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Editorial

Feature Papers in Catalysis in Organic and Polymer Chemistry

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1. Overview

Catalysis plays a key role in both organic chemistry and polymer chemistry. Catalysts enable more efficient, selective, and sustainable transformations, which are vital for industrial applications and fundamental research. In organic chemistry, catalysts are important for several reactions, such as hydrogenation [1], carbonylation [2], heterocyclization [3], cross-coupling [4], and asymmetric synthesis [5]. Catalysts not only accelerate the reactions but also provide precise control over product selectivity and stereochemistry. In polymer chemistry, catalysts are essential for controlling polymerization processes and modulating the characteristics and properties of the resulting materials [6]. Catalytic systems, in fact, allow the production of polymers with specific structures and configurations. These advancements have led to the creation of high-performance plastics, elastomers, and biodegradable polymers, addressing both industrial demands and environmental challenges. The role of catalysis in organic and polymer chemistry continues to expand, providing solutions to global challenges in energy, materials science, and green chemistry.

2. Special Issue Contributions

In this Special Issue, important contributions in the field of homogeneous and heterogeneous catalysis in organic synthesis and in polymer chemistry are reported. In particular, 26 papers have been published: 11 original research articles on homogenous catalysis in organic synthesis, 8 in heterogeneous catalysis, and 7 original papers in polymer chemistry.

2.1. Catalysis in Organic Chemistry

2.1.1. Homogeneous Catalysis

Copper-Catalyzed Reactions

In the first contribution, A. L. Gushchin et al. describe a new reaction for the oxidation of isopropylbenzene with oxygen, catalyzed by copper–BIAN complexes. The structures, electrochemical properties, and reactivity of copper(II) complexes with redox-active bis(imino)-acenaphthene (BIAN) ligands [R = 4-Me-Ph or 2-Me-Ph] have been thoroughly studied (Contribution 1). In the second contribution, the preparation, characterization, and application of copper(II) layered hydroxide salts (LHS) as catalysts in the copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction for the synthesis of 1,2,3-triazoles is reported. The reaction is carried out under solvent-free conditions, and J. Rafique et al. show that it is possible to degrade methyl orange with high efficiencies using some layered copper(II) hydroxide salt (Contribution 2). Another example of a CuAAC reaction for the synthesis of 1,2,3-triazoles is reported by V. Rosa et al. The authors present a new class of cationic heteroleptic copper(I) complexes [Cu(aryl-BIAN)(PPh_3)$_2$][X], where X = tetrafluoroborate,

Received: 4 January 2025
Accepted: 13 January 2025
Published: 17 January 2025

Citation: Cadierno, V.; Mancuso, R. Feature Papers in Catalysis in Organic and Polymer Chemistry. *Catalysts* **2025**, *15*, 83. https://doi.org/10.3390/catal15010083

triflate, or nitrate. The counter-ion influences in catalyst efficiency (Contribution 3). The fourth Contribution reported by D. S. Nesterov shows the synthesis, the theoretical study, and the use of copper(II) complexes $[Cu_4(pa)_4(Bae)_4]\cdot H_2O$ and $[Cu_4(eba)_4(Buae)_4\cdot H_2O$ (Hpa = propionic acid, HBae = 2-benzylaminoethanol, Heba = 2-ethylbutyric acid, and HBuae = 2-butylaminoethanol) as catalysts in the aerobic oxidation of *o*-aminophenol to phenoxazinone, in the amidation of cyclohexane with benzamide to give N-cyclohexyl benzamide and N-methyl benzamide, and in the oxidation of cyclohexane to cyclohexanol (Contribution 4). S. Díez-González et al. provide a new deuteration of terminal alkynes using technical acetone-d_6 as a deuterium source or a toluene/acetone-d_6 combination as the reaction media, catalyzed by the Copper–Diazabutadiene (DAB)-BF_4 complex $[[Cu(DABAnis)_2]BF_4$ where Anis = 4-MeO-C_6H_4] (Contribution 5).

Other Metal- and Non-Metal-Catalyzed Reactions

A new strategy for highly Markovnikov-selective hydrosilylation of terminal and internal alkynes is provided by M. Bolt et al. using both tertiary and secondary silanes and bulky N-heterocyclic carbene (NHC)–octacarbonyl dicobalt(0) complex as catalysts (Contribution 6). On the other hand, Y.Y. Titova reports on dynamic EPR spectroscopy studies for the formation of catalytically active nano-sized cobalt-containing structures in multicomponent hydrogenation systems based on the $Co(acac)_2$ complex and various cocatalysts, such as $AlEt_3$, $AlEt_2(OEt)$, Li-*n*-Bu, and $(PhCH_2)MgCl$ (Contribution 7). New palladium complexes of chiral non-racemic (*Sa*) and (*Ra*)-BisNap-Phos are synthesized by O. M. Demchuk et al. BisNap-Phos-palladium complexes are used in Suzuki-Miyaura coupling, including in the asymmetric version of this reaction, and are highly catalytically active in aqueous and anhydrous mediums (Contribution 8). In the ninth contribution, G. B. Shul'pin et al. provide a new strategy for the oxidation of hydrocarbons with hydrogen peroxide and alcohols with tert-butyl hydroperoxide catalyzed by mononuclear oxidovanadium(IV) complexes with BIAN ligands and with the addition of 2-pyrazinecarboxylic acid (PCA) as a co-catalyst. The reaction proceeds with the participation of hydroxyl radicals, and alkyl hydroperoxides are formed as the primary products (Contribution 9). M. Fochi et al. report a divergent reactivity of donor (D)–acceptor (A) cyclopropanes with thiocetic (and thiobenzoic) acid under phase-transfer catalyst (PTC) conditions. The decyanation-acetylation reaction competes with the typical cyclopropane ring-opening depending on the nature of the inorganic base (solid vs. aqueous) as a key factor (Contribution 10). The direct cross-coupling of secondary alkyl alcohols and benzylic alcohols (primary and secondary) with N-nucleophiles is reported by N. Ajvazi et al. in the eleventh contribution. The reaction is mediated by N-iodosuccinimide (NIS) as a non-metal precatalyst under mild conditions (Contribution 11).

2.1.2. Heterogeneous Catalysis

The first example of heterogeneous catalysis is report by Y. Ding et al. that describes the bioethanol conversion to butanol via the Guerbet coupling process in a fixed-bed reactor, catalyzed by MgAlOx and ZnAlOx porous mixed oxides supported copper catalysts. For Cu/MgAlOx, the conversion of ethanol and selectivity of butanol are 43.1% and 33.2%, respectively, whereas for Cu/ZnAlOx, the major product is ethyl acetate. The acid-base sites might determine the distribution of products, from which the catalysts with appropriate basic sites form the condensation products such as crotonaldehyde and butanol, whereas the catalysts with more acid sites form dehydrogenation products, such as ethyl acetate (Contribution 12). H. Sajiki et al. develop new palladium catalysts supported on silicon carbide [3% Pd/SiC and 3% Pd-Diethylenetriamine (DETA)/SiC] for chemoselective hydrogenation reactions. The 3% Pd/SiC heterogeneous system chemoselectively catalyzed the hydro-

genation of alkyne, alkene, azide, nitro, and aromatic N-Cbz functionalities. The silicon carbide-supported palladium catalysts reveal good reusability for at least three cycles under batch-reaction conditions. The 3% Pd(DETA)/SiC catalyst shows good chemoselectivity for the semihydrogenation of various mono- and disubstituted alkynes under batch- and flow-conditions (Contribution 13). In the fourteenth contribution, V. Ritleng et al. report an aerobic oxidation of N-methylisoquinolinium salts to the isoquinolones and sulfides to sulfoxides under visible-light irradiation by EY-APTES@PDA@PUF foam photocatalysis. The heterogeneous EY-APTES@PDA@PUF foam is synthesized by functionalization of a polydopamine-coated open-cell polyurethane foam (PDA@PUF) by silanization of the adhesive layer with 3-(triethoxysilyl)propan-1-amine (APTES) and the subsequent EDC-mediated coupling of the resulting amino-functionalized foam with Eosin (Contribution 14). Y. S. Zhou et al. provide a new example of photodegradation of organic pollutants over a heterojunction of BiOBr/protonated graphitic carbon nitride (*g*-C_3N_4). The photocatalytic activities of the BiOBr/g-C_3N_4 heterojunctions were evaluated by the degradation of RhB under visible-light irradiation ($\lambda \geq 420$ nm) (Contribution 15). G.P Romanelli et al. modify the surface of the polymeric matrix of polyacrylamide (PLM) by tungstophosphoric acid (TPA) to obtain a new series of composite materials (PLMTPA). PLMTPA materials are used as heterogeneous catalysts for the synthesis of 2-benzo[*c*]azepines (Contribution 16). In another contribution, G. V. Botteselle et al. report the preparation and characterization of iron-doped borophosphate glass (Fe@NaH_2PO_4-H_3BO_3 glass), applied as a catalyst for the hydrothiolation of alkynes under solvent-free conditions for the synthesis of vinyl sulfides in high stereoselectivity. The iron-doped borophosphate glass can be reused, and the scale-up of the reaction has been proven (Contribution 17). R. Luque et al. highlight that through mechanochemical incorporation of iron oxide precursors [alpha-Fe_2O_3 (hematite)] on silk cocoons as a sacrificial template, it is possible to synthesize natural nanostructured iron-based catalysts that are magnetically separable. The cocoon Fe-mag catalysts are promised materials for the oxidation of benzyl alcohol (Contribution 18). The last example of heterogeneous catalysis is reported by G.P. Romanelli et al., who prepare N-substituted pyrroles through a Paal–Knorr reaction of acetonylacetone with primary amines catalyzed by commercially available aluminas (CATAPAL200). The catalyst is easily separated from the reaction medium and reused up to five times without appreciable loss of its catalytic activity (Contribution 19).

2.2. Catalysis in Polymer Chemistry

The first paper is reported by J.-F. Carpentier et al. that provides a new synthetic strategy for the synthesis of 2,20-fluorenyl-linked bis(ansa-zirconocene)s and its use, combined with methylaluminoxane (MAO), in the homogeneous (co-)polymerization of ethylene, propylene, and ethylene/1-hexene (Contribution 20). On the other hand, W.-H. Sun et al. report another example of ethylene polymerization, with narrow polydispersity, catalyzed by 2-(arylimino)benzylidene-8-arylimino-5,6,7-trihydroquinoline Cobalt(II) chlorides, containing a fused ring and an inert phenyl group as a substituent at the imino-C atom, combined with MAO or modified methylaluminoxane (MMAO). The vinyl- or *n*-propyl-terminated polyethylene molecular weight can be regulated by controlling polymerization parameters (Contribution 21). In the twenty-second contribution, W.-H Sun again describe the ethylene polymerization, catalyzed by nitro-appended 2-(arylimino)pyridine-nickel catalysts. Para-nitro substituted 2-(arylimino)pyridine-nickel(II) bromide complexes, upon activation with either ethylaluminum dichloride ($EtAlCl_2$) or modified methylaluminoxane (MMAO), display good catalytic performance at 30 °C and 60 °C, with higher activities using $EtAlCl_2$ (Contribution 22). In the twenty-third contribution, T. Jiang et al. prepare three new nickel (II) complexes stabilized by PNP(NR_2)$_2$ (R = methyl, ethyl, isopropyl)

ligands, upon activation with EADC in a methylcyclohexane solvent, for ethylene oligomerization. The nickel-based PNP(NMe2)2 catalyst presents the greatest activity and selectivity in 1-butene derivatives (Contribution 23). L. D. Wilson et al. report the preparation of composite materials (Ag@P-CA) by immobilizing Ag nanoparticles (Ag NPs) onto citric-acid-modified polyaniline (PANI) as a semi-conductive support for the electrochemical oxidization of 2-nitrophenols and 4-nitrophenols, as a useful tool for the electrocatalytic remediation of these contaminants present in the water (Contribution 24). Z. Cai et al. provide a new synthesis of high-molecular weight norbornene (NB)/methyl acrylate (MA) copolymers by 2-(diarylphosphino)-N-phenylbenzenamine–nickel complexes-catalyzed copolymerization of NB and MA (Contribution 25). In the last contribution, A. Grassi et al. highlight the synthesis of poly(cyclohexene oxide) (PCHO) by cyclohexene oxide (CHO) polymerization-zinc complex [$Zn(C_6F_5)_2$(toluene)] catalyzed. On the other hand, poly(cyclohexene carbonate) (PCHC) can be obtained by copolymerization of CO_2 with CHO catalyzed by $Zn(C_6F_5)_2$(toluene)] catalyst (Contribution 26).

Author Contributions: Conceptualization, R.M. and V.C.; formal analysis, R.M.; writing—original draft preparation, R.M.; writing—review and editing, R.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

List of Contributions:

1. Fomenko, I.S.; Koshcheeva, O.S.; Kuznetsova, N.I.; Larina, T.V.; Gongola, M.I.; Afewerki, M.; Abramov, P.A.; Novikov, A.S.; Gushchin, A.L. Novel Copper(II) Complexes with BIAN Ligands: Synthesis, Structure and Catalytic Properties of the Oxidation of Isopropylbenzene. *Catalysts* **2023**, *13*, 849. https://doi.org/10.3390/catal13050849.
2. Marangoni, R.; Carvalho, R., E.; Machado, M.V.; Dos Santos, V.B.; Saba, S.; Botteselle, G.V.; Rafique, J. Layered Copper Hydroxide Salts as Catalyst for the "Click" Reaction and Their Application in Methyl Orange Photocatalytic Discoloration. *Catalysts* **2023**, *13*, 426. https://doi.org/10.3390/catal13020426.
3. Viana, M.S.; Gomes, C.S.B.; Rosa, V. Heteroleptic Copper Complexes as Catalysts for the CuAAC Reaction: Counter-Ion Influence in Catalyst Efficiency. *Catalysts* **2023**, *13*, 386. https://doi.org/10.3390/catal13020386.
4. Nesterova, O.V.; Pombeiro, A.J.L.; Nesterov, D.S. Tetranuclear Copper Complexes with Bulky Aminoalcohol Ligands as Catalysts for Oxidative Phenoxazinone Synthase-like Coupling of Aminophenol: A Combined Experimental and Theoretical Study. *Catalysts* **2022**, *12*, 1408. https://doi.org/10.3390/catal12111408.
5. Tarrach, X.; Yang, J.; Soleiman-Beigi, M.; Díez-González, S. Straightforward and Efficient Deuteration of Terminal Alkynes with Copper Catalysist. *Catalysts* **2023**, *13*, 648. https://doi.org/10.3390/catal13040648.
6. Bołt, M.; Zak, P. Bulky NHC–Cobalt Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes. *Catalysts* **2023**, *13*, 510. https://doi.org/10.3390/catal13030510.
7. Titova, Y.Y.; Dynamic EPR Studies of the Formation of Catalytically Active Centres in Multicomponent Hydrogenation Systems. *Catalysts* **2023**, *13*, 653. https://doi.org/10.3390/catal13040653.
8. Kapłon, K.; Frynas, S.; Mirosław, B.; Lipkowski, J.; Demchuk, O.M. An Efficient Asymmetric Cross-Coupling Reaction in Aqueous Media Mediated by Chiral Chelating Mono Phosphane Atropisomeric Biaryl Ligand. *Catalysts* **2023**, *13*, 353. https://doi.org/10.3390/catal13020353.
9. Fomenko, I.S.; Gongola, M.I.; Shul'pina, L.S.; Ikonnikov, N.S.; Komarovskikh, A.Y.; Nadolinny, V.A.; Kozlov, Y.N.; Gushchin, A.L.; Shul'pin, G.B. Mononuclear Oxidovanadium(IV) Complexes with BIAN Ligands: Synthesis and Catalytic Activity in the Oxidation of Hydrocarbons and Alcohols with Peroxides. *Catalysts* **2022**, *12*, 1168. https://doi.org/10.3390/catal12101168.

10. Bisag, G.D.; Viola, P.; Bernardi, L.; Fochi, M. Divergent Reactivity of D-A Cyclopropanes under PTC Conditions, Ring-Opening vs. Decyanation Reaction. *Catalysts* **2023**, *13*, 760. https://doi.org/10.3390/catal13040760.
11. Ajvazi, N.; Stavber, S. N-Iodosuccinimide as a Precatalyst for C–N Bond-Forming Reactions from Alcohols under Mild Reaction Conditions. *Catalysts* **2022**, *12*, 1368. https://doi.org/10.3390/catal12111368.
12. Liu, Z.; Li, J.; Tan, Y.; Guo, L.; Ding, Y. Copper Supported on MgAlOx and ZnAlOx PorousMixed-Oxides for Conversion of Bioethanol via Guerbet Coupling Reaction. *Catalysts* **2022**, *12*, 1170. https://doi.org/10.3390/catal12101170.
13. Yamada, T.; Yamamoto, H.; Kawai, K.; Park, K.; Aono, N.; Sajiki, H. Development of Silicon Carbide-Supported Palladium Catalysts and Their Application as Semihydrogenation Catalysts for Alkynes under Batch- and Continuous-Flow Conditions. *Catalysts* **2022**, *12*, 1253. https://doi.org/10.3390/catal12101253.
14. Peng, H.; Romero, T.; Bertani, P.; Ritleng, V. Polydopamine-Coated Polyurethane Foam as a Structured Support for the Development of an Easily Reusable Heterogeneous Photocatalyst Based on Eosin Y. *Catalysts* **2023**, *13*, 589. https://doi.org/10.3390/catal13030589.
15. Liu, J.; Guo, H.; Yin, H.; Nie, Q.; Zou, S. Accelerated Photodegradation of Organic Pollutants over BiOBr/Protonated g-C_3N_4. *Catalysts* **2022**, *12*, 1109. https://doi.org/10.3390/catal12101109.
16. Aguilera Palacios, E.X.; Palermo, V.; Sathicq, A.G.; Pizzio, L.R.; Romanelli, G.P. A New Series of Tungstophosphoric Acid-Polymeric Matrix Catalysts: Application in the Green Synthesis of 2-Benzazepines and Analogous Rings. *Catalysts* **2022**, *12*, 1155. https://doi.org/10.3390/catal12101155.
17. Catholico, N.; Tessari, E.A.; Granja, I.J.A.; de Sousa, M.J.A.; Felix, J.F.; Manarin, F.; Godoi, M.; Rafique, J.; Schneider, R.; Saba, S.; et al. Iron-Borophosphate Glass-Catalyzed Regioselective Hydrothiolation of Alkynes under Green Conditions. *Catalysts* **2023**, *13*, 1127. https://doi.org/10.3390/catal13071127.
18. Arancon, R.A.D.; Al Othman, Z.A.; Len, T.; Shih, K.; Voskressensky, L.; Luque, R. Naturally Nano: Magnetically Separable Nanocomposites from Natural Resources for Advanced Catalytic Applications. *Catalysts* **2022**, *12*, 1337. https://doi.org/10.3390/catal12111337.
19. Portilla-Zúñiga, O.; Bautista-Aguilera, O.M.; Martínez, J.J.; Rojas, H.; Macías, M.A.; Iriepa, I.; Pérez-Redondo, A.; Sathicq, A.; Castillo, J.-C.; Romanelli, G.P. Synthesis of N-Substituted Pyrroles Catalyzed by Low-Cost and Commercially Available Aluminas. *Catalysts* **2023**, *13*, 603. https://doi.org/10.3390/catal13030603.
20. Jende, L.N.; Roisnel, T.; Virginie Cirriez, V.; Welle, A.; Kirillov, E.; Carpentier, J.-F. An Asymmetric Dinuclear Bis(ansa-Zirconocene) Complex: Synthesis and Performance in Olefin (co-)Polymerization. *Catalysts* **2023**, *13*, 1108. https://doi.org/10.3390/catal13071108.
21. Zuo, Z.; Zhang, Q.; Han, M.; Liu, M.; Sun, Y.; Ma, Y.; Sun, W.-H. 2-(Arylimino)benzylidene-8-arylimino-5,6,7-trihydroquinoline Cobalt(II) Dichloride Polymerization Catalysts for Polyethylenes with Narrow Polydispersity. *Catalysts* **2022**, *12*, 1119. https://doi.org/10.3390/catal12101119.
22. Sage, D.D.; Zhang, Q.; Liu, M.; Solan, G.A.; Sun, Y.; Sun, W.-H. LLDPE-like Polymers Accessible via Ethylene Homopolymerization Using Nitro-Appended 2-(Arylimino)pyridine-nickel Catalysts. *Catalysts* **2022**, *12*, 961. https://doi.org/10.3390/catal12090961.
23. Cao, C.; Haonan Fan, H.; Zhang, J.; Ma, J.; Jiang, T. Nickel-Catalyzed Ethylene Dimerization Based on PNP(NR_2)$_2$ Ligands. *Catalysts* **2022**, *12*, 1008. https://doi.org/10.3390/catal12091008.
24. Khani, M.; Sammynaiken, R.; Wilson, L.D. Electrocatalytic Oxidation of Nitrophenols via Ag Nanoparticles Supported on Citric-Acid-Modified Polyaniline. *Catalysts* **2023**, *13*, 465. https://doi.org/10.3390/catal13030465.
25. Cao, L.; Li, M.; Cai, Z. Copolymerization of Norbornene and Methyl Acrylate by Nickel Catalyst Bearing 2-(Diarylphosphino)-Nphenylbenzenamine Ligands. *Catalysts* **2023**, *13*, 311. https://doi.org/10.3390/catal13020311.
26. Sokolovicz, Y.C.A.; Antonio Buonerba, A.; Capacchione, C.; Dagorne, S.; Grassi, A. Perfluoroaryl Zinc Catalysts Active in Cyclohexene OxideHomopolymerization and Alternating Copolymerization with Carbon Dioxide. *Catalysts* **2022**, *12*, 970. https://doi.org/10.3390/catal12090970.

References

1. Yan, Z.; Shi, P.; Wang, J.; Song, Y.; Ban, H.; Li, C. Understanding the Role of H_2O in Heterogeneous Catalysis of CO_x Hydrogenation. *ChemCatChem* **2024**, *16*, e202401135. [CrossRef]
2. Gabriele, B.; Mancuso, R.; Della Ca', N.; Veltri, L.; Ziccarelli, I. An Overview of Catalytic Carbonylative Double Cyclization Reactions. *Catalysts* **2023**, *13*, 1025. [CrossRef]
3. Kornet, M.M.; Thomas, J.J.; Müller, T.J.J. Recent Advances in Sequentially Pd-Catalyzed One-Pot Syntheses of Heterocycles. *Molecules* **2024**, *29*, 5265. [CrossRef] [PubMed]
4. Tian, T.; Uei, S.; Li, Z.; Nishihara, Y. A Highly Efficient Cross-Coupling Mode via the Release of Small Molecules: Transition Metal-Catalyzed Unimolecular Fragment Coupling (UFC). *ChemCatChem* **2024**, *16*, e202401190. [CrossRef]
5. Gaucherand, A.; Yen-Pon, E.; Domain, A.; Bourhis, A.; Rodriguez, J.; Bonne, D. Enantioselective Synthesis of Molecules with Multiple Stereogenic Elements. *Chem. Soc. Rev.* **2024**, *53*, 11165. [CrossRef] [PubMed]
6. Hu, S.; Zhao, Q.; Luo, M.; Xin, S.; Mao, G. Research Progress of Iron Catalysts with *N,N,N*-tridentate Ligands for Ethylene Polymerization. *ChemistrySelect* **2024**, *9*, e202303611. [CrossRef]