

Catalysts for Air Pollution Control: Present and Future

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Due to the continuous increase in both industrial activities and in the use of internal combustion engines, the quality of atmospheric air has progressively deteriorated, both in urban conglomerates and globally [1]. These facts prompt restrictions in emission limits, making it necessary to increase research efforts in this area, and the development of increasingly sophisticated processes becomes evident. For several years, the use of catalytic processes to reduce pollutants in the atmosphere has become essential, including those from fixed and mobile sources. A typical example is a complex system currently used for the simultaneous reduction of CO, VOCs, NO_x, and soot particles in the exhaust gases of diesel engines, for which a tandem of several catalytic reactors has been developed [2].

This Special Issue of Catalysts “Catalysts for Air Pollution Control: Present and Future” is dedicated to the diffusion of research results related to the basic and applied aspects of environmental catalysis. It is focused on the control of atmospheric pollution, with the aim of generating new ideas and stimulating research in this fascinating area. A collection of nine research papers is presented, covering different fields of catalytic processes, including the preparation, physicochemical characterization, and catalytic evaluation of different reactions that are of both academic and practical interest, and that result in valuable material for researchers in environmental catalysis.

Furthermore, different reactors are studied for specific applications, including control strategies and transport properties. In this vein, in a theoretical simulation study, Miranda et al. [3] present the dynamic closed-loop behavior of a reactor/feed-effluent heat exchanger/furnace (FEHE) system for the catalytic combustion of volatile organic compounds (VOCs). A 1D pseudo-homogeneous plug-flow model is proposed to simulate the non-steady state operation of a monolith reactor and the FEHE, while the furnace behavior is described by means of a heterogeneous model of lumped parameters. Positive energy feedback is a source of instability that leads to strong thermal oscillations (limit cycles) and may cause damage to the equipment and sintering of the catalyst. The design of a robust and flexible control system and an efficient control strategy are, therefore, required to ensure safe and stable operation. The authors conclude that the control strategy makes it possible to satisfy the main control objective (VOCs abatement) by avoiding situations such as the loss of controllability due to the saturation (closure) of the bypass valve, when almost all the feed has to be redirected to the FEHE. In addition, it minimizes the consumption of natural gas when the feed stream is more concentrated in VOCs or when the feed flowrate decreases. This prevents excessive overheating of the tube wall in the furnace.

One of the most studied reactions in environmental catalysis is VOC oxidation [4], with the results above being a good example. In the frame of this subject, Grahovski et al. [5] studied the catalytic oxidation of propane and n-hexane over a cobalt-loaded hierarchical MFI zeolite. ZSM-5 zeolites with different Si/Al ratios were modified with a buffer solution of HF and NH₄F. This acidic treatment led to the procurement of a material with secondary mesoporosity. It is shown that the catalysts obtained with treated ZSM-5 exhibit higher activity in the reactions of propane, and that n-hexane completes oxidation as opposed to the catalyst samples containing un-treated zeolite. Both the finer dispersion of metal oxide



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particles on the hierarchical sample and the presence of secondary mesoporosity improve the effectiveness of the active phase utilization via access to a larger number of active sites. In the same vein, Shah et al. [6] synthesized iron–manganese mixed metal oxide catalysts with a range of Fe–Mn ratios via co-precipitation using sodium carbonate. The catalysts were evaluated for total propane oxidation, with the $\text{Fe}_{0.50}\text{Mn}_{0.50}\text{O}_x$ catalyst being the most active for propane oxidation. The authors attributed this result to an increased surface area along with the formation of a Mn_2O_3 phase that was not present in the other catalysts with different compositions. The effect of the precipitating agent was also evaluated, with NH_4OH being the best performing one. This was thought to be due to the formation of a highly active mixed defect spinel structure.

Toluene and ethyl acetate are other VOC contaminants of great concern because they are widely used in petroleum processing, coating, pharmaceutical, and automobile manufacturing industries [7]. Such components usually exist in the mixture of VOCs emitted in the actual industrial production activities. Yuxi Liu et al. [8] found that $\text{Pt/CeMnO}_x/\text{Diatomite}$ is a highly active catalyst for the oxidation of toluene and ethyl acetate. In addition, this catalyst possesses good sulfur dioxide resistance during the toluene oxidation process. In the presence of SO_2 , some of the SO_2 molecules were adsorbed on diatomite, which protected the active sites from being poisoned by SO_2 to a certain extent. It is concluded that this work can provide a strategy to develop efficient catalysts with high catalytic activity, durability, low cost, and easy availability under actual working conditions.

Chlorinated volatile organic compounds (VOCs-Cl) represent a special case of VOCs and have gained attention in recent years due to their persistence and toxicity in the atmosphere [9]. One of the most effective ways to remove gaseous atmospheric pollutants in recent years has been through catalytic combustion, and, within it, by using inorganic structures of mixed oxides, specifically perovskites. Acosta Pérez et al. [10] synthesized $\text{LaCo}_x\text{Fe}_x\text{O}_3$ perovskites for their use in chlorobenzene catalytic combustion. To this end, a series of catalysts ($x = 0; 0.25; 0.5; 0.75; 1$) was synthesized using the citrate method, obtaining pure structures. It is observed that Fe doping in the original structure induces electronic environments capable of generating the $\text{Co}^{2+}/\text{Co}^{3+}$ redox couple. The characteristics observed in bulk are perfectly reflected on the surface, favoring the high resistance of solids to chlorine poisoning. Superior stability under reaction conditions was observed in the phase with the lowest Fe content ($x = 0.25$), remaining stable at 100% combustion of chlorobenzene during 100 h, without an observation of intermediate reaction products. These results open up a new avenue for designing and fabricating high-performance catalysts in the environmental field.

Photocatalysis is another interesting method for eliminating chlorobenzene. To this end, Aly Koné et al. [11] used a plasma/photocatalysis hybrid reactor. The mineralization of gaseous chlorobenzene was comparatively studied in a continuous reactor using three advanced oxidation processes: (i) photocatalysis, (ii) dielectric barrier discharge (DBD) plasma, and (iii) DBD/ TiO_2 -UV coupling. The reaction under study was influenced by the concentration, feed–flow rate, and the voltage injected into the reactor. Comparatively, the DBD/ TiO_2 coupling showed a good removal efficiency and it is proposed that a synergistic effect takes place. In addition, the study revealed that Cl^\bullet radicals are involved in CB decomposition, while OH^\bullet radicals react with Cl^\bullet in the medium to produce O^\bullet , another more powerful oxidant, which could mineralize the adsorbed CB.

There are examples in which the emissions of VOCs also contain nitrogen oxides, as seen in the cases of internal combustion engine exhausts and power plants that use methane combustion as an energy source [12]. An interesting approach to remove both contaminants is presented in the work by Serra et al. [13]. They propose the use of $\text{Cs}_x\text{Co}/\text{Na-Mordenite}$ powder coated on ceramic monoliths for the co-adsorption of hydrocarbon mixtures coupled with the selective catalytic reduction of NO_x . Zeolite catalysts have been widely used for both processes. In this work, Cs, as a basic component, favors the adsorption of hydrocarbons (toluene and butane mixture) and Co oxide is the component that promotes

the reaction between hydrocarbons and NO_x , giving non-toxic products. The coating of the powder onto a honeycomb structure is necessary for its use under high flow rates. The authors conclude that by combining Co^{2+} and Cs^+ cations in the same zeolite structure, an efficient material is obtained to adsorb a hydrocarbon mixture at a low temperature and retain it until a medium temperature is reached, where the SCR of NO_x begins to occur.

Carbon monoxide is another gaseous pollutant of great environmental concern because is highly toxic and it is present in a variety of effluents from combustion processes both in stationary and mobile sources. Low-temperature CO combustion is of both academic and practical interest. This is necessary, for example, in the case of indoor contamination such as that occurring in a mine shelter. Camposeco et al. [14] developed highly efficient Au/ZnO-ZrO₂ catalysts for CO oxidation at a low temperature. A series of gold catalysts on ZnO-ZrO₂ with ZnO loads of 3, 5, and 10 wt. % were synthesized using the sol-gel method, and gold-containing catalysts with loads between 1 and 3 wt. % were produced through the method of deposition-precipitation with urea. Their performance in the CO oxidation reaction at low temperature was evaluated. The HRTEM outcomes revealed high gold dispersion on the 3Au/5ZnO-ZrO₂ catalyst with a Zn/Zr atomic ratio of (5/95) and 3 wt.% of gold, which showed the highest CO conversion at low temperature (5 °C) under air treatment, when the reaction was carried out with a space velocity of $\sim 46,000 \text{ h}^{-1}$. The incorporation of ZnO to ZrO₂ provoked a high dispersion of the gold nanoparticles on the support and close size distribution. Moreover, the presence of Au^{1+} and Zr^{3+} species was increased by the Zr-O-Zn interaction, which was stronger than in the single Au/ZrO₂ and Au/ZnO catalysts. DRIFT/GCMS confirmed that the $\text{Au}^{1+}/\text{Au}^0$ ratio and formation of carbonate species played important roles in determining the CO conversion; likewise, the 3Au/5ZnO-ZrO₂ catalyst was stable at 10 °C for 24 h.

Soot particles emitted by modern diesel engines, despite having a significantly lower total mass, exhibit higher reactivity and toxicity than older black smoke engines, leading to serious health and environmental problems [15]. Leonardi et al. [16] carried out a study about the activity of catalytic ceramic papers loaded with Co, Ba, K and Ce, Co as catalysts, to remove soot particles, using different types of soot, obtained by burning diesel fuel in a vessel (Labsoot) or by filtering exhaust gases from a turbo diesel engine in a DPF filter (Benchsoot). They are compared with a commercial diesel soot, Printex U, which is by far the most commonly used as a model in the works reported in the literature. The authors conclude that both Co, Ce and Co, Ba, K structured catalysts exhibited reducibility properties that aided the oxidation of soot via redox mechanisms, which, in addition to the oxygen storage capacity of CeO₂ nanoparticles, allowed the catalytic burning of the different types of soot samples studied. The Co, Ce system preferentially improved T_M for the Printex U sample since it helped to supply active oxygen, absent in the surface of this model-type soot. On the other hand, the Co, Ba, K catalyst showed a higher catalytic effect on LabSoot since this type of soot exhibited the largest primary particles and a higher order of graphene layers, for which the catalyst containing potassium enhanced soot-to-catalyst contact, and for Co, Ba, K the contact with ceramic paper. T_M values between 390 and 425 °C were observed for both LabSoot and BenchSoot samples, which are close to the diesel exhaust gas temperature. Considering that the new generations of diesel engines produce lower amounts of NO_x , the transfer and reactivity of oxygen adsorbed on the catalyst to the soot particles become increasingly important in decreasing the regeneration temperature of the filter.

This Special Issue on “Catalysts for Air Pollution Control: Present and Future” provides an overview of the recent progress surrounding environmental catalysis, with a particular emphasis on the latest studies regarding the catalytic control of pollutants emitted by different sources. Depending on the type of contaminant, different strategies are presented, using a variety of catalysts and catalytic reactors. Emphasis is made on aspects such as reaction control, catalyst preparation and characterization, and reaction studies. We hope that our compilation will aid researchers in this field in generating new ideas and thus stimulate research surrounding this interesting subject.

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References

1. Serrano, J.R.; Novella, R.; Piqueras, P. Why the Development of Internal Combustion Engines Is Still Necessary to Fight against Global Climate Change from the Perspective of Transportation. *Appl. Sci.* **2019**, *9*, 4597. [\[CrossRef\]](#)
2. Martinovic, F.; Castoldi, L.; Deorsola, F.A. Aftertreatment Technologies for Diesel Engines: An Overview of the Combined Systems. *Catalysts* **2021**, *11*, 653. [\[CrossRef\]](#)
3. Miranda, A.F.; Rodríguez, M.L.; Serra, F.M.; Borio, D.O. Novel Control System Strategy for the Catalytic Oxidation of VOCs with Heat Recovery. *Catalysts* **2023**, *13*, 897. [\[CrossRef\]](#)
4. Brummer, V.; Teng, S.Y.; Jecha, D.; Skryja, P.; Vavrickova, V.; Stehlik, P. Contribution to Cleaner Production from the Point of View of VOC Emissions Abatement: A Review. *J. Clean. Prod.* **2022**, *361*, 132112. [\[CrossRef\]](#)
5. Grahovski, B.; Velinova, R.; Shestakova, P.; Naydenov, A.; Kolev, H.; Yordanova, I.; Ivanov, G.; Tenchev, K.; Todorova, S. Catalytic Oxidation of VOC over Cobalt-Loaded Hierarchical MFI Zeolite. *Catalysts* **2023**, *13*, 834. [\[CrossRef\]](#)
6. Shah, P.M.; Bailey, L.A.; Morgan, D.J.; Taylor, S.H. The Effect of Metal Ratio and Precipitation Agent on Highly Active Iron-Manganese Mixed Metal Oxide Catalysts for Propane Total Oxidation. *Catalysts* **2023**, *13*, 794. [\[CrossRef\]](#)
7. Sanz, O.; Banús, E.D.; Goya, A.; Larumbe, H.; Delgado, J.J.; Monzón, A.; Montes, M. Stacked Wire-Mesh Monoliths for VOCs Combustion: Effect of the Mesh-Opening in the Catalytic Performance. *Catal. Today* **2017**, *296*, 76–83. [\[CrossRef\]](#)
8. Li, L.; Liu, Y.; Deng, J.; Jing, L.; Hou, Z.; Gao, R.; Dai, H. Pt/CeMnOx/Diatomite: A Highly Active Catalyst for the Oxidative Removal of Toluene and Ethyl Acetate. *Catalysts* **2023**, *13*, 676. [\[CrossRef\]](#)
9. Guiotto, M.; Pacella, M.; Perin, G.; Iovino, A.; Michelon, N.; Natile, M.M.; Glisenti, A.; Canu, P. Washcoating vs. Direct Synthesis of LaCoO₃ on Monoliths for Environmental Applications. *Appl. Catal. A Gen.* **2015**, *499*, 146–157. [\[CrossRef\]](#)
10. Acosta Pérez, H.; López, C.A.; Furlong, O.J.; Nazzarro, M.S.; Marchetti, S.G.; Cadús, L.E.; Agüero, F.N. Highly Resistant LaCo₁-XFexO₃ Perovskites Used in Chlorobenzene Catalytic Combustion. *Catalysts* **2023**, *13*, 42. [\[CrossRef\]](#)
11. KONE, N.A.; Belkessa, N.; Serhane, Y.; Coulibaly, S.L.; Kamagate, M.; Mouni, L.; Loganathan, S.; Coulibaly, L.; Bouzaza, A.; Amrane, A.; et al. Chlorobenzene Mineralization Using Plasma/Photocatalysis Hybrid Reactor: Exploiting the Synergistic Effect. *Catalysts* **2023**, *13*, 431. [\[CrossRef\]](#)
12. Kansal, A. Sources and Reactivity of NMHCs and VOCs in the Atmosphere: A Review. *J. Hazard. Mater.* **2009**, *166*, 17–26. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Serra, R.M.; Gómez, L.E.; Tiscornia, I.S.; Deharbe, M.d.I.M.; Boix, A.V. Cs_xCo/Na-MOR Coating on Ceramic Monoliths for Co-Adsorption of Hydrocarbons Mixture and Selective Catalytic Reduction of NO_x. *Catalysts* **2023**, *13*, 106. [\[CrossRef\]](#)
14. Camposeco, R.; Maturano-Rojas, V.; Zanella, R. Highly Efficient Au/ZnO&ZrO₂ Catalysts for CO Oxidation at Low Temperature. *Catalysts* **2023**, *13*, 590. [\[CrossRef\]](#)
15. Meloni, E.; Palma, V. Most Recent Advances in Diesel Engine Catalytic Soot Abatement: Structured Catalysts and Alternative Approaches. *Catalysts* **2020**, *10*, 745. [\[CrossRef\]](#)
16. Leonardi, S.A.; Miró, E.E.; Milt, V.G. Activity of Catalytic Ceramic Papers to Remove Soot Particles: A Study of Different Types of Soot. *Catalysts* **2022**, *12*, 855. [\[CrossRef\]](#)

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