

Sustainable and Environmental Catalysis

Tommaso Tabanelli ^{1,*} , Daniele Cespi ^{2,*}  and Raffaele Cucciniello ^{3,*} 

¹ Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy

² NIER Ingegneria SpA, Via C. Bonazzi 2-40013-Castel Maggiore, 40013 Bologna, Italy

³ Department of Chemistry and Biology, “Adolfo Zambelli” Università di Salerno, Via Giovanni 6 Paolo II, 132, 84084 Fisciano, Italy

* Correspondence: tommaso.tabanelli@unibo.it (T.T.); d.cespi@nier.it (D.C.); rcucciniello@unisa.it (R.C.)

1. Introduction

Over the last few decades, an increasing amount of interest from academia and industry has been devoted to the application of the Twelve Principles of the Green Chemistry in order to pursue the Sustainable Development Goals (SDGs) recommended by the United Nations [1]. They are based on the fundamental idea of guiding research and innovation toward more environmental-friendly practices as well as socioeconomic sustainable solutions. Among them, catalysis plays a pivotal role able to address some important needs: (i) avoiding the use of stoichiometric amount of chemicals; (ii) increasing selectivity (i.e., decreasing the generation of waste), and (iii) decreasing energy demand. In this context, with the aim to eliminate environmental pollutants (NO_x, CO, SO_x, VOCs) and to design new catalytic routes for clean energy production, environmental and sustainable catalysis represents a noble and one of the most investigated research directions. Moreover, as recently suggested, sustainable and environmental catalysis allows for converting waste in value-added products, and the degradation of pollutants through catalytic combustion/photocatalysis are considered main topics in this context [2,3]. As a matter of fact, it is worth highlighting some recent research advances. The oxidation of chlorinated compounds by catalytic combustion on non-noble metals based oxides [4,5], NO_x reduction to nitrogen or by selective catalytic reduction (SCR) with ammonia in the presence of heterogeneous catalysts [6]; biofuel production from vegetable oils [7]; the development of new active catalysts for Fenton and photo-Fenton processes [8]; the development of supported nanoparticle catalysts for the treatment of the emission of harmful substances from automobiles, and the use of waste as source of metals for catalysts preparation [9]; the design of new active catalytic systems for the preparation of olefins from polyols [10]; the catalytic hydrotreatment in the valorization of bio-oils obtained from lignocellulosic biomass pyrolysis [11]; and the design of active catalysts for the preparation of organic carbonates from CO₂ or bio-based compounds are some examples in this framework [12,13].

This Special Issue aims to cover new and promising examples of sustainable and environmental catalysis with particular emphasis on the adoption of green chemistry principles at both a laboratory and industrial scale.

2. The Contents of the Special Issue

In this Special Issue, several fields of research on the sustainable catalytic valorization of biomasses are discussed. Therefore, we would like to sincerely thank all the authors who contributed with their excellent contributions to this Special Issue, which includes fourteen articles.

Cucciniello et al. investigated the use of iron-doped mayenite catalysts for trichloroethylene (TCE) oxidation in the gas phase. All the synthesized catalysts showed good performances for TCE oxidation, totally converted into CO₂, CO, and HCl. Mayenite loaded with 2% iron was found to be the best catalyst in terms of T₅₀ (300 °C). This result was correlated



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with an optimum combination of the oxidative properties of the mayenite active support with the redox properties of iron, as Temperature Programmed Reduction (TPR), X-ray photoelectron spectroscopy (XPS) and Raman results have shown [14].

Chevez Rivas et al. reported the preparation and characterization of natural purified mordenite treated with a hydrothermal ion exchange process in an acid medium with Fe^{2+} or Fe^{3+} salts. The set of samples was characterized regarding their textural properties, morphology, and crystallinity, and tested in the NO reduction with $\text{CO}/\text{C}_3\text{H}_6$. The activity in hydrocarbons-selective catalytic reduction (HC-SCR) (used as a reaction test) was found to depend on the ion exchange process [15].

Husnain et al. discussed the selective catalytic reduction of NO with NH_3 at low temperatures with natural iron ore catalysts. The results showed that the sample based on $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ calcined at $250\text{ }^\circ\text{C}$, achieved excellent selective catalytic reduction (SCR) activity (above 80% at $170\text{--}350\text{ }^\circ\text{C}$) and N_2 selectivity (above 90%, up to $250\text{ }^\circ\text{C}$) at low temperatures [16].

Ngoie et al. investigated the potential of a heterogeneous catalyst produced from mineral processing waste for biodiesel production. Tailings from the concentration of cupriferous minerals served as the starting material for synthesis of the catalyst. The nano-magnetic catalysts were prepared using coprecipitation and sol-gel methods, combined with zero-valent iron nanoparticles to form a hydride catalyst. Catalyst properties were assessed using SEM, TEM, BET, and EDX. The maximum yield obtained with this catalyst was 88% and an average of 27% decrease in biodiesel yield observed after four reaction cycles [17].

Muhammad Habib et al. discussed the preparation of two alternative catalysts ($\text{Co}_3\text{O}_4/\text{TiO}_2$ and 8 wt.% $\text{ZrO}_2\text{-Co}_3\text{O}_4/\text{TiO}_2$) for CO, HC, and NO_x conversions. These systems were produced along with a wire mesh-based substrate and tested by mounting them at the exhaust tailpipe of a motorcycle engine. Zirconia-promoted catalyst showed more promising towards NO_x conversion. The cobalt supported by the titania $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst showed a performance towards conversion of carbon monoxide, nitrogen oxides, and unburnt hydrocarbons to values of 78.1%, 61.9%, and 82.6% efficiency, respectively, at 1500 RPM; whereas, the conversion efficiency of zirconia promoted $\text{ZrO}_2\text{-Co}_3\text{O}_4/\text{TiO}_2$ catalyst was 81.3%, 78.6%, and 55.1% towards HCs, CO, and NO_x , respectively, at 1500 RPM value. Due to small crystalline size, thermal stability, and fouling inhibition, the ZrO_2 -promoted $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst showed better conversion efficiency towards CO and NO_x . The slightly lower efficiency of zirconia-promoted catalyst towards HCs is due to the nonavailability of the vacancies of oxygen for oxidation on Co_3O_4 . Both catalysts showed selectivity towards CO, NO_x , and HC, and had comparable performance with respect to the activity of a conventional catalyst [18].

Zhou et al. proposed a copper-based Fenton-like catalyst ($\text{Cu}/\text{Al}_2\text{O}_3/\text{g-C}_3\text{N}_4$) to achieve high degradation efficiencies for Rhodamine B (Rh B) in a wide range of pH (4.9–11.0). The $\text{Cu}/\text{Al}_2\text{O}_3$ composite was first prepared via a hydrothermal method followed by a calcination process. The composite was then stabilized on graphitic carbon nitride ($\text{g-C}_3\text{N}_4$). The characterizations show that Cu species were immobilized on the Al_2O_3 framework in the form of Cu^{2+} and Cu^+ , and the introduction of CN increased its specific surface area and adsorption capacity for Rh B. The $\text{Cu}/\text{Al}_2\text{O}_3/\text{CN}$ composite showed an excellent catalytic performance in a wide range of pH (4.9–11.0). The specific reaction rate constant of Rh B degradation was calculated as $(5.9 \pm 0.07) \times 10^{-9}\text{ m}\cdot\text{s}^{-1}$, and the activation energy was calculated to be 71.0 kJ/mol. The recycling experiment demonstrated its durability for Rh B removal and proved that the degradation reaction was surface dominated, with a negligible leaching of copper species in solution [19].

A novel method for preparing highly efficient glass fiber-supported Pt nanoparticle catalysts for the treatment of the emission of harmful substances from automobiles was proposed by Sasaki et al. The Pt catalyst was prepared by depositing a reactive chemically adsorbed monomolecular film with a thiol group at the molecular terminal on the surface of a hydrophilized glass fiber. The monomolecular film enabled the uniform and dense

grafting of Pt nanoparticles on the surface of the glass fiber as a single layer. Both catalysts exhibited catalytic performance at temperatures ≥ 200 °C. At 300 °C, the octane combustion rates (index for evaluating performances of the Pt and commercially available catalysts) of the catalysts were $\geq 80\%$. At 50–400 °C, the octane combustion rates of both catalysts were approximately the same. Pt catalysts were found to exhibit catalytic performance comparable to that of Pd catalysts under lean conditions, despite the lower price [20].

Research conducted by Villamarin-Barriga et al. showed that the residual sludge of galvanic industries can be used as catalytic materials (after thermal treatment) for the synthesis of materials. Researchers evaluated the sludge from three galvanic industries. Catalyst was obtained from a thermal process based on sludge dried between 100 and 120 °C, and calcination of sludges between 400 to 700 °C. Catalytic activity was analyzed by thermogravimetric analysis of a thermocatalytic decomposition of crude oil. The best conditions for catalyst synthesis were calcination between 400 and 500 °C, the temperature of reduction between 750 and 850 °C for 15 min. The catalytic material had mainly Fe as active phase and a specific surface between 17.68–96.15 m²·g⁻¹; the catalysts promoted around 6% more weight-loss of crude oil in the thermal decomposition compared with assays without the catalyst. To determinate the environmental sustainability of this process, the E-factor (mass of waste/mass of product) was calculated by obtaining values between 0.1 and 0.3; the ideal E-factor is zero [21].

In the manuscript of Klein Gebbink et al., two new tetradentate N-donor ligand-supported ReO₂⁺ complexes (cis-[(BPMEN)ReO₂]PF₆ and cis-[(BmdmPMEN)ReO₂]PF₆) were synthesized and fully characterized. They were found to be active in deoxydehydration (DODH) reactions of diols, suggesting that Re(V) dioxo complexes can be involved in DODH catalysis. Treatment of (N₂Py₂) ReO₂⁺ with an excess amount of water generates an active species for DODH catalysis; use of the Re-product of this reaction shows a much shorter induction period compared to the pristine complex. No ligand is coordinated to the “water-treated” complex, indicating that the real catalyst is formed after ligand dissociation. IR analysis suggested this catalyst to be a rhenium-oxide/hydroxide oligomer. The monodentate pyridine ligand is much easier to dissociate from the metal center than a tetradentate N₂Py₂ ligand, which makes the Py₄ReO₂⁺-initiated DODH reaction more efficient. For the Py₄ReO₂⁺-initiated DODH of diols and biomass-based polyols, both PPh₃ and 3-pentanol could be used as a reductant. Excellent olefin yields are achieved [22].

The manuscript of Ray et al. reports on the photocatalytic and antibacterial activity of ZnO nanoparticles. This activity is strongly related to the amount of surficial reactive oxygen species (ROS) and metal ions (Zn²⁺) which, in turn, is strictly dependent on the morphology of the nanomaterials. In this context, the authors managed to optimize the preparation of different ZnO nanospheres, nanopetals, and nanorods by varying the precipitation solvent ranging from PEG400, water, and toluene. These nanocatalysts (dimension ranging from 10 to few hundreds nanometers) were effective in killing 99% of bacteria at low concentrations in water while the photodegradation of caffeine using solar light was completed after 120 min using the optimized ZnO nanospheres. These results are promising; therefore, the mechanism of both the processes will be investigated in depth in future investigations [23].

The research work of Kaewkannetra and coworkers show the possibility to successfully valorize the triglyceride-rich palm-oil mill effluent (POME) through the combination of biological and thermochemical processes. In this complementary approach, the aqueous waste of the palm oil manufacture first undergoes an enzymatic hydrolysis with yield up to 90% in free fatty acids (FFA). Subsequently, FFA are efficiently converted into long chain hydrocarbon mixtures, suitable for jet fuel application, via the heterogeneously catalyzed hydrogenation reaction (Pd/Al₂O₃, 400 °C, 10 bar of H₂, 1 h). This innovative and complementary approach for the valorization of POME was never reported in literature and represents a new way to both alleviate the wastewater environmental issue and to obtain a high value-added product (jet fuels) for local biorefineries (e.g., Southeast Asia) [24].

Dutta et al. reported on the catalytic activity of Pd/SiO₂ for the selective oxidation of CO at low temperature. An extensive characterization of the catalytic materials (by FTIR, TGA–DSC, TEM, and XPS) allowed for investigating the influence of the thermal pretreatment on catalyst activity and stability. Interestingly, a structure–activity relationship was proposed, correlating the catalyst activation and CO oxidation hysteresis behavior with the information on both the palladium oxidation states and nanoparticle dispersion. In particular, the best low-temperature CO oxidation performance was achieved by calcining the catalyst at 450 °C [25].

In a comprehensive review, Paone et al. extensively discussed the potentials of catalytic hydrotreatment in the valorization of bio-oils obtained from either lignocellulosic biomass pyrolysis or by the physical pressing of oleaginous vegetable seeds. This treatment uses high-pressure hydrogen in order to both stabilize the bio-oil and decrease the amount of oxygenated compounds, in this way obtaining mixtures suitable for direct use as drop-in biofuels. In particular, the current state-of-the-art on the reaction pathways, catalyst formulations, and reactor technology (i.e., traditional vs. membrane) were analyzed in-depth [26].

Zhang et al. proposed an innovative series of binuclear aluminum complexes as highly active and selective homogeneous catalysts for the cycloaddition reaction of epoxides and carbon dioxide. The reaction is of interest because the market for organic carbonates is steadily increasing due to their utilization as solvents, electrolytes, and monomers for high-performance polymers (i.e., polycarbonates, polyurethane, and polyureas), as well as a way to valorize CO₂ as a feedstock. Interestingly, the bifunctional tridentate tetrammino phenoxyimino-phenoxy aluminum complex is also active in very mild conditions, i.e., 100 °C and low CO₂ pressure (≤2 atm), which allows for obtaining good to excellent conversions of the parental epoxides. Kinetic investigations showed a first-order dependence on the concentration of the epoxide for the target reaction [27].

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References

1. Cespi, D.; Esposito, I.; Cucciniello, R.; Anastas, P.T. Beyond the beaker: Benign by design society. *Curr. Res. Green Sustain. Chem.* **2020**, *3*, 100028. [[CrossRef](#)]
2. Fasolini, A.; Cespi, D.; Tabanelli, T.; Cucciniello, R.; Cavani, F. Hydrogen from Renewables: A Case Study of Glycerol Reforming. *Catalysts* **2019**, *9*, 722. [[CrossRef](#)]
3. Bellè, A.; Tabanelli, T.; Fiorani, G.; Perosa, A.; Cavani, F.; Selva, M. A Multiphase Protocol for Selective Hydrogenation and Reductive Amination of Levulinic Acid with Integrated Catalyst Recovery. *ChemSusChem* **2019**, *12*, 3343–3354. [[CrossRef](#)]
4. Cucciniello, R.; Intiso, A.; Castiglione, S.; Genga, A.; Proto, A.; Rossi, F. Total oxidation of trichloroethylene over mayenite (Ca₁₂Al₁₄O₃₃) catalyst. *Appl. Catal. B Environ.* **2017**, *204*, 167–172. [[CrossRef](#)]
5. Intiso, A.; Martinez-Triguero, J.; Cucciniello, R.; Proto, A.; Palomares, A.E.; Rossi, F. A Novel Synthetic Route to Prepare High Surface. *Catalysts* **2019**, *9*, 27. [[CrossRef](#)]
6. Chen, Z.; Liu, Q.; Guo, L.; Zhang, S.; Pang, L.; Guo, Y.; Li, T. The promoting mechanism of in situ Zr doping on the hydrothermal stability of Fe-SSZ-13 catalyst for NH₃-SCR reaction. *Appl. Catal. B Environ.* **2021**, *286*, 119816. [[CrossRef](#)]
7. Ricciardi, M.; Falivene, L.; Tabanelli, T.; Proto, A.; Cucciniello, R.; Cavani, F. Bio-Glycidol Conversion to Solketal over Acid Heterogeneous Catalysts: Synthesis and Theoretical Approach. *Catalysts* **2018**, *8*, 391. [[CrossRef](#)]
8. Prete, P.; Fiorentino, A.; Rizzo, L.; Proto, A.; Cucciniello, R. Review of aminopolycarboxylic acids-based metal complexes application to water and wastewater treatment by (photo-)Fenton process at neutral pH. *Curr. Opin. Green Sustain. Chem.* **2021**. [[CrossRef](#)]
9. Cova, C.M.; Zuliani, A.; Manno, R.; Sebastian, V.; Luque, R. Scrap waste automotive converters as efficient catalysts for the continuous-flow hydrogenations of biomass derived chemicals. *Green Chem.* **2020**, *22*, 1414–1423. [[CrossRef](#)]
10. Scioli, G.; Tonucci, L.; Di Profio, P.; Proto, A.; Cucciniello, R.; D’Alessandro, N. New green route to obtain (bio)-propene through 1,2-propanediol deoxydehydration. *Sustain. Chem. Pharm.* **2020**, *17*, 100273. [[CrossRef](#)]
11. Kang, S.; Li, X.; Fan, J.; Chang, J. Hydrothermal conversion of lignin: A review. *Ren. Sustain. Energy Rev.* **2013**, *27*, 546–558. [[CrossRef](#)]
12. Aomchad, V.; Cristofol, A.; Della Monica, F.; Limburg, B.; D’Elia, V.; Kleij, A. Recent progress in the catalytic transformation of carbon dioxide into biosourced organic carbonates. *Green Chem.* **2021**. [[CrossRef](#)]

13. Tabanelli, T.; Giliberti, C.; Mazzoni, R.; Cucciniello, R.; Cavani, F. An innovative synthesis pathway to benzodioxanes: The peculiar reactivity of glycerol carbonate and catechol. *Green Chem.* **2019**, *21*, 329. [[CrossRef](#)]
14. Cucciniello, R.; Intiso, A.; Siciliano, T.; Palomares, A.P.; Martinez-Triguero, J.; Cerrillo, J.L.; Proto, A.; Rossi, F. Oxidative Degradation of Trichloroethylene over Fe₂O₃-doped Mayenite: Chlorine Poisoning Mitigation and Improved Catalytic Performance. *Catalysts* **2019**, *9*, 747. [[CrossRef](#)]
15. Rivas, F.C.; Rodriguez-Iznaga, I.; Berlier, G.; Ferro, D.T.; Concepcion-Rosabal, B.; Petranovskii, V. Fe Speciation in Iron Modified Natural Zeolites as Sustainable Environmental Catalysts. *Catalysts* **2019**, *9*, 866. [[CrossRef](#)]
16. Husnain, N.; Wang, E.; Fareed, S. Low-Temperature Selective Catalytic Reduction of NO with NH₃ over Natural Iron Ore Catalyst. *Catalysts* **2019**, *9*, 956. [[CrossRef](#)]
17. Ngoie, W.I.; Weiz, P.J.; Ikhu-Omoregbe, D.; Oyekola, O.O. Heterogeneous Nanomagnetic Catalyst from Cupriferous Mineral Processing Gangue for the Production of Biodiesel. *Catalysts* **2019**, *9*, 1047. [[CrossRef](#)]
18. Rehman, M.H.U.; Noor, T.; Iqbal, N. Effect of Zirconia on Hydrothermally Synthesized Co₃O₄/TiO₂ Catalyst for NO_x Reduction from Engine Emissions. *Catalysts* **2020**, *10*, 209. [[CrossRef](#)]
19. Zhou, C.; Liu, Z.; Fang, L.; Guo, Y.; Feng, Y.; Yang, M. Kinetic and Mechanistic Study of Rhodamine B Degradation by H₂O₂ and Cu/Al₂O₃/g-C₃N₄ Composite. *Catalysts* **2020**, *10*, 317. [[CrossRef](#)]
20. Sasaki, T.; Horino, Y.; Ohtake, T.; Ogawa, K.; Suzaki, Y. A Highly Efficient Monolayer Pt Nanoparticle Catalyst Prepared on a Glass Fiber Surface. *Catalysts* **2020**, *10*, 472. [[CrossRef](#)]
21. Villamarin-Barriga, E.; Canacuan, J.; Londono-Larrea, P.; Solis, H.; De La Rosa, A.; Saldarriaga, J.F.; Montero, C. Catalytic Cracking of Heavy Crude Oil over Iron-Based Catalyst Obtained from Galvanic Industry Wastes. *Catalysts* **2020**, *10*, 736. [[CrossRef](#)]
22. Li, J.; Lutz, M.; Gebbink, R.J.M.K. N-Donor Ligand Supported "ReO²⁺": A Pre-Catalyst for the Deoxydehydration of Diols and Polyols. *Catalysts* **2020**, *10*, 754. [[CrossRef](#)]
23. Thakur, S.; Neogi, S.; Ray, A.K. Morphology-Controlled Synthesis of ZnO Nanostructures for Caffeine Degradation and *Escherichia coli* Inactivation in Water. *Catalysts* **2021**, *11*, 63. [[CrossRef](#)]
24. Muanruksa, P.; Winterburn, J.; Kaewkannetra, P. Biojet Fuel Production from Waste of Palm Oil Mill Effluent through Enzymatic Hydrolysis and Decarboxylation. *Catalysts* **2021**, *11*, 78. [[CrossRef](#)]
25. Al Soubaihi, R.M.; Saoud, K.M.; Myint, M.T.Z.; Gothelid, M.A.; Dutta, J. CO Oxidation Efficiency and Hysteresis Behavior over Mesoporous Pd/SiO₂ Catalyst. *Catalysts* **2021**, *11*, 131. [[CrossRef](#)]
26. Bagnato, G.; Sanna, A.; Paone, E.; Catizzone, E. Recent Catalytic Advances in Hydrotreatment Processes of Pyrolysis Bio-Oil. *Catalysts* **2021**, *11*, 157. [[CrossRef](#)]
27. Zhang, Z.; Wang, T.; Xiang, P.; Du, Q.; Han, S. Syntheses, Characterization, and Application of Tridentate Phenoxyimino-Phenoxy Aluminum Complexes for the Coupling of Terminal Epoxide with CO₂: From Binary System to Single Component Catalyst. *Catalysts* **2021**, *11*, 145. [[CrossRef](#)]