Synthesis design of Cu/Al$_2$O$_3$ catalysts to decrease copper leaching in the catalytic wet peroxide oxidation of phenol

N.A. Sacco [a], M.E. Lovato [b], F.A. Marchesini [a], A.V. Devard [a,*]

[a] *Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (UNL-CONICET), Facultad de Ingeniería Química, Santiago del Estero 2829, 3000 Santa Fe, Argentina*
[b] *Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), (Universidad Nacional del Litoral and CONICET), Intec I. CCT Santa Fe, Colectora de la Ruta Nacional No. 168, Km. 472.5, 3000 Santa Fe, Argentina*

A R T I C L E   I N F O

A B S T R A C T

This work aims to study the catalytic performance of Cu/Al$_2$O$_3$ catalysts in the catalytic reaction of oxidation of phenol. The addition of La and Mn to Al$_2$O$_3$ support and the calcination temperature influence on the catalytic performance and Cu leaching were studied. The addition of either La or Mn to the support triggered less Cu leaching compared to the unmodified support. The catalysts modified with Mn and calcined at 650ºC and 900 °C yielded low Cu leaching values and high phenol conversions at 120 min of reaction, achieving total consumption of H$_2$O$_2$. The catalysts prepared in the same way but modified with La and calcined at 900 °C, achieved 100% phenol conversion and higher TOC conversion. Copper leaching was higher when the support was modified with La, but improved when compared to the unmodified support, suggesting that the presence of Mn allowed a better anchoring of Cu on the support. However, this was not beneficial for the reaction since a certain amount of Cu in the homogeneous phase was required for the reaction to start. Cu-La-Al$_2$O$_3$ showed stability after consecutive reaction cycles with the corresponding calcinations in each cycle.

1. Introduction

Access to safe drinking water is a fundamental right for humans. Despite this, the majority of water pollutants are generated by anthropogenic activity although pollutants may also originate from natural sources (volcanic eruptions or evaporation) (Gusain et al., 2020). Phenols and halogenated phenols are among the toxic substances present in the wastewater of various industries such as steel, coal conversion coking, pharmaceuticals, pesticides, plastics, mining, petrochemicals, and oil refining (Anon, 2020; Ac, 2019). The World Health Organization (WHO) has set the phenol and phenolic compounds concentration to 1 µg/L and 0.1 µg/L in drinking water, and the UK regulators have set the maximum concentration in the discharge wastewater of hospitals to be less than 10 ppm (Wilson et al., 1995). Since the concentrations of phenol in wastewaters from some industries are much higher than those limits (Al-Obaidi et al., 2020), efficient treatment techniques for phenol removal from industrial wastewaters are required.

In recent years, many researchers have focused on the remediation of phenolic compounds by catalytic wet peroxide oxidation (CWPO) processes using H$_2$O$_2$ as the liquid oxidant (Samandari et al., 2021; Jiang et al., 2022).

The Copper-based catalysts have been extensively studied for wet oxidation (Jiang et al., 2022; Covinich et al., 2016; Maduna et al., 2018) and are regarded as one of the candidates that could replace those catalysts containing noble metals as active phases in some heterogeneous catalytic processes since the high price of noble metals restricts their use for catalytic oxidation. Despite the good catalytic performance of copper under oxidizing conditions, it can leach into the reaction matrix due to poor stability in acidic media (Li et al., 2021; Wu et al., 2020; El Gaidoumi et al., 2019). Santos et al. (Santos et al., 2005) observed an increase in the leaching of Cu when pH dropped below 4 due to the formation of acid intermediates through the oxidation. The authors reported that metal leaching could be promoted by both the pH decrease and Cu-take off from the surface during the redox reaction. On the other hand, Cu leaching is not only linked to the catalysts stability but also alters the reaction mechanism and as a consequence influences on the oxidation rate of phenol and its intermediates (Santos et al., 2005). In addition to the toxicity caused by Cu itself, toxic effects were found among Cu in solution and with the oxidation intermediate (Santos et al., 2004).

Therefore, it is practically important to develop a solid catalyst with high stability to metal deactivation and leaching (Maduna et al., 2018).

In a previous work, Devard et al. (Devard et al., 2019) prepared Cu (5 wt%)/Al_2O_3 by the wet impregnation method and applied it in the CWPO of phenol. Surface Cu^{2+} suffered a reduction process during the reaction due to the drop of the pH value, and the reduced Cu was leached to the liquid phase. However, even though the increase in the calcination temperature (900 °C) produced a decrease in this reduction extent, the remaining amount of Cu in the solution exceeded the regulatory limit values, which are stablished in 1.3 ppm (Xie et al., 2022).

As it is well known, the nature of the support strongly influences the catalytic performance of a supported catalyst as it not only affects the dispersion and stability of the active phase, but also may participate in some reactions.

It has been reported that the addition of La to the alumina support can considerably improve its thermal stability (Schaper et al., 1983; Li et al., 2019) by preventing sintering of alumina and its phase transformation through the formation of a lanthanum aluminate surface layer (Li et al., 2019). Stoyanova et al. (Stoyanova et al., 2011) found that the addition of La suppressed the transformation of the alumina support to α-Al_2O_3, and its interaction with the active phase produced aluminates. In addition, they showed that modification of the support with La increased the number of active sites in the catalyst.

On the other hand, the modification of γ-Al_2O_3 with Mn promoted a greater dispersion of Cu on the surface of the support (González-Arias et al., 2022). Moreover, López-Benítez (López-Benítez et al., 2017) found that the modification of alumina with Mn modified the nature of the oxide species and its interaction with the support.

This work aims to improve the synthesis of the catalysts to suppress the copper leaching by modifying the support with the addition of La and Mn. As mentioned above, their oxides could promote the interaction between copper and alumina, and thermally stabilize the support.

2. Experimental

2.1. Preparation of the supports x-Al_2O_3 (x = La or Mn)

The alumina support Al_2O_3 (Puralox®, SBa 230) was modified by the wet impregnation of $La(NO_3)_2$.6 H_2O or $Mn(NO_3)_2$.4 H_2O in order to obtain 20 wt% x loading. The suspension was dried at 80 °C and calcined at three different temperatures (400ºC, 650ºC, and 900 °C) for 4 h at 10 °C/min.

2.2. Synthesis of Cu/ x-Al_2O_3

The catalysts were prepared via wet impregnation of 2 g of support using a 0.03 mol.L^{-1} of $Cu(NO_3)_2$.3 H_2O (Merck, p.a.) to obtain 5 wt% Cu loading. The suspension was dried at 80 °C and calcined at three different temperatures (400ºC, 650ºC, and 900 °C, as well as the support where it was impregnated) for 4 h at 10 °C/min.

The samples were named **Cu/x-Al_2O_3 T**, where **x** is La or Mn, depending on the precursor used in the support modification, and **T** the temperature at which catalysts were calcined.

2.3. Catalytic tests

The reaction was carried out in a glass vessel under continuous stirring and subjected to refluxing, as described in Fig. S1.A. A certain volume of solution was heated until the reaction temperature was reached. Then, 100 mg of catalyst was added, and finally a large excess of peroxide 100 vol was also added; this moment being considered the beginning of the reaction (t_0). Samples were taken from the reaction medium for quantifying the remaining phenol, H_2O_2, and total organic carbon (TOC).

The reaction conditions were 70 °C, 100 mg of catalyst in 100 ml of 1000 ppm initial phenol solution, 10 ml of H_2O_2, and 2 h of reaction.

Among the various reaction mechanisms associated with copper in solution or on a solid catalyst that have been proposed, there are two

possible routes: a redox mechanism involving Cu^+ and Cu^{2+}, and the formation of intermediate hydroperoxide complexes, which subsequently generate the hydroxyl radical. In the latter case, the Cu(II) complexes activate the hydrogen peroxide for the oxidation of organic compounds, and the peroxide activation mechanism involves the formation of a hydroperoxide complex, which then oxidizes the organic matter (Covinich et al., 2016). Fig. S1. B shows a simplified reaction pathway phenol oxidation, over Cu-based catalysts, proposed by Zhang et. al (Zhang et al., 2022).

2.4. Catalyst stability and reusability

The stability and reusability of the most efficient catalyst were studied by repeatedly using the sample for three consecutive reaction cycles (with intermediate drying of the catalyst). In addition, a stability test was performed with an intermediate regeneration of the catalyst by calcining it in air using the same temperature ramp at which it was synthesized, to evaluate if the deactivation of the catalyst, if present, occurred preferentially by deposition of reaction intermediates on the active sites or by leaching of the catalytic material.

2.5. Characterization

Catalysts were characterized by X-ray diffraction to elucidate the crystalline phases present.

The quantification of the different reagents was carried out using the following techniques:

H_2O_2. The H_2O_2 concentration was determined by titration with 0.1 mol.L^{-1} $KMnO_4$ using H_2SO_4 as an acidifying agent.

Phenol. The remaining phenol was quantified by colorimetry according to the 5530-D proposed by *Standard Methods for the examination of water and wastewater using* a Cole Parmer 1100 Spectrophotometer (Rice et al., 2017). The phenol conversion was calculated taking into account the concentration measured initially and at different reaction times.

Total organic carbon (TOC). TOC was determined according to ISO 8245 (1999) in an Elementar Vario Toc Cube/Trace model.

Copper. The composition of copper in the catalysts was performed by atomic absorption spectroscopy with Perkin Elmer Atomic Absorption equipment, model AAnalyst 800 flame atomization system (air/acetylene and nitrous oxide/acetylene), automatic sampler series AS-90, and Graphite Furnace with automatic sampler series AS-800.

3. Results

3.1. Catalytic performance

The catalysts containing lanthanum (Fig. 1. A) reached 100% phenol conversion within 10–15 min after starting the reaction, and no significant differences between catalysts calcined at different temperatures were observed.

For catalysts containing Mn (Fig. 1. B), the one calcined at 400 °C reached total phenol conversion after 15 min while those catalysts calcined at 650 °C and 900 °C, achieved total conversion after 120 min (97.4% and 99.7%, respectively).

After 120 min, the solution was colorless in all reactions, evidencing the elimination of colored by-products such as hydroquinones and benzoquinones, among others (see Fig. S1. B) (Rice et al., 2017). These products were then cleaved to short-chain carboxylic acids and also mineralized, whereupon the solution acquired a low pH (around 2–3) and simultaneously became discolored. As these products still contributed to the organic carbon content of the reaction medium, it was necessary to evaluate the degree of mineralization, i.e., the proportion of the original phenol that was converted to CO_2 and H_2O.

The TOC values were determined after completion of reactions (after 120 min) to analyze the degree of mineralization. For the calculation of
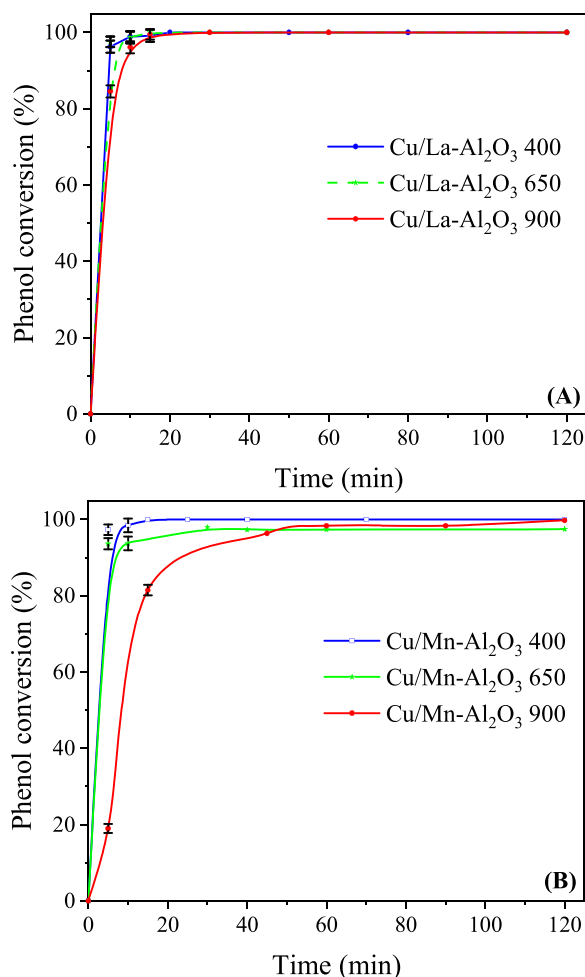
Fig. 1. Phenol conversion (%) as a function of time with **(A)** Cu/La-Al$_2$O$_3$-T. **(B)** Cu/Mn-Al$_2$O$_3$-T.

Table 1
Cu leached (%), and phenol, H$_2$O$_2$ and TOC conversion (%).

| Catalyst	Leached Copper (%)	TOC conversion (%)	Maximum phenol Conversion % (min)	H$_2$O$_2$ Conversion % (120 min)
Cu/La-Al$_2$O$_3$ 400	53	96	100 (15 min)	66
Cu/La-Al$_2$O$_3$ 650	53	98	100 (15 min)	66
Cu/La-Al$_2$O$_3$ 900	25	86	100 (15 min)	38
Cu/Mn-Al$_2$O$_3$ 400	35	96	100 (15 min)	100
Cu/Mn-Al$_2$O$_3$ 650	29	94	97 (120 min)	100
Cu/Mn-Al$_2$O$_3$ 900	11	56	100 (120 min)	24
Cu/Al$_2$O$_3$ 400 (Devard et al., 2019)	64	90	100 (10 min)	75
Cu/Al$_2$O$_3$ 650 (Devard et al., 2019)	60	91	100 (15 min)	54
Cu/Al$_2$O$_3$ 900 (Devard et al., 2019)	36	86	100 (10 min)	53
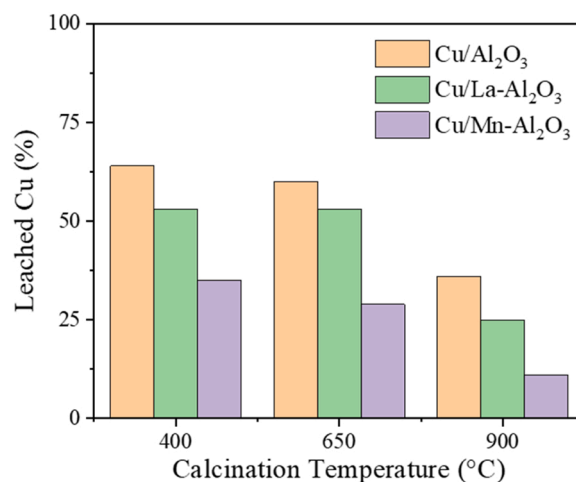
Fig. 2. Copper leaching after the reaction as a function of the calcination temperature for catalysts supported over Al$_2$O$_3$ (Ferrandon et al., 2001), La-Al$_2$O$_3$, and Mn- Al$_2$O$_3$.

TOC conversion, it was considered all the initial organic carbon came from phenol.

Table 1 summarizes the Cu leaching percentage, and phenol, H$_2$O$_2$, and TOC conversion (%).

All catalysts calcined at 400°C and 650 °C achieved a high degree of mineralization (above 95%). On the other hand, the catalysts calcined at 900 °C achieved both a lower TOC conversion and Cu leachate, with the manganese catalyst being the one that achieved the lowest degree of mineralization. These observed differences were related to the different copper species available that contributed to the development of the reaction. In comparison with results obtained in a previous work (Devard et al., 2019), the addition of either Mn or La to the supports formulation had a beneficial effect, both on leachate reduction and on TOC conversion.

The catalysts with lanthanum are very promising since, for 100% phenol conversion, high TOC conversions were achieved; and the percentage of copper lost improved compared to the catalyst containing only Cu in its formulation. The catalysts with manganese, although showing a lower proportion of leaching, achieved total phenol conversion only when calcined at 400 °C.

Fig. 2 shows the leached Cu (expressed as %) after phenol oxidation, as a function of the calcination temperature for Cu/Al$_2$O$_3$ ((Devard et al., 2019)), Cu/La-Al$_2$O$_3$, and Cu/Mn-Al$_2$O$_3$. In those catalysts containing Mn, as the calcination temperature increased, the formation of copper species more strongly anchored to the alumina structure was achieved; and therefore, the leaching of the active phase was lower. On the other hand, those catalysts containing lanthanum and calcined at 400°C and

650 °C presented the same copper loss %. Thus, it can be affirmed that even La is not exerting its fixing effect on Cu at this temperature. However, this effect could be evidenced in the catalyst calcined at 900 °C since that was the one that presented the lowest Cu loss after the reaction.

Overall, the observed trends were congruent; the higher the calcination temperature, the lower the leaching. Calcination at higher temperatures induced the formation of a stronger interaction between the Al of the support and the supported Cu species. The presence of the second metal (La or Mn) modified and reinforced this interaction, allowing Cu to bind to the support and leach in a lower proportion. Moreover, it is important to note that, as with Cu, leaching of La and Mn into the reaction solution decreased as the temperature increased (see Table S1).

Catalysts were characterized by X-ray diffraction to provide information about crystalline phases present in the samples not yet studied in depth. Fig. 3 shows diffractograms of Cu-based catalyst supported onto (A) Al_2O_3, (B) La-Al_2O_3, and (C) Mn-Al_2O_3, and calcined at 900 °C since those catalysts which were prepared at 400°C and 650 °C did not show signals corresponding to copper species (Devard et al., 2019). All
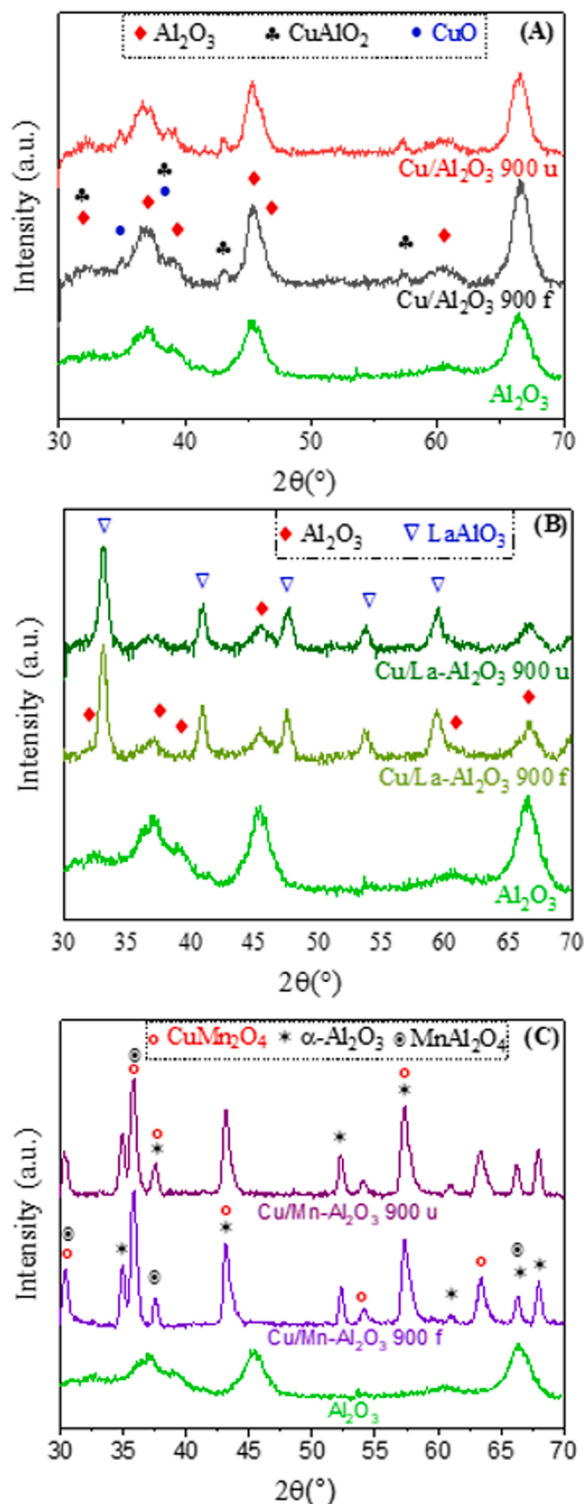
diffractograms were contrasted with the diffractogram corresponding to the support. In addition to the diffractograms of the fresh catalysts (marked with the letter "f" after the nomenclature), those corresponding to the catalysts after being used in the reaction ("u") were shown. In catalyst supported on.

unmodified alumina, in addition to the signal corresponding to γ-Al_2O_3 (JCPDS 10–0425), the presence of CuO (JCPDS 002–1040) and $CuAlO_2$ (JCPDS 009–0185) was also observed. On the other hand, no significant differences were found in the intensity of the signals in the catalysts before and after being used in the reaction.

For La-modified catalysts, diffraction peaks corresponding to copper species were not observed. This could be attributed to the high dispersion of Cu on the support since the presence of La could promote the dispersion of the active phases (Ferrandon et al., 2001; Chen et al., 2002; Barrera et al., 2001). On the other hand, $LaAlO_3$ perovskite (JCPDS 031–0022) was present, and its formation on the surface of alumina could be associated with a strong interaction between La^{3+} and Al^{3+} and the coherence in the interfacial structure of La-AlO_3- γ-Al_2O_3 (Kathiraser et al., 2013).

For the Mn-modified catalysts, unlike the other systems, no signals corresponding to γ-Al_2O_3 were observed, but the presence of α-Al_2O_3 (JCPDS 046–1212) was detected. This behavior was also observed by Yalfani et al. (Yalfani et al., 2007), who found that the addition of transition metals, such as Fe or Mn, promoted the formation of α-Al_2O_3 at relatively low temperatures. This would imply a reduction in specific surface area and consequently, a lower oxidation activity than for the γ-Al_2O_3-supported catalyst. In addition, the formation of the spinel $MnAl_2O_4$ (JCPDS 001–1302), also detected in the diffractograms, would be related to a reduction of the surface area of the catalyst. This reduction in surface area due to the presence of MnO_X species and to the phase change of the support would explain the lower mineralization (see Table 2, TOC values) obtained for the Mn-modified catalyst (Jiang et al., 2022; Massa et al., 2011).

3.2. Catalyst stability and reusability

Reusability experiments were carried out with the most promising catalyst (Cu/La-Al_2O_3-900) to assess catalyst stability. Table S2 shows the phenol conversion values after 120 min of reaction for the 3 reaction cycles carried out with dried or calcined intermediate catalyst (Cu/La-Al_2O_3 900). The TOC values obtained after each reaction cycle are also shown. The formulation Cu/La-Al_2O_3 900 showed very good catalytic stability both after drying and calcination in each reaction cycle. However, the catalyst reached 100 percent conversion in all 3 reaction cycles after being calcined, while the conversion activity decreased slightly when only heated.

4. Conclusions

Cu/La-Al_2O_3 and Cu/Mn-Al_2O_3 catalysts were synthesized by the wet impregnation method, calcined at 400°C, 650°C and 900 °C, and evaluated in the CWPO of phenol. All catalysts presented good catalytic performances in the CWPO of phenol under mild reaction conditions (70 °C, 1 atm).

Those catalysts prepared with alumina modified with La or Mn presented less Cu leaching with respect to the catalyst with unmodified alumina in the CWPO of phenol.

The catalysts calcined at 400°C and 650 °C, both with La and Mn, allowed to achieve mineralization higher than 93%, whereas the catalyst modified with Mn and calcined at 900 °C had the lowest mineralization, probably due to the possible decrease of the specific surface area by phase transformation of the support.

The active phase leachate analysis for the manganese-containing catalysts indicated that, at a higher calcination temperature, less copper amount was lost to the reaction medium. However, in the case of 650 °C and 900 °C, this decrease in leachate was accompanied by a

Fig. 3. X-ray diffractograms of fresh and after reaction catalysts. (A) Cu/Al_2O_3 900 fresh and after reaction, (B) Cu/La-Al_2O_3 900, and (C) Cu/Mn-Al_2O_3 900. All diffractograms were contrasted with the diffractogram corresponding to the support.

decrease in conversion. For La-Al$_2$O$_3$ catalysts, although no difference in the amount of copper lost for the catalysts calcined at 400ºC and 650 °C was observed, it was lower compared to the catalysts with unmodified alumina.

Financial support of FIQ

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2022.100059.

References

C.O. Ac, Removal of Phenol from Steel Plant Wastewater in Three Dimensional Electrochemical (TDE) 1 Introduction, (2019).

Al-Obaidi, I.M., Kara-Zaitri, M., Mujtaba, C., 2020. Wastewater Treatment by Reverse Osmosis Process. CRC Press,.

AnonSpringer, Nanosensor Technologies for Environmental Monitoring, 2020. https://link.springer.com/bookseries/15921%0Ahttp://link.springer.com/10.1007/978–3-030–45116-5.

Barrera, A., Viniegra, M., Bosch, P., Lara, V.H., Fuentes, S., 2001. (Formula presented) catalysts prepared by sol-gel: characterization and catalytic activity in the NO reduction by H2. Appl. Catal. B: Environ. 34, 97–111. https://doi.org/10.1016/S0926-3373(01)00206-5.

Chen, Y.Z., Liaw, B.J., Lai, W.H., 2002. ZrO2/SiO2- and La2O3/Al2O3-supported platinum catalysts for CH4/CO$_2$ reforming. Appl. Catal. A: Gen. 230, 73–83. https://doi.org/10.1016/S0926-860X(01)00996-6.

Covinich, L.G., Massa, P., Fenoglio, R.J., Area, M.C., 2016. Oxidation of hazardous compounds by heterogeneous catalysis based on Cu/Al2O3 system in Fenton-type reactions. Crit. Rev. Environ. Sci. Technol. 46, 1745–1781. https://doi.org/10.1080/10643389.2016.1267449.

Devard, A., Brussino, P., Marchesini, F.A., Ulla, M.A., 2019. Cu(5%)/Al$_2$O$_3$ catalytic performance on the phenol wet oxidation with H2O2: influence of the calcination temperature. J. Environ. Chem. Eng. 7, 103201 https://doi.org/10.1016/j.jece.2019.103201.

El Gaidoumi, A., Doña-Rodríguez, J.M., Pulido Melián, E., González-Díaz, O.M., Navío, J. A., El Bali, B., Kherbeche, A., 2019. Catalytic efficiency of cu-supported pyrophyllite in heterogeneous catalytic oxidation of phenol. Arab. J. Sci. Eng. 44, 6313–6325. https://doi.org/10.1007/s13369-019-03757-2.

Ferrandon, M., Ferrand, B., Björnbom, E., Klingstedt, F., Neyestanaki, A.K., Karhu, H., Karhu, H., Väyrynen, I.J., 2001. Copper oxide–platinum/alumina catalysts for volatile organic compound and carbon monoxide oxidation: synergetic effect of cerium and lanthanum. J. Catal. 202, 354–366. https://doi.org/10.1006/jcat.2001.3303.

González-Arias, J., González-Castaño, M., Sánchez, M.E., Cara-Jiménez, J., Arellano-García, H., 2022. Valorization of biomass-derived CO$_2$ residues with Cu-MnOx catalysts for RWGS reaction. Renew. Energy 182, 443–451. https://doi.org/10.1016/j.renene.2021.10.029.

P.S. Gusain, D, Bassin, J., Tian, K., & and Yulia Milshina, Water Conservation and Wastewater Treatment in BRICS Nations, Candice Janco, Amsterdam, Netherlands, 2020.

Jiang, S., Zhao, Z., Cui, K., Tang, Y., Du, X., He, B., Li, M., Feng, J., Yu, B., Xiong, W., 2022. Catalytic wet peroxide oxidation of phenolic wastewater on novel Cu/Mn-UiO-66@Al$_2$O$_3$ ceramic tube membrane catalysts. Chem. Eng. J. 430 https://doi.org/10.1016/j.cej.2021.132787.

Y. Kathiraser, W. Thitsartarn, K. Sutthiumporn, S. Kawi, Inverse NiAl 2 O 4 on LaAlO $_3$ − Al $_2$ O $_3$: Unique Catalytic Structure for Stable CO 2 Reforming of Methane, (2013).

Li, C., Goetz, V., Chiron, S., 2021. Peroxydisulfate activation process on copper oxide: Cu (III) as the predominant selective intermediate oxidant for phenol and waterborne antibiotics removal. J. Environ. Chem. Eng. 9, 105145 https://doi.org/10.1016/j.jece.2021.105145.

Li, H., Su, S., Peng, Y., Wu, L., Xu, K., Liu, L., Qing, M., Hu, S., Wang, Y., Xiang, J., 2019. Effect of La-Modi fi ed Supporter on H2S Removal Performance of Mn/La/Al$_2$O$_3$. Sorbent in a Reducing Atmosphere. https://doi.org/10.1021/acs.iecr.8b05923.

López-Benítez, A., Berhault, G., Guevara-Lara, A., 2017. NiMo catalysts supported on Mn-Al$_2$O$_3$ for dibenzothiophene hydrodesulfurization application. Appl. Catal. B: Environ. 213, 28–41. https://doi.org/10.1016/j.apcatb.2017.04.058.

Maduna, K., Kumar, N., Aho, A., Wärnå, J., Zrnčević, S., Murzin, D.Y., 2018. Kinetics of catalytic wet peroxide oxidation of phenolics in olive oil mill wastewaters over copper catalysts. ACS Omega 3, 7247–7260. https://doi.org/10.1021/acsomega.8b00948.

Massa, P., Ivorra, F., Haure, P., Fenoglio, R., 2011. Catalytic wet peroxide oxidation of phenol solutions over CuO/CeO$_2$ systems. J. Hazard. Mater. 190, 1068–1073. https://doi.org/10.1016/j.jhazmat.2011.03.033.

Rice, P.E.W., Baird, R.B., Eaton, A.D. (Eds.), 2017. Standard methods for the examination of water and wastewater., 23rd ed.,. American Public Health Association, American Water Works Association, Water Environment Federation.

Samandari, M., Manesh, A.T., Hosseini, S.A., Mansouri, S., 2021. Mg-Al LDH and calcined LDH: Green nanocatalysts for wet peroxide oxidation of phenol in wastewater. J. Water Environ. Nanotechnol. 6, 72–80. https://doi.org/10.22090/jwent.2021.01.007.

Santos, A., Yustos, P., Quintanilla, A., García-Ochoa, F., Casas, J.A., Rodriguez, J.J., 2004. Evolution of toxicity upon wet catalytic oxidation of phenol. Environ. Sci. Technol. 38, 133–138. https://doi.org/10.1021/es030476t.

Santos, A., Yustos, P., Quintanilla, A., Ruiz, G., Garcia-Ochoa, F., 2005. Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: causes and effects. Appl. Catal. B: Environ. 61, 323–333. https://doi.org/10.1016/j.apcatb.2005.06.006.

Schaper, H., Doesburg, E.B.M., Reijen, L.L.V.A.N., 1983. The influence of lanthanum oxide on the thermal stability of gamma alumina catalyst supports. Lab. Inorg. Phys. Chem. 7, 211–220.

Stoyanova, D.D., Ivanov, G.M., Khristova, M.S., 2011. Effect of lanthanum on the activity and thermal stability of copper-cobalt oxide catalysts supported on alumina. Izvestiya po Khimiya Bulgarska Akademiya na Naukite 43, 477–482.

J.R. Wilson, E.N. Corlett, John R. Wilson, NIGEL CORLETT Evaluation of Human Work, (1995).

Wu, Y., Zhang, H., Yan, Y., 2020. High efficiency of phenol oxidation in a structured fixed bed over Cu-ZSM-5/PSSF prepared by ion-exchanged method. Chem. Eng. J. 380, 122466 https://doi.org/10.1016/j.cej.2019.122466.

Xie, M., Zhao, J., Mai, X., Chen, Y., Zhao, W., Sun, M., Yu, L., Yu, H.-J., 2022. A dual-function luminescent probe for copper(II) ions and pH detection based on ruthenium (II) complex. Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 277, 121265 https://doi.org/10.1016/j.saa.2022.121265.

Yalfani, M.S., Santiago, M., Pérez-Ramírez, J., 2007. In situ studies during thermal activation of dawsonite-type compounds to oxide catalysts. J. Mater. Chem. 17, 1222–1229. https://doi.org/10.1039/b615264c.

Zhang, W., Ye, B., Zhong, Z., Jiang, Y., Zhou, R., Liu, Z., Hou, Z., 2022. Catalytic wet air oxidation of toxic containments over highly dispersed Cu(II)/Cu(I)-N species in the framework of g-C3N4. J. Hazard. Mater. 424, 127679 https://doi.org/10.1016/j.jhazmat.2021.127679.