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Editorial

Catalysts: Advances in the Catalytic Behavior of Ion-Exchange Resins

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Ion-exchange resins have been embraced as a relevant scientific development of the 20th century. They have been widely recognized as useful materials for industrial chemical transformations because of their broad applicability to water softening, environmental remediation, hydrometallurgy, chromatography, biomolecular separation, and the heterogeneous catalysis of organic reactions such as etherification, hydration, dehydration, esterification, alkylation, oligomerization, and hydrogenation [1,2].

These organic solid materials, which are mostly but not exclusively styrene–DVB copolymers, are insoluble, which makes them suitable replacements for homogeneous catalysts such as sulfuric acid. They are also environmentally adaptable to batch and continuous processes because of their easy separation from the process mixture and subsequent recyclability [3]. However, they have limited thermal stability at temperatures up to 120–150 °C, a feature that sometimes represents a drawback. Despite this, ion-exchange resins can selectively catalyze—with recognizable activity—thermodynamically favorable reactions at low/mild temperatures with catalytic performance comparable to that of conventional catalysts such as alumina or zeolites.

In contribution 1, Dorado et al. perform the H_2O_2/KBr/sulfonic acid method for secondary hydroxy fatty ester oxidation. They propose and test the heterogenization of this process by means of sulfonic acid substitution with a sulfonated solid polymer (Aquivion PW97S, Aquivion P98, Nafion NR50, Amberlyst 15, Dowex 50 W × 8, and Dowex 50 W × 2). They also successfully apply the same procedure to the oxidation of other alcohols. Methyl 9(10)-hydroxystearate, a secondary fatty alcohol, is used as a substrate to assess the catalytic resins' performance and compare it to that of the homogeneous method using two sulfonic acids of different strengths (p-toluenesulfonic and triflic acids) under the experimental conditions described in the available literature. Their results show that sulfonic resin introduction improves the alcohol oxidation procedure.

Patiño et al. (contribution 2) elucidate the potential application of ion-exchange resins in biorefineries through three different reactions for biomass upgrading. In the continuous gas-phase synthesis of poly(oxymethylene) dimethyl ethers for fuel additives, the resin Amberlyst 15 shows selectivity values close to 100% when the reaction is performed at temperatures over 60 °C. These results are significantly better than those obtained with different mineral acids, ionic liquids, carbon materials, and solid superacids, and they are comparable with those over HZSM-5 zeolite. In the in situ discontinuous transesterification of the lipid phase of sludge to produce biodiesel, Amberlyst IR-120 shows good catalytic performance (yield around 6.7%) and stability (six cycles) in the presence of water. The resin's acidity and swelling capacity explain its catalytic performance. Finally, in the aqueous-phase condensation of furfural and levulinic acid to obtain platform molecules, the mesoporous nature of the resins Amberlyst 36 and IR-120 overcomes the diffusional limitations found in the aldol condensation of platform molecules using an acidic zeolite, H-β-25, at a mild temperature (125 °C).

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In contribution 3, Abidin et al. report the successful two-stage synthesis of biodiesel from waste cooking oil using a combination of ion-exchange resins. Purolite D5081, a hyper-cross-linked resin, shows a free fatty acid conversion rate of 92% for the esterification step, while Diaion PA306s gives the best catalytic performance, with 75% triglyceride conversion, for the transesterification of a pre-treated substrate with methanol at low temperatures. This resin presents similar catalytic activity after being reused for three consecutive cycles.

The porosity of ion-exchange resins depends on their morphology and swelling capacity. Gel-type (1–8% DVB) and macroporous (more than 8% DVB) resins have very different intrinsic porosity (dry state): macroporous resins have mesopores, whereas the gel-type resins are impervious. However, because of interactions with the medium (liquid or gaseous), they develop variable porosity; this allows for a high surface area and pore volume increase, creating new spaces for reactions and facilitating the reactants' access to functional groups. Despite the low thermal stability of most resins, their morphology is suitable for acting as a metal support for bifunctional catalysis. Bifunctional catalysts supported on resins have drawn increased interest for redox reactions (hydrogenation, oxidation) conducted at moderate temperatures.

In contribution 4, Badia et al. review the role of ion-exchange resins as catalysts or catalyst supports in the gas- and liquid-phase hydrogenation of alkenes, alkynes, carbonyls, arenes, and nitroaromatics, among other families of organic molecules, reported in the literature back to the early 2000s. This work highlights the potential of bifunctional catalysts obtained via the inclusion of metals into polymeric resin backbones. The high yields, reusability, and recyclability associated with these resins make them promising solid catalysts for assorted industrial applications that entail multistep reactions.

The variable morphology of ion-exchange resins is due to their interactions with reaction media causing a swelling phenomenon, resulting in some regions of the polymer becoming accessible to reactants [4] and making their catalytic behavior complex to describe. Moreover, their catalytic activity is a function of their acid capacity and acid strength, the latter being challenging to comprehensively characterize. This makes it difficult to establish a reliable qualitative/quantitative relationship between the morphology and structure of resins and their catalytic performance as solid supports.

Godoy et al. (contribution 5) focus on assessing the active site accessibility of vinyl–trivinyl acidic resins with different cross-linker contents in glycerol acetylation. Their results show that the mean catalytic efficiency linearly decreases with an increase in the trimethylolpropane triacrylate (TMPTA) content, demonstrating the effect of reduced accessibility in dense polymer networks. Statistical and kinetic models allow for a representation of the experimental results and support the development of strategies to improve the resin formulation and synthesis conditions.

Finally, knowledge about effectiveness factors is a keystone feature of chemical reactor design. However, these factors have not been successfully estimated for reversible reactions, especially for reactions performed using catalysts whose morphology changes with the reaction medium composition, as is the case with ion-exchange resins. In contribution 6, Rios et al. provide an outstanding solution by expressing effectiveness factors for bimolecular reversible reactions in terms of an irreversible nth-order Thiele Modulus (specifically written for the nth-order forward reaction), the thermodynamic equilibrium constant, the ratios of effective diffusivities, and the ratios of surface concentrations. The methodology is applied to ethyl acetate and acetaldehyde dimethyl acetal synthesis, with errors ranging from 1.2% to 3.4% in the predicted concentration profiles for six experimental conditions.

In this Special Issue, the potential of ion-exchange resins as catalysts for green and sustainable heterogeneous chemical processes is envisaged. The contributions also provide insights into the morphological, physical, and chemical characterizations of these resins, improving our general understanding of their catalytic performance.

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List of Contributions:

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