at 90 °C. The reaction performed with NHPI, the linker (3-(glycidoxypropyl) trimethoxysilane (GPTMS)), SiO_2 , and $Co(OAc)_2$ altogether could convert only 14.1% of toluene with a benzaldehyde selectivity of 73%. Catalyst **I**, composed of all the same components as the previous test, was able to achieve a conversion of toluene much higher of 42.5% but with a decrease of selectivity to 52.6% and the formation of benzoic acid. This increase in the conversion showed that the combination of NHPI and the Co^{2+} ions is more effective when supported together than when supported in their homogeneous state. An interesting aspect of this reaction was the effect of the temperature. When the temperature is 50 °C or below the conversion of toluene is very slim (2.3%) increasing exponentially at 70 °C reaching 27.9% with good selectivity toward benzaldehyde 64%. The continuous increase in temperature up to 110 °C leads to an increase in conversion up to 52% but at the cost of the benzaldehyde selectivity, which decreases to 36% in favor of the formation of benzoic acid. The reusability tests revealed an important decrease in conversion between the first and second cycle which the authors attributed to the desorption of physisorbed NDHPI which was not washed totally during the synthesis. After that, until the fifth cycle, the catalyst maintained an almost similar conversion of toluene ca. 30% with a selectivity toward benzaldehyde of 55%.

A similar system was reported in the same year by Xu et al.,⁴² where cobalt oxides were supported over SiO_2 and tested in conjugation with NHPI, molecular oxygen, and HFIP. In a reaction of 8 h at 30 °C this system was able to convert 98.5% of toluene with a significantly high selectivity to benzaldehyde of 62.5% with the main secondary product being the benzoic acid. This result was obtained with 0.15 mmol of NHPI, 1 atm of O_2 , and 0.6 g of the prepared catalyst. This result was considered the best by the authors, but another very interesting one is the one obtained at only 4 h and in the presence of 0.15 g of catalyst. In the last conditions although only 68.5% of the toluene is converted, the selectivity of the benzaldehyde is still higher (64.8%) with the main byproduct in this instance being the benzyl alcohol. Not only did this condition avoid overoxidation but also achieved a very good conversion with less catalyst and in less time. The authors also demonstrated the reusability of the catalyst prepared by different methods, and the one reported here by coprecipitation was able to make 3 catalytic cycles without losing any activity.

Alegria et al.⁴³ studied the ultrasound and photoassisted oxidation of toluene using oxidovanadium(V) complex (**J**), **Figure 8**. The study compared different energy inputs from photo to conventional heating including ultrasonic bath and probe. The reactions were performed in the presence of 10 μ mol of catalyst, a 2:1 ratio H_2O_2 :toluene, and a small addition

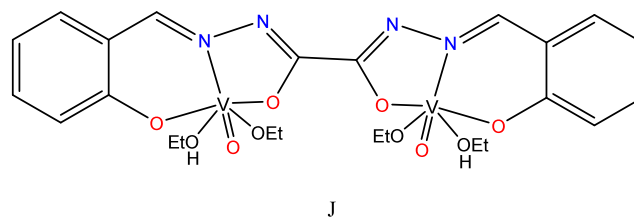


Figure 8. Representation of the oxidovanadium(V) complex, catalyst **I**. Adapted with permission from ref 43. Copyright 2022 Elsevier.

of HNO_3 ($n_{acid}/n_{cat} = 25$). The photo and ultrasonic reactions were performed at room temperature, and the final temperature did not pass 35 °C, while the conventional heating achieved its best result at 80 °C. When comparing the results, it is possible to observe the dominance of the ultrasonic reaction with the probe (6.2% total yield and 67% selectivity to benzaldehyde) and bath (5.4% yield and 61% selectivity) achieving high yields in a short reaction time (0.5 and 1 h, respectively) at room temperature. Compared to conventional heating, it has achieved a similar yield, 7.6%, with a slightly higher selectivity of 75% toward benzaldehyde but only after 6 h and at 80 °C.

The liquid phase oxidation of toluene using nickel nanoparticles was tested by Ádám et al., in 2022.⁴⁴ The nickel particles were shown to be crystalline and possess three different crystal phases (hcp, fcc, and fcc+hcp). All were tested as catalysts for the oxidation of toluene under the following conditions: 5 mL of toluene, 0.5 mL of water (additive), 6 mg of catalyst, and 50 mg of phenyliodine(III) diacetate (PIDA), under reflux for 60 min. Outstandingly all of the phases achieved full conversion of toluene, and although having similar behavior in terms of activity to convert toluene, the different phases were shown to have different selectivities in the reaction. For instance, an fcc Ni-NP favors the formation of benzyl alcohol (82%) with the rest being benzaldehyde, while the hcp Ni-NP were shown to be more active in oxidation being the major product from the benzoic acid (55%). It was important to analyze the stability of the Ni-NP, and it was reported that after the reaction both the fcc and mixed-phase recrystallized into an α -Ni(OH)₂/ β -Ni(OH)₂/fcc Ni mixture, while the hcp Ni phase completely transformed into the fcc-phase counterpart. These transformations were also possible to observe on the recycling tests performed since there were changes in the selectivity for the products, although maintaining the full conversion of toluene. In the end, the three forms are unable to become selective for benzaldehyde, with its yield being almost constant in all 3 catalysts (between 15 and 20%).

In 2023 Deng et al.⁴⁵ investigated the possibility of the selective oxidation of toluene in the liquid phase using as a catalyst a Mn@ZIF-8 derived material. This system is contrary to most of the ones reported before application of a high temperature of 180 °C under an O_2 pressure of 1 MPa for two and half hours. The reaction performed solvent-free was able to convert 6.5% of toluene with only a 31.6% selectivity for the benzaldehyde. This is followed by benzyl alcohol being the major product obtained with 38.7%. One interesting aspect of this report is the influence of the calcination temperature. At lower temperatures as 300 °C, the catalyst presents the highest activity previously reported. When this temperature is increased to 500 or 700 °C, the conversion of toluene drops to half, 3.4%, but the selectivity toward benzaldehyde increases

from 31.6% to 46.0%. The recyclability of the catalyst was evaluated over 5 cycles, in which it was observed that the catalyst was able to maintain its activity.

In the same year Long and co-workers⁴⁶ published the application of a polyoxometalate loaded on activated carbon (AC) as a catalyst for the oxidation of toluene by air. The reaction took place in an autoclave where toluene, the catalyst, and acetic acid were added. Then the system was pressurized at 2 MPa, air was introduced at 500 mL/min, and the system was maintained at 220 °C for 2 h. Several parameters such as pH during the synthesis, temperature, and metal ratios were optimized, and the best catalyst was $\text{Na}_{3.1}\text{La}_{0.7}\text{CoMn}_{0.3}\text{Mo}_{11.7}\text{O}_{40}\cdot 22.05\text{H}_2\text{O}@AC$. The catalyst was able to convert 13.2% of toluene with a benzaldehyde selectivity of 40.43%. These last two reports represent a step down in terms of energy consumption since they apply very high temperatures without resulting in outstanding results.

The conjugation of HFIP and NHPI was again reported by Zhang et al.⁴⁷ In 2023, Co-Mn-Al oxides were used as catalysts for the oxidation of toluene using O_2 . The reaction took place at 50 °C for 20 h with an oxygen flow of 18 mL/min, and five different oxides with different compositions were screened (Co_4Al , Co_3MnAl , $\text{Co}_2\text{Mn}_2\text{Al}$, CoMn_3Al , Mn_4Al). The most active catalyst was CoMn_3Al with the bioxides being the least active, showing the importance of the presence of multiple metals for this system. CoMn_3Al was able to convert 81% of toluene after 20 h of reaction with a benzaldehyde yield of 47%, 15% of benzoic acid, and the rest into benzyl alcohol. The stability of the catalyst was evaluated by multiple catalytic cycles. The conversion of toluene was relatively the same over the cycles varying between 52% and 40%, but the most interesting aspect was the product distribution. Over the cycles, it is possible to observe changes in the distribution which does not follow any specific rule; sometimes the benzoic acid yield increases (2nd), the following is the benzaldehyde (3rd), and even benzyl alcohol (5th). This shows a bit of fluctuation in the system, and some surface analyses could shed light on this factor.

Another example of a multicomponent catalyst was reported by Liu et al.⁴⁸ and tested in a solvent-free oxidation of toluene. The new catalyst was prepared by supporting $\text{Co}_2(\text{PO}_4)\text{Cl}$, ZrO_2 , P_2O_5 , and WO_3 into the ZSM-5 zeolite. The reaction took place at 90 °C for 8 h, and H_2O_2 30% aq. was added in a proportion of 250 toluene/oxidant mols. In the best conditions, the catalyst can convert 16.6% of toluene with an outstanding selectivity to benzaldehyde of ca. 90%. The stability of the catalyst was also evaluated. The first 3 cycles maintained the same activity being able to maintain its conversion and selectivity; however, the fourth and fifth cycles demonstrated a decrease in conversion while keeping the high selectivity to benzaldehyde. This decrease is attributed to the small amount of catalyst recovered since no adjustments in the reaction quantities were made afterward. In a sense of value, the conversion is lower but if the authors were to calculate the specific activity of the catalyst it would be higher or remain stable.

■ PHOTOCATALYSIS

Photocatalytic systems have been known to be systems with very low energy input and in which the reaction tends to be performed with high selectivity to the desired product. The treatment of effluents has been one of the main focuses for the application of this technology,⁴⁹ and several companies like

Novartis, Pfizer, and Merck among others have been developing methodologies and technology to scale up the application of this new synthesis method to be incorporated and substitute some currently utilized processes.⁵⁰

In 2016 Yuan et al.⁵¹ reported the application of doped Bi_2WO_6 with palladium as an active catalyst for the photooxidation of toluene. The authors first tested the different structures that Bi_2WO_6 could form depending on the pH during its synthesis and found that the flower-like structure was the most active among the other three structures. This structure was able to convert 1.47% of toluene with a high selectivity toward benzaldehyde of 92% (representing production of $500 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$), while the others achieved less than 1% of conversion. The loading of a cocatalyst onto a photocatalyst is an effective means to enhance the photocatalytic performance by improving the charge separation efficiency.⁵² It improves the catalytic activity and stabilizes the overall process, allowing it to have a higher cycle rate while maintaining its original structure. The doping with 0.1 wt % of palladium resulted in an increase in the toluene conversion to 3.42%, maintaining its high selectivity toward benzaldehyde. With a 300 W Xe lamp with a light cutoff at 400 nm, 1 atm of O_2 and after 5 h the benzaldehyde production was $1140 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$. The catalyst in the end has proven to be stable up to 7 cycles, stabilizing its activity after the third cycle with a small decrease in the activity but always maintaining its high selectivity.

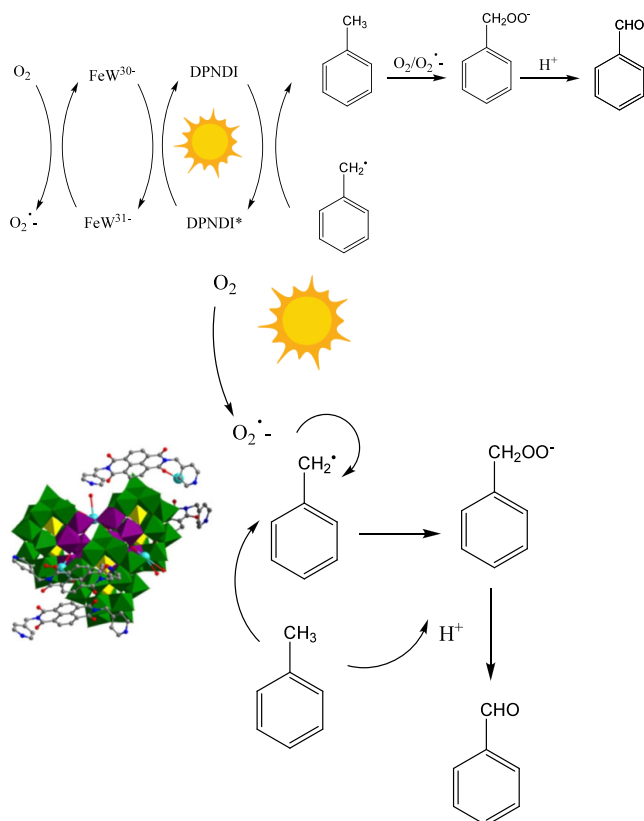
Cai et al.⁵³ published in 2019 the synthesis of Bi_2MoO_6 nanosheets and their application as photocatalysts in the oxidation of toluene under visible light. Two types of nanosheets prepared with water ($3\text{-}1 \mu\text{B}\text{O}$) and with ethylene glycol ($3\text{-}1 \text{BMO}(\text{EG})$) were presented in this study. The catalytic system used benzotrifluoride as a solvent, a flow of oxygen of 3 mL/min, and a 300 W Xe lamp with a 400 nm cutoff. The catalysts $3\text{-}1 \mu\text{B}\text{O}$ and $3\text{-}1 \mu\text{B}\text{O}(\text{EG})$ were able to achieve a conversion of 10.2 and 12.7%, respectively, both with high selectivity toward benzaldehyde (over 95%). The highest production obtained was $778 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$ for $3\text{-}1 \mu\text{B}\text{O}(\text{EG})$ in the standard conditions and $708 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$ when the reaction was performed without solvent. During the tests in which they were compared with the nanosheet produced with Na_2MoO_4 (BMO), it was observed that the conversion of these photocatalysts follows an order of $\text{BMO} < 3\text{-}1 \mu\text{B}\text{O} < 3\text{-}1 \mu\text{B}\text{O}(\text{EG})$ independent of solvents applied. This trend is parallel to the importance of the thickness of Bi_2MoO_6 sheets in which the thinner the sheets, the higher the catalytic activity. In the end, the recycling properties of $3\text{-}1 \mu\text{B}\text{O}(\text{EG})$ were tested, and after 5 cycles it maintained its activity and morphology.

Ding et al.⁵⁴ reported in 2019 the synthesis of the heterostructure, Bi_2MoO_6 quantum dots (QDs) supported on graphitic carbon nitride nanosheets. The structures were synthesized with different Bi_2MoO_6 QDs mass ratios between 10 to 30%. The best catalyst was revealed to have a mass ratio of 20% (BMCN-20) and achieved a production of benzaldehyde of $850 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$, equivalent to a toluene conversion of 1.26%. BMCN-20 was revealed to have the highest BET-specific surface area and porous structure among the catalysts which contributed to an enhancement of photocatalytic properties by displaying more active sites. The reaction was performed in a solvent-free way, with a flow of O_2 of 3 mL/min, and the visible light had a cutoff at 400 nm. The recycling tests showed the stability of the catalyst in terms of

activity and the ability to maintain the same production and selectivity over consecutive cycles.

In 2020, Li et al.⁵⁵ reported the application of a hybrid polyoxometalate $K_6(H_2O)_8H_{24}(C_{26}H_{16}N_4O_4)_8-[P_6W_{48}Fe_6O_{180}] \cdot 6H_2O$ (FeW-DPNDI) as a photocatalyst for the oxidation of toluene using O_2 under mild condition. The catalysts took advantage of the interactions between anion $\cdots\pi$, C–H \cdots O hydrogen bonds, and electrostatic interactions between the $[P_6W_{48}Fe_6O_{180}]^{30-}$ anion and π -acidic DPNDI skeletons. This leads to an easier charge transfer achieving the activation of molecular oxygen under mild conditions and consequently the oxidation of the C–H bond. In this system, white light was utilized as an energy source (peak wavelength at 450 nm and intensity of 320 mW/cm²), and the reaction occurred in the presence of acetonitrile as the solvent, O_2 as oxidant, and 2 mol % of catalyst for 24 h at room temperature. The result obtained was very impressive with a conversion of 63% and a selectivity over 99% (66 $\mu\text{mol/g}_{\text{cat}} \cdot \text{h}$) toward the benzaldehyde, which the authors reported being the highest when compared with other systems^{56–58} which achieved 25/91, 2.1/98.8, and 70.1/19.3 conversion/selectivity, respectively. The high selectivity of this system could be due to the presence of the Fe(III)-Lewis site, as explained by the authors. The catalyst was reused for 5 cycles after washing and drying, and it maintained its selectivity toward the benzaldehyde only with a slight decrease in the conversion of toluene. The two proposed mechanisms for the reaction are presented in Scheme 5. The first mechanism involves the excitation of DPNDI, acting as a photosensitizer under white light and

Scheme 5. Proposed Mechanisms by the Authors for the Photo-Oxidation of Toluene^a



^aAdapted with permission from ref 55. Copyright 2020 Elsevier.

generating DPNDI* holes. This led to the activation of toluene, resulting in the formation of a cationic. During the substrate reaction, a photoinduced electron transfer occurred, leading to the production of FeW^{31-} . Simultaneously, O_2 was reduced to a superoxide radical, namely, $O_2^{\bullet-}$. Consequently, either $O_2^{\bullet-}$ or O_2 reacted with the cationic radical, resulting in the generation of benzaldehyde. The second proposed pathway involves FeW-DPNDI as an n-type semiconductor. The photogenerated electrons on the conduction band reduced O_2 to $O_2^{\bullet-}$ radicals, while holes on the valence band activated toluene. The resulting cationic radicals reacted with $O_2^{\bullet-}/O_2$ to form benzaldehyde.

Yin and co-workers⁵⁹ published in the same year the synthesis and application of octahedral CdS-ZnS composites (Figure 9) with high photocatalytic activity on the selective

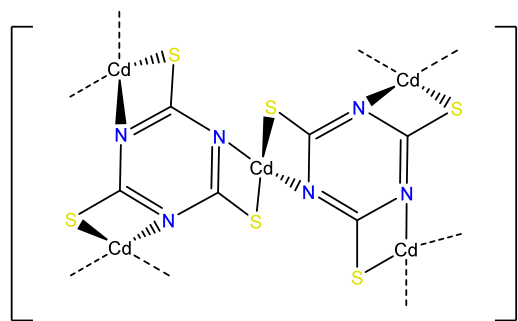
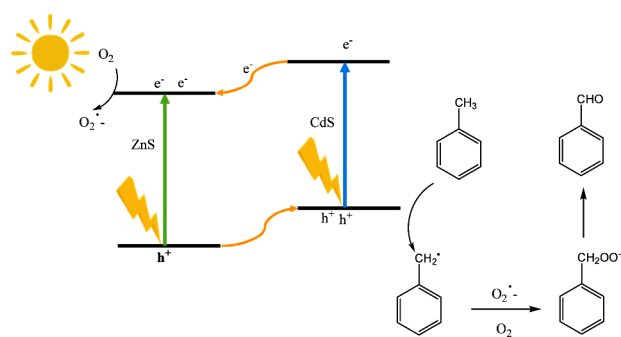


Figure 9. Representation of a unit cell of the CdS-ZnS composite. Adapted with permission from ref 59. Copyright 2020 American Chemical Society.

oxidation of toluene. The system reported used a 300 W Xe lamp as a light source, and O_2 was bubbled into the mixture (toluene + catalyst) at a rate of 3 mL/min. Four different catalysts (using various CdS:ZnS mass ratios CZ-1 10.9; CZ-2 4.79; CZ-3 2.80 and CZ-4 1.00) were tested under those conditions. The best result achieved was obtained in the presence of CZ-2 where the catalyst achieved a conversion of 1.68% (corresponding to a production of 1078 $\mu\text{mol/g}_{\text{cat}} \cdot \text{h}$). This result was achieved after 3 h under the light and corresponded to a benzaldehyde selectivity of 98%. The correspondent sources of Cd and Zn only achieved 664 and 195 $\mu\text{mol/g}_{\text{cat}} \cdot \text{h}$ respectively demonstrating the importance and the impact of the synergy of both metals in the reaction. The catalyst CZ-2 was recycled up to 5 catalytic cycles, maintaining its activity, morphology, and phase structure conforming to its stability. The stability and activity of the composite are attributed to two important factors. The junction of the two metals allows protection of CdS from photocorrosion and on the other hand prevents the release of S^{2-} achieved by covering ZnS on the surface of CdS. Finally, the author conducted a free-radical-capture experiment which resulted in the proposed mechanism of Scheme 6.

The immobilization of vanadyl acetylacetonate over graphitic carbon nitride was studied by Verma et al.,⁶⁰ in 2016 followed by its application as a catalyst for C–H activation. The most active catalyst VO@g-C₃N₄ (10% (v)) was tested in the oxidation of several cycle alkanes, including toluene. When applied in the optimized conditions, (substrate (1 mmol), VO@g-C₃N₄ (25 mg), H₂O₂ (1.5 mmol), acetonitrile as solvent 40 W domestic bulb at room temperature), it has achieved an isolated yield toward benzaldehyde of 94%. The

Scheme 6. Simplification of the Mechanism by the Authors for the Photo-Oxidation of Toluene^a



^aAdapted with permission from ref 59. Copyright 2020 American Chemical Society.

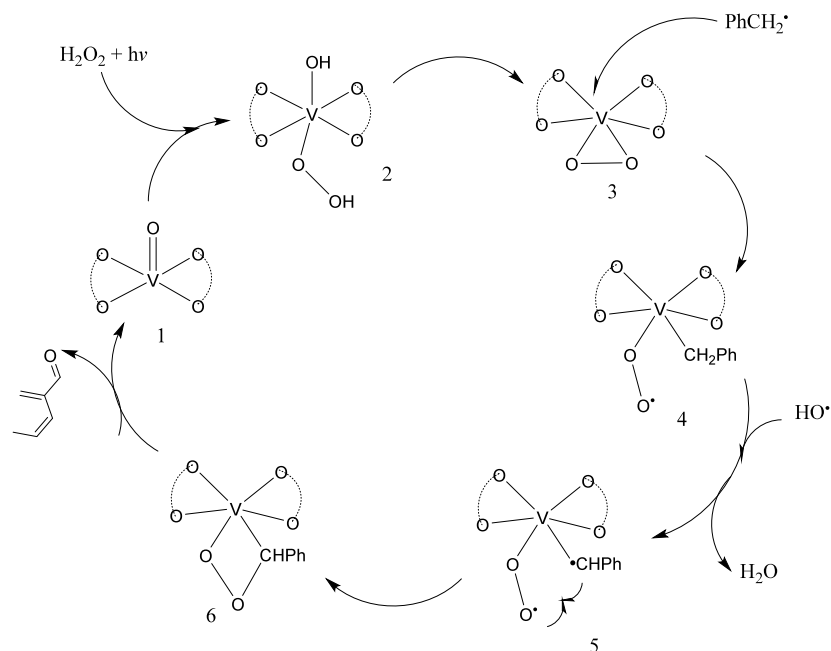
authors proposed a possible mechanism (Scheme 7) for the active catalyst and this reaction. The reactional pathway would involve the decomposition of H_2O_2 , with light, into radicals HO^\bullet , H^\bullet , and HOO^\bullet . The HO^\bullet radical would then abstract a proton from the toluene creating the alkyl radical PhCH_2^\bullet . In the catalyst, the H_2O_2 would first coordinate with the metal complex and create the intermediary oxirane analogue of vanadium (3). This new species could be attacked by the alkyl radical. A hydroxy radical HO^\bullet would then abstract the proton from the alkyl radical now coordinated (5) and by a rearrangement and elimination (6) mechanism form the benzaldehyde as a product leaving the metal complex and regenerating to its original form (1).

In 2020 Qiu et al.⁶¹ reported a new $\text{BiOCl}/\text{BiCl}_3\text{Br-CTA}$ heterostructure and its photocatalytic application for the selective oxidation of toluene. The heterostructure is composed of BiOCl nanoplates and the organic layer $\text{BiCl}_3\text{-Br-CTA}$ and possesses an abundance of oxygen vacancies

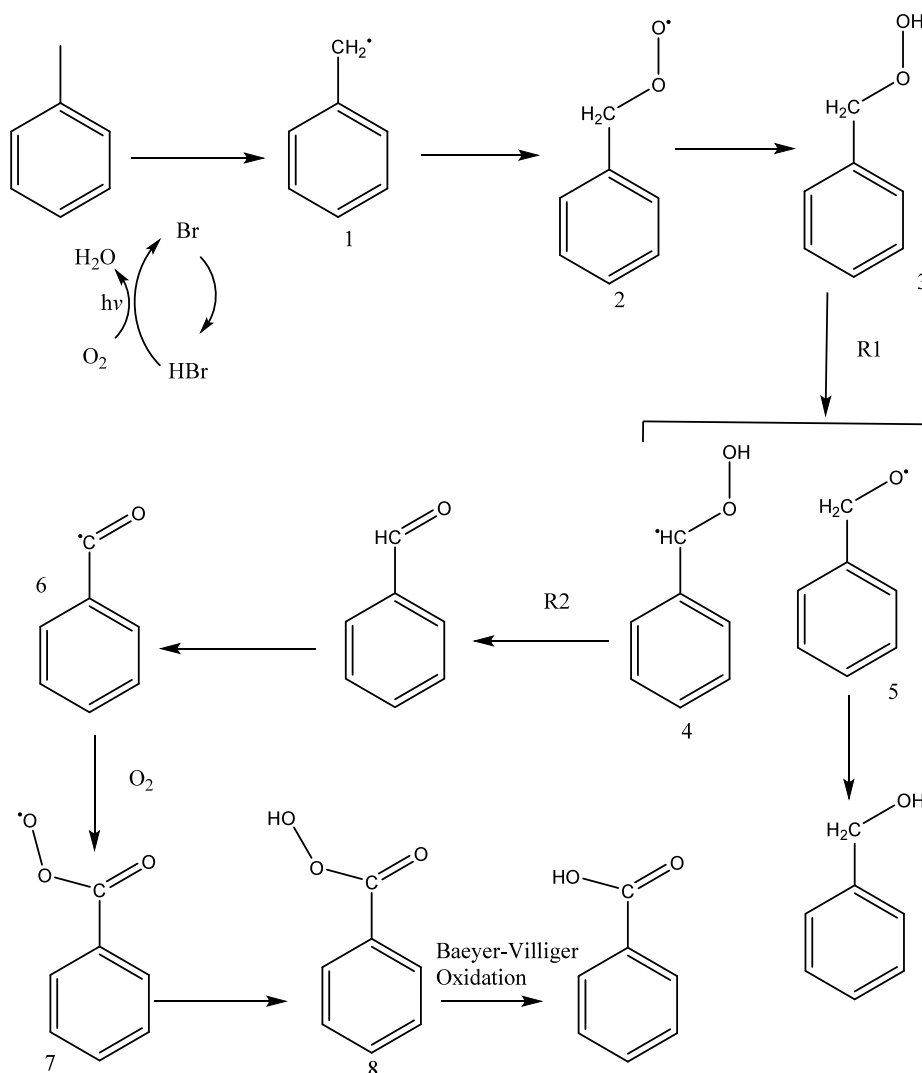
which combined with broad light absorption and enhanced electron–hole separation efficiency allows the absorption and activation of O_2 and toluene. The reaction was performed in the presence of a 6.5 mol % catalyst in acetonitrile under an O_2 atmosphere (approximately 1 atm) and full-spectrum irradiation or visible light ($\lambda > 400$ nm) for a total of 6 h. Different parameters were optimized during the work, and two highlighted since were found to produce very interesting effects. The catalyst preparation utilized different surfactants in its synthesis, and their impact on the catalytic outcome was observed. Most of the catalysts could not achieve a conversion of toluene over 10% besides the one prepared with CTAB, which proved to be the most active with a conversion of toluene of 31.6% (Bz production of $527 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$). This result proves that the other surfactants such as octadecyltrimethylammonium chloride (OTAC), sodium laurylsulfonate (SDS), and poly(vinylpyrrolidone) (PVP) did not enhance the photocatalytic activities of the BiOCl nanoplates. The second important factor highlighted was the influence of the optical power density. When this parameter was increased from 200 to $400 \text{ mW}/\text{cm}^2$, it allowed a higher conversion of toluene (31.6 vs. 44.8%) without loss of the selectivity to benzaldehyde, which during the study remained over 99% (final Bz production of $747 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$).

The same group published in the same year⁶² an iron-doped Bi_2/WO_6 photocatalyst which followed a previous study reported here by Yuan et al., where the doping of palladium enhanced the catalytic activity of the catalyst. As in the previous report by this group, a similar system was applied but with a lower oxygen flow of only 1 mL/min and a 300 W Xe lamp with a light cutoff filter at 420 nm for 5 h. Several catalysts with different loads of iron were prepared $\text{Fe}(x)\text{-BWO}$ ranging from ($x = 0.10$ up to 1.04 mol % of iron). The $\text{Fe}(0.26)\text{-BWO}$ catalyst was shown to be the most active under these conditions, achieving 1.35% of toluene conversion with

Scheme 7. Mechanism Proposed by the Authors for the Photo-Oxidation of Toluene Using $\text{VO}@g\text{-C}_3\text{N}_4$ ^a



^aAdapted with permission from ref 60. Copyright 2016 American Chemical Society.

Scheme 8. Mechanism Proposed by the Authors for the Photo-Oxidation of Toluene using HBr^a 

^aAdapted with permission from ref 66. Copyright 2021 Elsevier.

96.8% of selectivity. The continuous increase of the iron load did not increase the conversion of toluene as expected from the photoluminescence studies. The emission intensity of Bi_2/WO_6 is the strongest, whereas $\text{Fe}(0.26)\text{-BWO}$ is the weakest, indicating that Fe doping in Bi_2/WO_6 can effectively inhibit charge recombination. The other catalysts also presented a high emission intensity as the Bi_2/WO_6 . Further analyses were performed and were presented in the supplementary information, which validates the catalytic results obtained. The stability and recyclability of the catalyst were tested over 5 cycles and compared to the Bi_2/WO_6 . The $\text{Fe}(0.26)\text{-BWO}$ shows higher stability stabilizing after 3 cycles, and when analyzed by XRD, SEM, and ERS, the doped iron catalyst was still able to conserve its flower-like structure, while Bi_2/WO_6 had completely lost its structure after the 5 cycles. In the end, this system was able to achieve a Bz production of $1303.8 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$.

Another photocatalytic system that took advantage of generating more oxygen vacancies in semiconductors was reported by Li et al.⁶³ This system utilizes Pd nanoparticles 1 wt % deposited on BiOBr nanosheet-assembled structures as catalysts under UV-vis irradiation ($200 \text{ mW}/\text{cm}^2$) in

acetonitrile for 5 h and using molecular oxygen atmosphere as the oxidant. The load of Pd was investigated, and similar to what was reported by the Benxia Li group to the iron doped behavior follows a "Gaussian" curve where it starts by increasing the conversion of toluene reaching its maximum in this case at 1% and then starts to decrease. In this report, the authors claimed the decrease in activity was due to an increase in the palladium nanoparticles sizes which led to a decrease in the active sites available. One other interesting effect is the irradiation intensity, which was above $300 \text{ mW}/\text{cm}^2$, led to a decrease in the conversion of toluene probably due to the plasmonic effect on the Pd-NP generating a reverse flow of electrons into the semiconductor unlike what was reported earlier in the case with the $\text{BiOCl}/\text{BiCl}_3\text{Br-CTA}$ catalyst. In the optimized conditions, the catalyst achieved production of $476.8 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$ with the only product being the benzaldehyde. This corresponded to a conversion of 23.8% which is considerably high when compared to other photocatalytic systems but with a lower production since the ratio catalyst substrate is very high. When this ratio is decreased, the conversion decreases to 1.6%, but the production rate increases up to $6022 \mu\text{mol}/\text{g}_{\text{cat}}\cdot\text{h}$, one of the highest values reported.

Lastly, like the other heterogeneous catalysts, this system was shown to be stable for up to 5 cycles maintaining its structural integrity and its activity.

A nitrogen-modified Nb₂O₅ nanomesh material was reported by Su et al.⁶⁴ as an active visible light photocatalyst for the selective oxidation of toluene. The study compared the new material with its commercial counterpart Nb₂O₅ and other modified nanomeshes with different elements such as sulfur and phosphorus. The Nb₂O₅-N was overall the most active of the catalysts achieving 4× more conversion than the second-best at 1.56% conversion (using 6W LEDs centered at 455 nm, O₂ 1 atm, 12 h, and 40 °C). When compared to the commercial material, the production is 37 times higher (0.66 vs 25 μmol/g_{cat}·h), but when compared to previous reports, the conversion and production obtained are considerably lower mainly due to the longer reaction time where the average is normally 5 h.

In 2021 Tan et al.⁶⁵ reported the application of a CdIn₂S₄-CdS composite as a catalyst taking advantage again of the defects induced this time by the sulfur vacancies. This composite was able to convert 50.9% of toluene only after 2 h and 80.3% after 6 h in the presence of acetonitrile as a solvent, an oxygen atmosphere, and with a 300 W Xe lamp with a 420 nm cutoff. The composite was able to maintain a selectivity toward benzaldehyde over 95% during the process. The CdS and CdIn₂S₄ materials part of the composite, were also tested and showed some activity, achieving a conversion of 15.6 and 24.7% respectively. This result shows the benefit of the junction of the two parts and the synergy created, allowing for higher activity and conversion. The CdIn₂S₄-CdS catalyst achieved a high production rate when compared to other photocatalytic systems (1201 μmol/g_{cat}·h at 2 h and 631 μmol/g_{cat}·h at 8 h).

In the same year, Kaboudin and co-workers⁶⁶ studied the performance of tetrabutylammonium tribromide (TBATB) as the catalyst and two different LED lights, blue (430 nm) and violet (400 nm), as sources for the oxidation of toluene under an O₂ atmosphere. After optimization of the reaction conditions such as solvent and amount of catalyst, TBATB performed well under both the blue and violet light resulting in a conversion of toluene of 61 and 84% only after 3 h, respectively. Although the violet sourced has a higher conversion, this value does not translate into a higher benzaldehyde yield; in fact, in both cases, the yield to benzaldehyde is similar, ca. 50%. The increment observed, in the total conversion, with the violet light is due to the increase in the benzoic acid yield, which went from 1%, when the blue light was used, up to 22%. The authors proposed a mechanism (Scheme 8) for the reaction which started with the bromide radicals produced via photodissociation of Br₂, being provided for the catalyst, which will react with toluene creating the benzyl radical. HBr, which forms during the activation of toluene, can further convert into the bromo radical through an aerobic photooxidation process. Initially, benzyl radical 1 can abstract molecular oxygen, resulting in the formation of peroxy radical 2. This peroxy radical 2 then abstracts hydrogen, leading to the production of benzyl hydroperoxide 3. At higher concentrations of benzyl hydroperoxide 3, the self-reaction (R1) becomes notably more likely than other reactions. Consequently, hydroperoxybenzyl radical 4 and benzyloxy radical 5 are generated. These radicals subsequently transform into benzaldehyde (R2) and benzyl alcohol, respectively. The aldehyde C–H bond in benzaldehyde, subject to dissociation

by free radicals that arise in the photooxidation reaction, can yield compound 6. The abstraction of O₂ by compound 6 leads to the creation of compound 7, which subsequently converts into perbenzoic acid 8 through hydrogen trapping. Finally, benzoic acid can be produced via a nonradical Baeyer–Villiger-type oxidation reaction.

As previously mentioned, Alegria et al.⁴³ screened a complex for the oxidation of toluene using alternative heating methods including photocatalyst. In the system, the catalyst was able to convert 3.9% of toluene in a 1 h reaction with a surprisingly high benzaldehyde production of 16302 μmol/g_{cat}·h.

In 2023 Singha et al.⁶⁷ studied the oxidation of toluene over WO₃ nanostructures (nanocubes (WNCs) hexagonal nanosheets (WNSs) and nanorods (WNRs)) driven by visible light. The new nanostructures (0.02 g) were tested using acetonitrile as the solvent under a white LED light and 0.1 MPa of O₂ to act as an oxidant. From the three structures, only the WNC showed activity for oxidation after 2 h of reaction. In these conditions, the catalyst was able to convert 1.3% of toluene with a benzaldehyde production of 650 μmol/g_{cat}·h. The conversion of toluene could be further increased to 3.9% when the reaction is left to react for up to 8 h with only a slight decrease in the selectivity for benzaldehyde (94.3%) leaving the production at 8 h 460 μmol/g_{cat}·h. Interestingly the catalyst tends to become more active under blue-light irradiation, being able to convert 2.3% of toluene with a benzaldehyde production of 1016 μmol/g_{cat}·h. This new activity comes with a bit of loss of selectivity since benzoic acid started to form to a higher extent having now 10.2% selectivity on the reaction. The use of the blue light over the white one also raised the temperature of the reaction from 30 to 45 °C.

In the same year, Bai et al.⁶⁸ reported a lead-free double perovskite ((DETA)BiBr₆/Cs₂AgBiBr₆, (DCABB), DETA³⁺ = NH³⁺(CH₂)₂NH²⁺(CH₂)₂NH₃₊) with photocatalytic properties and applied on the oxidation of toluene. The reaction took place in the presence of visible light, an oxygen atmosphere, and acetonitrile as the solvent, and after 2 h, the catalyst had converted 78.9% of toluene into benzaldehyde (3945 μmol/g_{cat}·h). This system reported a 92% selectivity for the benzaldehyde with benzyl alcohol as its only byproduct. The main product obtained with this catalyst changes when the reaction is performed for over 5 h with benzoic acid being now the majority product (60%) with benzaldehyde taking the rest in a full conversion of toluene. The stability of DCABB was evaluated by recycling tests. After 5 cycles the catalyst maintained its initial activity and selectivity, and the XRD of the used samples revealed that the structure remained largely intact.

A similar system was reported by Caruso and co-workers⁶⁹ where Cs₂AgBiBr₆ was supported over g-C₃N₄. The system applied a 500 W Hg(Xe)-lamp for 4 h under an oxygen atmosphere and acetonitrile as solvent. Three different composites (with different amounts of Cs₂AgBiBr₆ 10, 20, and 30 wt %) were prepared and tested for the oxidation of toluene. The best result was obtained with a wt % of 20 reporting a benzaldehyde production of 1088 μmol/g_{cat}·h, representing a selectivity toward the production of benzaldehyde of over 96%. The stability of the catalyst was evaluated, demonstrating stability up to three catalytic cycles and a continuous 12-h reaction. After 12 h the authors noticed a slowing in the conversion of toluene to decomposition of the perovskite triggered by the presence of water in the system. This shows the vulnerability of the catalyst for the application

of this reaction to the oxidation of an industrial stream since it is expected in the presence of water vapor.

Teixeira and co-workers⁷⁰ screened the application of single-atom catalysts, namely iron, and manganese, supported on poly(heptazine imide) (PHI). The photooxidation of toluene took place under an irradiation light of 410 nm and 100 W of power, oxygen atmosphere (1 atm), acetonitrile as a solvent, and sulfuric acid (10 μ L). Both iron and manganese catalysts were shown to be active for the oxidation of toluene with iron presenting a high conversion of 96% with 92% selectivity toward benzaldehyde (166 μ mol/ $g_{cat}\cdot h$) with a lower iron load (0.5%) after 20 h of reaction. For the manganese catalyst, a high benzaldehyde yield is obtained (86% of toluene conversion with 90% selectivity) in the presence of 1% of the metal load (w/w%) after 12 h of reaction. This system was able to achieve a final production of benzaldehyde of 152 μ mol/ $g_{cat}\cdot h$ and 166 μ mol/ $g_{cat}\cdot h$, for the Mn-PHI and Fe-PHI respectively.

Zeng et al.⁷¹ studied the effect that doping Ce over Bi₂MoO₆ could result in the photocatalytic activity of the catalyst. The doping of Ce introduced the redox ion pairs Ce³⁺/Ce⁴⁺ and generated oxygen defects in Bi₂MoO₆ responsible for increasing the activity of the catalyst in the presence of O₂ since it allows a better activation of the oxidant. The reaction was performed in a solvent-free system where oxygen flowed at 1 mL/min through a solution of toluene and the catalyst irradiated by a 300 W Xe lamp. The system could achieve a benzaldehyde production of 3745 μ mol/ $g_{cat}\cdot h$, representing a selectivity of 85% with benzyl alcohol being the secondary product produced. XRD and SEM analysis of the catalyst before and after cycles were important to understand the behavior of the catalyst in the recycling tests since a decrease in the toluene conversion rate was observed. This reduction is explained by the gathering of the nanosheets during the catalytic process decreasing the surface area and therefore the number of active sites.

The application of perovskite in this case CsPbBr₃ was again explored this time by Yi et al.,⁷² with support over a hierarchical TiO₂ nanoflake. The photocatalytic system applied acetonitrile as the solvent and visible light with a cutoff at 420 nm and 300 W of power. The authors started by studying the effect of the ratio toluene:solvent and reported as optimal conditions for this system a ratio 1:2 with a toluene conversion of 10200 μ mol/ $g_{cat}\cdot h$ and a benzaldehyde production of approximately 8600 μ mol/ $g_{cat}\cdot h$. Increasing the concentration of toluene, it starts by increasing the production of benzaldehyde due to the increased possibility of interaction between the toluene molecules and the photogenerated charges. However, the catalysts reach a "saturation" point where the existence of a high amount of toluene adsorbed in the catalyst slows the desorption of the products of the reaction and by that decreases the oxidation rate. The amount of catalyst was optimized next, and the blank tests of TiO₂ and CsPbBr₃ showed no or very low activity (a conversion rate of 520 μ mol/ $g_{cat}\cdot h$) respectively. The hybrid catalysts were able to achieve a higher production with 10% of CsPbBr₃ over TiO₂ able to produce ca. 4000 μ mol/ $g_{cat}\cdot h$ reaching 10200 with 20%. The further increase in the concentration of perovskite did not lead to a further increase in the production, possibly due to aggregates of large particles, which will lead to longer migration distances of charge carriers and increase the charge recombination or the reduction of the exposed surface area, inhibiting the adsorption of toluene molecules. Lastly, the

catalyst was shown to be very stable in the recycling tests, being able to perform 4 cycles without a decrease of activity.

The synergy between amorphous BiOCl nanosheets and TiO₂ was investigated by Wang et al.⁷³ in 2023. The reaction was performed in acetonitrile, under a O₂ atmosphere and irradiated with a xenon lamp (500 mW/cm²) for 2 h. Several Bi:Ti molar ratios were screened, and a crescent tendency is visible in the conversion of toluene (and in the benzaldehyde selectivity) until 0.01 is reached. After that point, the conversion of toluene tends to decrease intensely, although maintaining a high selectivity to benzaldehyde. The best photocatalytic system reported a 10% conversion of toluene with 85% selectivity toward benzaldehyde representing a production of benzaldehyde of 1700 μ mol/ $g_{cat}\cdot h$. This represents a significant value in terms of conversion, since most systems reported conversions below 5%. When comparing the activity of the photocatalyst 0.01BiOCl/TiO₂ with its base counterparts an increase is observed of 5.6 and 3.7 times to TiO₂ and BiOCl. The stability of the catalyst was tested over 5 catalytic cycles. Although a small decrease in the conversion of toluene between the first and second cycles was observed, the activity remained stable for the rest of the tests.

Another example of an active photocatalyst with TiO₂ combined this time with Cs₃Bi₂Br₉ was published by Cui et al.⁷⁴ (2023). The new composite was tested in a free-solvent reaction with an irradiation density of 400 mW/cm² provided by a 300 W Xe-lamp and in the presence of Na₂SO₄ (to remove the water content in the medium) and O₂ bubbled into the reaction. The new composite was able to achieve a benzaldehyde production of 9692.5 μ mol/ $g_{cat}\cdot h$, which represents an increase of 15 and 4 times to the pure phases that constituted the composite. The catalyst stability was evaluated over 4 catalytic cycles in which it maintained its activity. This result represents one of the highest productions reported in the past few years.

In 2024 Zhou et al.⁷⁵ explored the importance of Lewis acid sites in (110) facet-exposed BiOBr (EC-BiOBr) when compared to (001) facet-exposed BiOBr (H-BiOBr) as an active photocatalyst. For the reaction, a 300 W xenon lamp was utilized, acetonitrile was used as the solvent, and an oxygen atmosphere was used as the oxidant. The results demonstrated the change in activity between the two catalysts. It was observed a benzaldehyde production rate increased from 233 to 1623 μ mol/ $g_{cat}\cdot h$, representing an increase of 7 times in the production of benzaldehyde. Unfortunately, this increase led to a decrease in the selectivity of benzaldehyde, which was >99% to only 66% with benzoic acid as the major secondary product. The catalyst was finally submitted to 5 cycles, where the production of benzaldehyde slightly decreased to 1250 μ mol/ $g_{cat}\cdot h$ but remained stable afterward.

Deng et al.⁷⁶ prepared a heterogeneous composite constituted by two known active photocatalysts for this reaction, BiOBr nanosheets, and Cs₃Bi₂Br₉ perovskite nanoparticles. For the oxidation of toluene, a 300 W Xe lamp was utilized as well as acetonitrile as the solvent in which the substrate and the catalyst were added. The reaction was then performed under an O₂ atmosphere at room temperature. The new composite Cs₃Bi₂Br₉/BiOBr was synthesized with different concentrations of Cs₃Bi₂Br₉ (5 to 20%, wt %). The results showcase the synergy obtained from the two catalysts. The addition of 5% led to an increase in the selectivity toward benzaldehyde from 65/72% (Cs₃Bi₂Br₉ and BiOBr alone respectively) to 83% maintaining the conversion around 17%.

The best result was obtained with 10% (22.5% conversion and 96.2% selectivity), and it was observed that the further increase in the $\text{Cs}_3\text{Bi}_2\text{Br}_9$ concentration did not lead to a further increase in either the conversion or selectivity. XRD data showed the decomposition of the catalyst mainly due to the high polarity of acetonitrile and water formed during the reaction. When the reaction was performed in a solvent-free way, the catalyst remained unchanged. The final benzaldehyde production with this system was calculated as $1082 \mu\text{mol}/\text{g}_{\text{cat}} \cdot \text{h}$.

TOTAL OXIDATION

Over the past few years, the total oxidation of toluene has been an extensively explored topic, with several articles published each year and more catalysts and materials being tested to optimize the process. The solution with this application trades the emission of toluene and other organic compounds known to be harmful to the environment and public health with the emission of only two gases, one being water and the other being CO_2 . Known not to be very toxic, CO_2 could be a great alternative if not for the current global warming and the dangers of greenhouse gases. Most of the research focuses on mimicking industrial residue streams that would be emitted into the atmosphere without considering alternatives such as capturing and reusing CO_2 to produce for example plastics,⁷⁷ methanol,^{78,79} among other uses.⁷⁹ And although very few CO_2 solutions have been found and implemented in industries, this topic continues to be a hot topic and very popular among researchers. Over the last year, some reviews about this topic focusing on specific aspects or types of catalysts have been published. More information about the topic can be referenced here.^{80–88}

In Table 1 a summary of some of the reports published from 2013 to 2017 is presented.

This section will briefly touch on some examples over the years that have contributed to the research in the field and the advances accomplished. This will include reports from 2017 forward, and it will focus on not only the lowest temperatures achieved for the reaction but also the different metals and

Table 1. Brief Overview of Some of the Best Results Reported Each Year from 2013 up to 2017

year	catalyst	reaction conditions	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	ref
2013	ACMn1.0	600 ppm, WHSV = 84000	240	262	91
2013	20% CMC/ZrO ₂	5000 ppm, WHSV = 24000 mL/g·h	170	205	92
2014	Pt/HWT1	300 ppm, WHSV = 30000 mL/g·h	175	200	93
2014	8% CuO/ Ce _{0.8} Zr _{0.2} O ₂	4400 ppm, WHS V = 33000 mL/g·h	217	225	94
2015	Pt-1.9/ZSM-5	1000 ppm, WHSV = 60000 mL/g·h	147	153	95
2015	Mn ₃ O ₄	1000 ppm, GHSV 19100 h ⁻¹	225	240	96
2016	MnNit-Hap	800 ppmv, WHSV = 500 mL/g·h	203	210	97
2016	Au/MnO ₂ wires	1000 ppm, WHSV = 48000 mL/g·h	196	212	98
2017	Cu ₂ S/Hap	800 ppm, GHSV = 15000 h ⁻¹	215	231	99

materials to be applied to this reaction as well as their stability and reusability of the catalysts.

Typically, the reported systems follow very similar conditions and studies with very few changes.

A certain mass of catalyst ranging from 50 mg up to almost 500 mg is usually placed in a U-shape or fixed-bed reactor in which the stream will pass through. The stream is usually a mixture of air or oxygen diluted with an inert gas like argon or helium, and a maximum of 1000 ppm of toluene is present. The bigger difference comes with the flow utilized, which can vary from 30 mL/min up to 100 mL/min, which combined with the different catalyst loads gives different weight hourly space velocity (WHSV). This factor can vary from 15000 mL/g·h up to 60000 mL/g·h.

For these systems, the comparison factors are usually the energy of activation (E_a) calculated through the Arrhenius equation plus the temperature at which the conversions reach 10%, 50%, and 90% called $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$. In the end, the catalyst reusability is usually evaluated through consecutive cycles, continuous reaction tests (lifetime), and the presence of moisture, which could leave a huge impact on the system, as it will be possible to observe later.

The research published focuses on very specific metals and properties very well-defined; therefore, this section will be divided into the most characteristic metal or groups of metals that can perform this reaction.

MANGANESE OXIDE AND MATERIALS

By far, the most studied metal for this reaction is manganese, being in its more crystalline oxide form (α , β , γ , and δ MnO₂) or just simply by doping other materials or metals. The long interest in this metal is due to the fact it usually is accumulated by oxygen vacancies which are of extreme importance for the success of this reaction as exemplified by the mechanism proposed by Mars Van Krevelen⁸⁹ and most used to explain the mechanism of this reaction even with other metals.

Table 2 summarizes some manganese systems reported, their best results, the stability test effectuated, and the interesting aspects of the catalytic system.

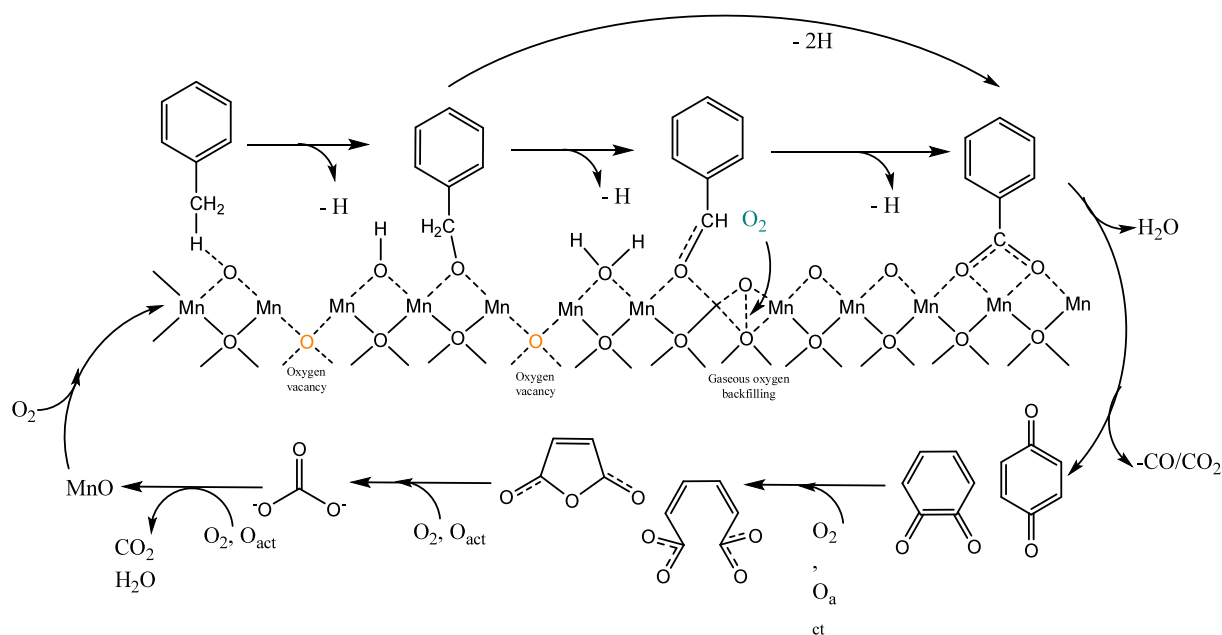
Zeng et al. (entry 2, Table 2) prepared a novel ordered mesoporous γ -MnO₂ (meso- γ -MnO₂) and applied it to the oxidation of toluene. This new material possessed a high specific surface area and a rich surface oxygen vacancy, which are important factors in this reaction. The activity of meso- γ -MnO₂ was compared, under the same conditions, with α -MnO₂ nanorods and γ -MnO₂ microrhynchins. The lowest $T_{10\%}$, 179 °C is obtained in the presence of meso- γ -MnO₂ followed by α -MnO₂ nanorods at 200 °C. The same is observed at $T_{90\%}$: the meso- γ -MnO₂ can convert at the lower temperature of 219 °C when compared to the other two catalysts. This system presents one of the lowest $T_{90\%}$ values, demonstrating the importance of a rich surface oxygen vacancy for the success of the reaction. As a final test, the stability of the catalyst was evaluated. The catalyst was run in four catalytic cycles (two of them sequentially, followed by a 40 continuous reaction at 220 °C, ending with the last two cycles). During the tests, a loss in activity in the catalyst was not observed either during the cycles or the continuous experiment. It would be important to evaluate the activity of the catalyst in the presence of water since usually, industrial VOC emissions contain water and could impact the conversion of toluene.

Yang et al. (entry 4, Table 2) screened the activity of different phases of MnO₂ (α , β , γ , and δ) for the

Table 2. Resume of the Results Obtained with Manganese Catalysts^a

entry	catalyst	[toluene] ppm	WHSV (mL/g·h)	T _{90%} (°C)	E _a (kJ/mol)	stability	reference
1	octahedral molecular sieve	1000	60000	263	96.9	A	100
2	mesoporous γ -MnO ₂	1000	40000	219	68.0	A/B	101
3	MnO _x @nanohallow-HZSM-5	1000	15000	255	101.3	C	102
4	δ -MnO ₂	1000	60000	245	55.0	A/C	90
5	MnO _x -ET (Ethanol in the synthesis)	1000	60000	225	93.1	A/C	103
6	rod-like MnCeO _x molar ratio Mn:Ce 3:2	1000	30000	236	48.9	A/C	104
7	15%Mn@iron-palygorskite	1000	20000	227	125.7	B/C	105
8	β -MnO ₂ ^b	1000	48000	228	n.a.	C	106
9	CuMnO ₂	500	60000	241	38.4	B/C	107
10	α -MnO ₂ doped with copper	1000	30000	224	28.84	A/C	108

^an.a. not available. A – lifetime test; B – recycling test; C – test in the presence of moisture. ^bSynthesized by ozone oxidation with a hydrothermal temperature of 160 °C.

Scheme 9. Mechanism Proposed by the Authors for the Total of Toluene Using MnO₂^a

^aAdapted with permission from ref 90. Copyright 2020 Elsevier.

decomposition of toluene. In the first screening, β -MnO₂ showed no activity below 220 °C. On the other hand, δ -MnO₂ displayed a toluene conversion of 40% at the same temperature. The T_{90%} is reached between 240 and 260 °C for most catalysts with δ being 245 °C followed by α at 255 °C and γ at 260 °C. On that range of temperatures, β -MnO₂ could not even convert 50% of toluene with its T_{50%} being at 278 °C and T_{90%} at 295 °C. The stability of the catalyst was tested over 48 h as well as its water resistance. It was able to maintain its activity for the tested period, with no significant loss of activity. The introduction of water in the system (5% vol) led to a loss in conversion (ca. 15%) and regained its high activity (ca. 80%) when the water addition stopped, thus demonstrating that the catalyst was free of additional surface hydroxyl groups resulting from water. The mechanism for this reaction was also explored by the authors and is presented in Scheme 9. The system starts with the adsorption of toluene onto the surface through interaction between the methyl group and the surface-adsorbed oxygen. A one-step dehydrogenation leads to the formation of benzyl alcohol species, and a swift dehydrogenation process succeeds, resulting in the accumulation of

benzoate species at room temperature (RT). This process is possible with the assistance of substantial amounts of surface-adsorbed oxygen (presented from the molecular oxygen) over δ -MnO₂ that are crucial for the success of the reaction. Benzoate species can undergo further oxidation above 120 °C, following a potential mechanism: benzoate → benzoquinone → maleate, and maleic anhydride → manganese carbonate → CO₂ and H₂O.

Another interesting report comes from Zhang et al. (entry 6, Table 2) where the application of rod-like MnCeO_x (derived from MOFs) for the oxidation of toluene was explored. Overall, the MnCeO_x catalysts presented a higher activity than the monometal oxides with the catalysts with a Mn:Ce molar ratio of 3:2 (Mn₃Ce₂) being the most active. This catalyst was able to fully convert the toluene into CO₂ at 255 °C with T_{90%} being 236 °C. From the data presented, it was possible to observe the importance of Ce in the catalyst since the catalysts with higher loads tend to perform better. One important parameter that seriously impacts the system is the WHSV. When this value was increased from 30000 to 90000, the activity of the catalyst decreased (the T_{90%} increased from 236

Table 3. Summary of the Results Obtained with Co Catalysts^a

entry	catalyst	[toluene] ppm	WHSV (mL/g·h)	T _{90%} (°C)	E _a (kJ/mol)	stability	reference
1	Co-CO ₃	1000	40000	256	196.0	A/B	110
2	CoxOy@AC	10000	66000	235	n.a.	A	111
3 ^b	Co ₃ O ₄ /TiO ₂ -H	200	30000	178	32.99	C	112
4	Cu _{0.2} Co	1000	40000	240	n.a.	A	113
5	MgCo ₃ O ₄	500	20000	250	38.5	A/B	114
6	Ni _x Co _y O ₄ (Ni/Co ratio of 1.5)	9000	5700	175	n.a.	-	115
7	Co-350D	1000	440000	257	n.a.	A/B/C	116
8	CoCeO _x -2-NP	1000	60000	209	n.a.	A/C	117

^an.a. not available. A – lifetime test; B – recycling test; C – test in the presence of moisture. ^bPhotocatalytic system 300 W xenon lamp (908 mW/cm²).

to 263 °C). A lower WHSV increases the molar ratio between oxygen and toluene promoting its degradation. The higher activity detected for the Mn₃Ce₂ catalyst when compared to the others reported (MnCe, Mn₂Ce₃, MnCe₄, Mn₃O₄, Mn₄Ce, CeO₂) could be explained by the Mars Van Krevelen mechanism⁸⁹ in which the presence of more oxygen vacancies promotes the catalytic degradation of toluene. Other reports showed that the high presence of Mn³⁺ in the dominant active sites tends to make it more active for this reaction. This fact occurs in Mn₃Ce₂ which has more Mn³⁺ in the active sites than the other catalysts of the study. The stability of the catalyst was evaluated over 48 h at 240 °C. It maintained the activity over that time. The result obtained in the presence of water was similar to the one accomplished in dry toluene, demonstrating the great stability of the catalyst.

Jiang et al. (entry 10, Table 2) screened the effect of doping α-MnO₂ with different metals such as copper, cerium, cobalt, and iron. From the catalysts produced the MnCu showed the highest activity reaching T_{90%} at 224 °C followed by MnCo, MnCe, and α-MnO₂ ca. 240 °C. The calculated activation energy for MnCu was reported as 28.84 kJ/mol the lowest reported here although with a higher T_{90%} achieved than entry 2 which has an E_a ca. 2.5 times higher. The stability of the catalyst was evaluated at the end with a continuous reaction over 24 h at two different temperatures in which the catalyst was able to maintain the conversion of toluene over time. The effect of the presence of water on the stream was also evaluated, and it is observed a small decrease when the content reached 20% vol of water exists a significant drop on the conversion which is further accentuated when the content rises to 40%. When the water is removed from the system, the catalyst regains its activity.

■ COBALT OXIDES

Another very explored metal for this reaction is cobalt. Similar to manganese, multiple structures, phases, and oxides have been used in this reaction. Table 3 presents the summary conditions of the reports here for easier reading.

Xia et al. Xia et al. (entry 2, Table 3) published the removal, through oxidation, of toluene using a Co_xO_y/AC as a catalyst (AC – activated carbon). Four catalysts bearing 20 wt % of cobalt oxides (CC250, CC300, CC350, CC400) prepared at calcination temperatures of 250 °C, 300 °C, 350 °C, and 400 °C, respectively, were tested. The catalytic activity of Co_xO_y/AC catalysts for toluene oxidation in air exhibited a dramatic change with the calcination temperature, with the maximum catalytic efficiency achieved at 350 °C. CC350 exhibited exceptional performance, removing over 90% of toluene at 235 °C and approaching 100% removal at higher temperatures. In

contrast, CC250, prepared at a lower calcination temperature, showed significantly reduced catalytic activity, leading to a 94.6% removal of toluene but with a substantial increase in temperature, 280 °C. Low calcination temperatures result in poorly crystalline, while high calcination temperatures reduce surface active oxygen species. The CC350 catalyst, prepared at an intermediate calcination temperature, exhibits an optimal combination of physicochemical properties, including appropriate crystallinity, a Co²⁺/Co³⁺ ratio, and a high reducible oxygen species content. To finalize, the stability of CC350 was evaluated over 700 min of continuous reaction. It is observed that the catalyst can maintain its activity when applied to temperatures of 240 and 250 °C.

In 2022 Yang et al. (entry 4, Table 3) studied the photothermal catalytic oxidation of toluene by utilizing a cobalt oxide and titanium oxide composite. The catalyst Co₃O₄/TiO₂ is modified by treatment under a H₂ (Co₃O₄/TiO₂-H) or argon (Co₃O₄/TiO₂-Ar) flow of 200 °C creating oxygen vacancies. The oxygen vacancies are known to be important activity enhancers in heterogeneous catalysts, especially for the oxidation of toluene. Co₃O₄/TiO₂-H was the catalyst which performed better reporting the lowest T_{50%} (120 °C) and T_{90%} (170 °C) followed by Co₃O₄/TiO₂-Ar (T_{50%} = 140 °C, T_{90%} = 178 °C). The catalyst without treatment could lead to T_{90%} only at 200 °C, demonstrating the important role of the oxygen vacancies in the reaction and activity in this reaction. The calculated activation energies for the catalyst were 32.99 and 35.28 kJ/mol for Co₃O₄/TiO₂-H and Co₃O₄/TiO₂-Ar, respectively. When the photothermal catalytic system was compared to the nonphoto system, the complete degradation of toluene occurred only at 240 °C demonstrating the synergy effect between the photo and thermal. This is further confirmed by the activation energy in which the thermal system has a higher value of 59.33 kJ/mol, while the photothermal system has an energy of 32.99 kJ/mol. The stability tests were reported; for this catalyst, the presence of water seemed to impact its stability, and with the presence of 1 vol % of water vapor the toluene conversion dropped to 60%. When the water is eliminated from the system the catalyst can convert up to 70% (20% less than they could before the presence of water).

Kouotou and co-workers (entry 5, Table 3) published the effect of the addition of magnesium to Co₃O₄ and its activity as a catalyst for the oxidation of toluene at low temperatures. The new catalyst was compared to Co₃O₄ and MgO. MgO was not able to allow a toluene conversion higher than 40% at 400 °C. As is known and by the reports already referenced, cobalt oxides tend to be active for this reaction. Co₃O₄, under the conditions described above, was able to achieve full conversion

of toluene at 315 °C. Interestingly, the addition of magnesium to the cobalt oxide provides an enhancement in its catalytic activity: $T_{100\%}$ decreased by 122 °C, a huge difference, reaching it at 255 °C. The activation energy for the catalysts was calculated, with the MgCo_3O_4 being 38.5 kJ/mol and the Co_3O_4 alone being 1.8 times higher at 68.9 kJ/mol. The stability of the new catalyst was then evaluated with a continuous test being placed at 260 °C for over 30 h of reaction, where it is possible to observe a small decrease in the conversion, 4.4%, after the 10 h of reaction and maintaining its stability until the end. The recyclability was also evaluated with 4 catalytic cycles in which the catalyst was able to keep its initial activity in all the tests.

In the same year, Giroir-Fendler and co-workers (entry 7, Table 3) investigated the effect of the calcination process on Co_3O_4 catalysts and their impact on the oxidation of toluene. Four catalysts were produced and evaluated (Co-350D, Co-350S, Co-550S, and Co-550D), with two different calcination temperatures (350 and 550 °C), and at each temperature two different environments were applied, static air (S) and dynamic airflow (D). The four catalysts behave differently at the start; $T_{10\%}$ for Co-350D is 200, while the highest is for Co-550S at 229, a 29-degree difference. But this difference is less evident at $T_{50\%}$ and $T_{90\%}$ where the difference is less than 10 °C. Overall the catalyst with the lowest calcination temperature tends to perform better than the catalysts at higher ones. The same can be said about static air and dynamic air, in which the dynamic samples tend to be able to convert a certain percentage of toluene at lower temperatures than the others. This article also included the oxidation of propane in which the difference between the catalysts is more significant, with $T_{90\%}$ with differences between 20 to 40 °C. The stability of Co-350D was evaluated; in three catalytic cycles, it was able to maintain the same behavior and activity. The catalyst was then evaluated over time, in which its activity decreased from 80% to 40% in 3 h and adopted a wavy behavior ca. 53% for the next 60%. Interestingly the authors explained that once the toluene stream was cut off, a large amount of CO_2 was released immediately, due to the fast decomposition of coke that had been accumulating in the catalysts. Once the catalysts were fully regenerated it was continuous for another 20 h with the same behavior as before.

In 2024, Zhu et al. (entry 8, Table 3) studied the activity of cobalt-doped cerium dioxide as a possible catalyst for the oxidation of toluene. These nanoparticles were synthesized with different Co/Ce molar ratios ($\text{CoCe}_x\text{-Y-NP}$, $Y = 0.5, 1,$ and 2) and evaluated their influence on the activity. The $T_{50\%}$ and $T_{90\%}$ of the catalysts demonstrated the positive effect of the doping of cobalt over the cerium dioxide, since all were able to achieve the conversion at lower temperatures than the cerium dioxide and the cobalt oxide alone (over 250 °C). In this case, the best ratio was 2 with the catalyst $\text{CoCe}_{0.5}\text{-2-NP}$ being able to convert 50% toluene at 203 °C and 90% at 209. The load of cobalt has a very big impact on these results since 0.5 has a difference of 42 and 50 °C for the $T_{50\%}$ and $T_{90\%}$, while the 1 molar ratio catalyst had a smaller difference, 25 and 43 °C. This increment of activity with the increase of the ratio may be due to the synergistic effect between cobalt and cerium, which leads to the distortion of the ceria lattice and produces oxygen vacancies known to be an important factor for the success of the reaction. The stability of $\text{CoCe}_{0.5}\text{-2-NP}$ was evaluated. In the durability test, the catalyst was kept at its $T_{90\%}$ temperature for 72 h. At the end of the test, it is possible to observe that

there was not a decrease in the activity of the catalyst with this being capable of converting during this time at its high potential. The effect of the presence of water in the reaction mixture was also evaluated. The introduction of water a 5 vol % did not have a big influence on the conversion, but the consecutive increase to 10, 15, and 20% led to a decrease in the conversion of toluene, reaching at the end 75%. The presence of water was also studied to observe if the catalyst can regain its activity once water is removed from the system. Therefore, in a continuous test at the 4 h mark, 20 vol % of water was introduced into the system leading to the decrease seen previously. Later after 10 h from starting the test, the supply of water to the system is shut down, and the catalyst starts to regain its activity showing its stability to the presence of water and its ability to regenerate. To end, the reusability of the catalyst was evaluated in 4 catalytic cycles in which the catalyst was able to remain active between them.

■ MANGANESE WITH COBALT

The activity of both metals has been proven very high individually; therefore, the study of both metals together is an interesting part since it could result in a very active catalyst. As reported here previously Jian et al. tried to study this synergy, but in their case, it was not successful due to the low concentration of Mn^{3+} which is important in creating oxygen vacancies as the key role for the success of the reaction.

Nevertheless, other authors tried to study this synergy and some with great success, for example:

Wang et al.¹⁰⁹ in 2018 reported the synthesis and application of a flower-like (Figure 10) $\text{Co}_3\text{-xMn}_x\text{O}_4$ spinel as a catalyst for

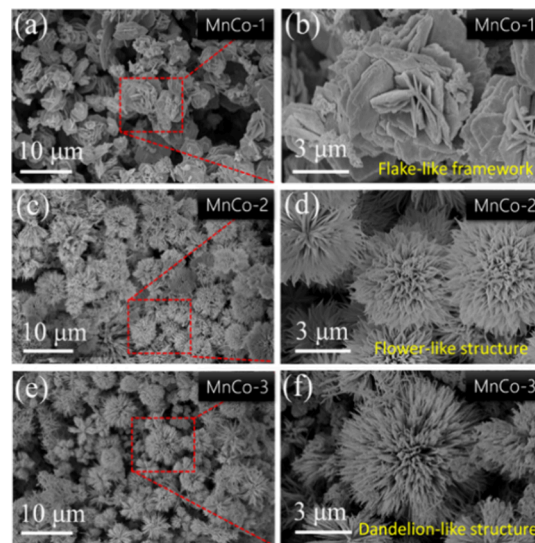


Figure 10. SEM and FESEM images of (a, b) MnCo-1, (c, d) MnCo-2, and (e, f) MnCo-3. Reused with permission from the author.¹⁰⁹ Copyright 2018 Chemistry Europe.

the oxidation of toluene. Three mixed oxide catalysts ($x = 0.75, 1,$ and 1.5) were screened. The increase in toluene conversion is linked to growth of the Co/Mn ratio. $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ was the catalyst performing worst (having a $T_{50\%}$ and $T_{90\%}$ of 240 and 255 °C), while $\text{Co}_{2.5}\text{Mn}_{0.75}\text{O}_4$, which has a higher Co/Mn ratio, can achieve the same conversion at much lower temperatures, 214 and 229 °C. This result suggests that in this case, the cobalt centers are more responsible for the oxidation of toluene than manganese, which is known to be

Table 4. Resume of the Results Obtained with Pt or Pd Catalysts^a

entry	catalyst	[toluene] ppm	WHSV (mL/g·h)	$T_{90\%}$ (°C)	E_a (kJ/mol)	stability	reference
1	Pt ₃ Pd ₁ @TiO ₂	51.74	15000	110	n.a	A/B	118
2	Pt@Y-6h	1000	60000	149	66.5	-	119
3	0.05Pd@UiO-66-Oxy	1000	26400	274/237 ^b	75.6/36.4 ^b	A/B/C	120
4	0.5% Pd@halloysite	1000	30000	185	n.a	A/B/C	121
5	Pt-Cu-Mn lamellar oxides	1000	30000	228	33.2	A	122

^an.a. not available. A – lifetime test; B – recycling test; C – test in the presence of moisture. ^bDecrease in the temperature after the 2nd cycle.

active based on the numerous articles published on this topic. Importantly, the stability of the Co_{2.5}Mn_{0.75}O₄ in a continuous reaction was evaluated over 70 h, and there was no observed decrease in conversion over time.

Dong et al.¹²³ (2019) studied the catalytic activity of a spinel CoMn₂O₄ for the total oxidation of toluene. CoMn₂O₄ was able to lead to 50% conversion of toluene at 202 °C which reached 90% at 210 °C. The spinel catalyst performed better than the oxides (Co₃O₄ and MnO_x) including mixed-metal oxides (Co₃O₄/MnO_x) which were only able to convert 90% of toluene at temperatures above 220 °C. The authors present the calculus for the activation energy for the catalysts. The spinel catalyst had the lowest energy necessary (35.5 kJ/mol). CoMn₂O₄ stability was evaluated at 220 °C for 700 min: over 98% toluene was converted within the test duration. The resistance of water was also evaluated: the presence of 2 vol% of water did not affect the activity of the catalyst which was able to maintain the high toluene conversion.

■ PALLADIUM AND PLATINUM

Tu et al. (entry 1, Table 4) published in the same year the application of Pt_xPd_y/TiO₂ as a possible catalyst for the oxidation of toluene. Pt₃Pd₁/TiO₂, Pt₁Pd₃/TiO₂, Pt₁Pd₁/TiO₂, Pd/TiO₂, and Pt/TiO₂ were screened in the standard conditions. Among the catalysts tested, Pt₃Pd₁/TiO₂ presented the highest activity with a toluene conversion of 94.7% at 110 °C. At this same temperature Pt₁Pd₃/TiO₂ could only convert 64% of toluene with the other catalysts behind with the lowest (Pt₁Pd₁/TiO₂) achieving only 24.5%. One of the parameters studied was the effect of the calcination temperature on the activity of the catalyst. Therefore, the most active catalyst was then synthesized at different temperatures. This alteration exhibited some changes in the activity, with the catalysts being calcinated at 400 °C having the highest activity mainly due to the highest proportion of Pd²⁺ and Pt²⁺ on the surface. The results showed that tendency, higher temperatures, 500 °C, 600 °C are more active than lower temperatures 300 °C with the maximum being at 450 °C. The catalysts also showed they were not influenced by the increase of the concentration of toluene nor by the increase of the WSHV, maintaining the same level of activity. To finalize, the stability was evaluated over 5 consecutive cycles and over a continuous period of 24 h in which the catalyst also was able to maintain its activity over 90%.

Zhang et al. (entry 3, Table 4) investigated the influence of palladium species on the catalytic activity of UiO-66 (XPd-U-H, where X is the load of palladium in wt %) for the oxidation of toluene. The poor activity of UiO-66 was visible, having less than 10% at 400 °C but was sharply improved by the addition of Pd. The $T_{90\%}$ values of 1Pd-U-H, 0.5Pd-U-H, 0.25Pd-U-H, 0.1Pd-U-H, and 0.05Pd-U-H were 234 °C, 254 °C, 263 °C, 269 °C, and 314 °C, respectively. The catalytic activity was directly proportional to the Pd loading. Interestingly even a

small amount of palladium in the MOF improved the reaction. Due to the high price of the rare metals, the rest of the tests were performed with the catalysts with the lowest content of palladium. The recyclability test was performed, and a very interesting phenomenon occurred. The catalyst performance improved with the second cycle lowering the $T_{90\%}$ from 314 to 269 °C. The authors explained that a similar phenomenon occurred previously with a silver catalyst.¹²⁴ From that experience, the authors modified the catalyst by submitting the catalysts to a pretreatment with oxygen (0.05Pd-U-H-O). The new catalyst, 0.05Pd-U-H-O was shown to be more effective than its predecessor, achieving 90% of toluene conversion only at 274 °C, while before it was 314 °C. The recyclability test showed again the same phenomenon in which after the fourth cycle the $T_{90\%}$ decreased to 237 °C (0.05Pd-U-H-O-fourth). The effect of water on the system was also evaluated. It was observed that for 0.05Pd-U-H this factor had a huge impact on the conversion that the catalyst could perform (decreasing almost 50%), especially in the presence of 10 vol% of water. This effect becomes less impactful in the 0.05Pd-U-H-O and becomes null for 0.05Pd-U-H-O-fourth. In the end, the activation energies for the catalyst were calculated, 84 kJ/mol for 0.05Pd-U-H, 75.6 kJ/mol for 0.05Pd-U-H-O, and 36.4 kJ/mol for 0.05Pd-U-H-O after the fourth cycle.

The application of palladium/halloysite (*x*% Pd/A-Hal) nanotubes (entry 4, Table 4) as a catalyst for the oxidation of toluene was researched by Wang et al. Different metal loads (*x* = 0.1, 0.3, 0.5, 0.7, and 1.0 wt %) were synthesized and tested in a fixed-bed reactor. In the initial screening, it was possible to observe the influence of the catalytic load on the conversion of toluene. When looking at the $T_{10\%}$ it is possible to conclude that the higher the palladium concentration higher the activity since it goes from 160 to 100 °C. This effect is not observed in the lower conversion at $T_{50\%}$; the difference between the lowest concentration and the highest is only 40 °C, but interestingly after 0.5 wt % the difference between them is null being all similar in temperature. The same is applied in the $T_{90\%}$ in which 0.5%, 0.7%, and 1% all have the same temperature for that conversion of 185 °C. This means that for the low conversions, the load of metal in the catalyst is important, but for the higher conversions this effect is more diluted, and it is possible to achieve good results with the load content of the metal. The reusability of the 0.5% Pd/A-Hal was tested, and over 5 catalytic cycles, it was possible to see a change between the first and second cycle where the $T_{90\%}$ increased 5 °C. The stability in the presence of water vapor was also investigated by the introduction of 5 and 10 vol% into the system. This introduction did not create an impact on the reaction conversion being maintained at its high during all the tests.

■ GROUP 11 METALS

Ibrahim et al.¹²⁵ screened the activity of copper–manganese hydroxyapatite (Hap) materials in the oxidation of toluene.

Three bimetallic catalysts (Cu₂MnHap, CuMnHap, and CuMn₂Hap) and two mononuclear catalysts (with each of the metals, MnHap and CuHap) were tested in a continuous-flow fixed-bed. Most of the catalysts were shown to be very active for this reaction presenting a $T_{50\%}$ ca. at the same temperature between 196 °C (Cu₂MnHap) and 210 °C (MnHap). The blank test of hydroxyapatite showed that the support is very inactive, not reaching 50% of toluene conversion at 390 °C. The worst new catalyst was indeed the copper supported in Hap, since it has an increment of 45 °C from the next active catalyst. The best catalyst, Cu₂MnHap, was able to achieve a $T_{90\%}$ below 220 °C. The stability of the catalysts was evaluated at 200 °C over time. In all cases, an enormous decrease in conversion from 90% to ca. 20% in less than 3 h was observed. The increase in temperature of the test to 390 °C resulted in a slight increase in the conversion, but the same tendency of deactivation was noticed.

Zhang and colleagues¹²⁶ explored the activity of metal oxides (CuO, CeO₂, and CuO-CeO₂) supported on ZrO₂ derived from UiO-66 MOF for the oxidation of toluene. The blank test for the ZrO₂ support shows very little activity for the reaction, needing 381 and 460 °C to reach the $T_{50\%}$ and $T_{90\%}$. The introduction of the metals improved the catalytic activity decreasing the temperature needed for the reaction to occur. It is also observed that the presence of copper oxide is more beneficial than that of cerium since the first one can achieve $T_{90\%}$ at 320 °C, while at that temperature the supported cerium oxide can reach only 50% of toluene conversion. The addition of both metals leads to a small decrease in the required temperatures (10 °C for copper oxide, reaching $T_{50\%}$ and $T_{90\%}$ at 277 and 310 °C, respectively).

Cui and co-workers¹²⁷ reported the application of silver nanoparticles supported on UiO-66 derivative as a catalyst for the oxidation of toluene. Four catalysts with different Ag loads (2, 6, 10, and 14 wt %) were evaluated in the conditions above-described. The support itself (UiO-66) showed very low activity leading to only $T_{10\%}$ at 400 °C. The addition of silver nanoparticles resulted in an enhancement of the activity, being able to get a $T_{10\%}$ as low as 280 °C, 281 °C, 248 °C, and 285 °C with the increase of the silver load (2, 6, 10, and 14 wt % respectively). The best catalyst, silver load 10 wt % (10Ag-U), was able to convert 90% of toluene at 295 °C followed by the catalyst with 14% of silver at 298 °C. The stability tests for recyclability and the effect of the water content were also evaluated for the best catalyst. The 10Ag-U showed great recyclability with an increase of only 10 °C after 4 fully catalytic cycles, and in a separate test, the catalyst was able to maintain its conversion for 24 h straight. The introduction of 10 vol % of water in the system led to a small increase in the conversion temperatures for this catalyst ($T_{10\%}$, 248 °C vs. 267 °C; $T_{50\%}$, 277 °C vs. 286 °C; and $T_{90\%}$, 295 °C vs. 300 °C). The authors attribute this inhibition to the competitive adsorption between water and toluene. The introduction of water in the reaction at 300 °C did not influence the catalyst's conversion, even when the content increased to 20 vol%, illustrating the stability of the catalyst in the presence of water at this temperature.

CONCLUSIONS AND PERSPECTIVES FOR THE FUTURE

The oxidation of toluene has been extensively studied from both perspectives. From an emissions standpoint, its conversion to CO₂ appears to be a more straightforward

solution, easier to implement. However, until an efficient method for managing CO₂ fixation is found, this option is not feasible (transforming a harmful product into another hazardous product is not worthwhile). Furthermore, the catalysts under investigation often require a significant amount of energy to effectively convert toluene. When coupled with the use of complex heterogeneous catalysts, occasionally composed of two or three costly metals such as platinum or palladium, the feasibility of such a proposal is questionable amidst the current climate crisis. On the other hand, although benzaldehyde is a very high in-demand product, its oxidation reaction still requires substantial improvements in terms of yields, selectivity, and the development of catalysts suitable for industrial-scale production. Most of the systems are liquid, which would require an investigation into the reaction in a gas–liquid state. Nevertheless, as evidenced by the pharmaceutical and agrochemical industries, there is considerable interest in photocatalytic systems. With continued refinement, scalability, and the advent of new technologies, the oxidation of toluene under photocatalytic conditions could emerge as a viable option.

The focus for the future should be the continued research of new systems not only to help supply the demand for benzaldehyde but also other oxygenate products prevent from alkane oxidation, while the topic of CO₂ utilization continues to be explored and optimized.

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Notes

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ABBREVIATIONS

AC, activated carbon; BTC, 1,3,5-benzene tricarboxylic acid; GPTMS, 3-(Glycidioxypropyl) trimethoxysilane; Bz, benzaldehyde; $g-C_3N_4$, carbon nitride; E_a , energy of activation; fcc, face-centered cubic; CTAB, hexadecyltrimethylammonium bromide; HFIP, hexafluoropropan-2-ol; hcp, hexagonal closed packed; MOF, metallic organic framework; MW, microwave; NB, nanobars; NHPI, N-hydroxyphthalimide; OTAC, octadecyltrimethylammonium chloride; PIDA, phenyliodine(III) diacetate; PVP, poly(vinylpyrrolidone); QDs, quantum dots; SDS, sodium laurylsulfonate; TBATB, tetrabutylammonium tribromide; *t*-BuOOH, *tert*-butyl hydroperoxide; PHI, poly-(heptazine imide); VOC, volatile organic compound

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