

Editorial

Catalysis on Zeolites and Zeolite-like Materials II

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This Special Issue is a continuation of the previous successful Special Issue, “Catalysis on Zeolites and Zeolite-Like Materials”, which presented the latest developments and advances in the synthesis, characterization, and application of zeolites and zeolite-like materials as catalysts by renowned scientists. Recent research results indicate that the potential of zeolitic molecular sieves is far from exhausted. Scholars in various fields, including chemistry, physics, biology, and chemical reaction engineering, are increasingly interested in this class of substances. The eleven Contributions in this Special Issue once again demonstrate that zeolites and zeolite-like materials are ideal for a wide range of applications as adsorbents and catalysts in chemical technology due to their regular pore systems, with cavities and channels in sub-nanometer dimensions, and their surface properties.

In their Contributions, Al-Shammari et al. Contribution 1 and Echevsky et al. Contribution 2 report on progress in the preparation and modification of zeolite-containing catalysts for processes in the petrochemical industry.

In Contribution 1, a series of FCC catalysts with different zeolite-to-matrix ratios was prepared using USY zeolite and an amorphous matrix. The performance evaluation of FCC catalysts was conducted in a fixed-bed microactivity test unit, with hydrotreated vacuum gas oil (VGO) as feed at 550 °C. The surface area and acidity of all FCC catalyst samples were found to increase as the zeolite-to-matrix ratio increased, but this occurred to different extents for steamed and fresh samples. In both cases, increasing the zeolite-to-matrix ratio resulted in increased production selectivity of dry gas, liquified petroleum gas, and coke, coupled with a steady decrease in gasoline and heavy end products. Thus, it was concluded that an increase in the zeolite-to-matrix ratio enhanced secondary reactions, such as overcracking of liquid products, more than the primary VGO cracking reaction.

Contribution 2 describes a new method for the synthesis of micro-mesoporous silicoaluminophosphate SAPO-31 using tetraethoxysilane as a source of silicon based on the Stöber process approach. This method allows for controlling the mesopore diameter and volume and, hence, the external surface area of the synthesized material. The proposed methods of depositing the hydro-dehydrogenating component on the synthesized SAPO-31 can be applied to obtain highly efficient bifunctional hydroisodeparaffinization catalysts with platinum or palladium content exceeding 0.2 wt.%. As a result, the process temperature can be decreased by 50–60 °C compared to known analogs.

The Contributions by Traa et al. Contribution 3, Seifert et al. Contribution 4, and Seames et al. Contribution 5 focus on the development of new zeolite systems, tools for their modification, and scale-up process development for promising applications of zeolite-based catalysts in environmental catalysis.

Contribution 3 focuses on the production of basic chemical acrylic acid from bio-based lactic acid as an important step towards sustainability. The gas-phase dehydration reaction of lactic acid to acrylic acid was performed over eight-membered ring PHI-type zeolites in Na⁺- and K⁺-form. Variations in the synthesis process of PHI-type zeolite resulted in significant differences in performance during the catalytic reaction due to differences in surface area and pore accessibility. For Na,K-PHI with a low surface area, catalysis tends to occur on the outer surface, while for Na,K-PHI with a high surface area, catalysis can also



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take place within the pore system. This has a considerable influence on the selectivity of the catalysts. The high acetaldehyde selectivity of the high surface area materials is due to secondary reactions promoted by diffusion limitations.

The authors of Contribution 4 investigated the conversion of guaiacol, a surrogate for complex lignin-based biomass resources, using an inert silica carrier material with different d-metal impregnation (Mo, W, Re, Fe, Co, Ni, Cu, Pd, Ag) to reveal the reasons for different product selectivity to hydrogenated and deoxygenated hydrocarbon products. It was shown that for ring hydrogenation, a geometrical correspondence (i.e., hexagonal symmetry with optimal atomic spacing) combined with an energetic correspondence (i.e., a not fully occupied d-shell) are necessary. For deoxygenation prevailing at high temperatures, product selectivity depends on the aromatic products on the center of the d-band, correlating with oxophilicity. The results are summarized in a pseudo van Krevelen diagram and interpreted as complex interdependency from Sabatier's principle of the geometric correspondence of hexagonal metal surface for hydrogenation, electronic correspondence for hydrogen activation, and oxophilicity for deoxygenation from the d-band center model.

Contribution 5 examines the extent to which two laboratory-scale reactions that can be used to convert bio-based levulinic acid into 2-methyltetrahydrofuran (2-MeTHF) can be transferred and optimized to a continuous bench-scale unit. 2-MeTHF is an important monomer for producing liquid polyols, which are used in polymer foam products. First, a hydrogenation reaction transforms levulinic acid into γ -valerolactone (GVL) using isopropanol and a Zr- β -zeolite catalyst. Next, GVL is reacted with hydrogen to form 2-MeTHF utilizing a CuO/Al₂O₃ catalyst. Both reactions were optimized in bench-scale continuous flow reactors to produce 2-MeTHF in one step. Using a single pass in each reaction, an overall yield of 81 mol.-% was achieved. This yield is projected to increase to 87 mol.-% when first-reaction intermediates are recovered and recycled back into the first reactor.

Popova et al. Contribution 6 and Valtchev et al. Contribution 7 investigated the heterogeneous catalyzed hydrogenation of CO₂ to single-carbon (C₁) products as an efficient option for developing more environmentally friendly products compared to fossil-based ones.

In Contribution 6, the authors addressed a series of Ni- and/or Ru-modified ZSM-5 zeolite catalysts, prepared by the wet impregnation method, to determine the influence of Ni content, the addition of Ru, and the sequence of modification by two metals on the physicochemical and catalytic properties of the catalysts in CO₂ methanation (the Sabatier process). It was found that the zeolite structure and modification procedure determined the type of formed metal oxides, their dispersion, and reducibility. An XPS study revealed that the surface became richer in nickel and poorer in ruthenium for bimetallic catalysts. Correspondingly, a TPR study confirmed the facilitated reducibility of nickel oxide particles in the presence of noble metal. Among the studied catalysts, the 10Ni5RuZSM-5 composition showed the highest activity and high selectivity for methane formation, reaching equilibrium conversion and 100% selectivity at 400 °C.

Contribution 7 focuses on the mechanistic aspect of methanol synthesis from CO₂ hydrogenation on Cu-based catalysts with ultrafine Cu clusters smaller than 2.0 nm encapsulated in nanosized silicalite-1 zeolite through direct crystallization in the presence of Cu(en)₂²⁺ complex ions as the metal precursor. The obtained composite material, as a model catalyst, allows for CO₂ activation and hydrogenation to methanol. The methanol space-time yield is comparable with the benchmark test utilized, using a commercial Cu/ZnO/Al₂O₃ catalyst. A preliminary in situ FTIR study identifies a series of surface-adsorbed carbonyl, formyl, carbonate, and formate species when the material was exposed to CO₂ and H₂. Among these, the adsorbed formate decayed most rapidly upon cofeeding CO₂ and H₂, implying that the most probable pathway toward methanol formation for this material is via the formate-mediated mechanism.

The Contributions by Hartmann et al. Contribution 8, Derewinski et al. Contribution 9, Dzwigaj et al. Contribution 10, and Vorontsov et al. Contribution 11 are devoted to new methods of synthesis and in-depth characterizations of the physico-chemical properties of obtained microporous nanosized zeolites with a number of useful applications.

In Contribution 8, it was shown that the combination of spray drying and steam-assisted crystallization (SAC) can improve the efficiency of hydrothermal synthesis of aluminum-containing nanoscale MFI-type zeolites. At spray-drying temperatures between 300 and 400 °C, the amorphous material was converted via SAC into zeolite particles without extra addition of a template. Kinetic studies of SAC revealed that about 4 to 8 days are needed to achieve the formation of a 100% crystalline product. The newly formed crystalline phase crystallized on the surface of the nanosized zeolites and led to a slight increase in primary particle size while preserving the macroscopic morphology of the spray-dried aggregates. This work demonstrates that the combination of spray drying and SAC are useful tools in supplementing the hydrothermal synthesis of nanosized zeolites.

The authors of Contribution 9 report a simple and scalable method to increase the Al pair distribution in siliceous SSZ-13 zeolite (Si/Al~10) by synthesis in the presence of Sr(OH)₂. Al distribution was shown to be key to the exchange of larger amounts of divalent metal cations (e.g., Co(II) and Pd(II)) atomically dispersed in the SSZ-13 micropores. The resulting materials demonstrate the ability to adsorb NO_x pollutants under various conditions. They have remarkable hydrothermal stability, withstanding exceptionally harsh hydrothermal aging conditions (such as those in vehicle exhaust gases) at 900 °C and not losing their full NO_x adsorption capacity at even higher temperatures for both catalytic and adsorption applications. This Contribution reveals a previously unexplored route to produce zeolites and metal/zeolite composites with tailored proportions of paired sites and beneficial properties (stability, activity) not previously available.

Contribution 10 deals with the preparation of potential catalysts, Co all-silica and Co Al-containing zeolites beta, for use in the selective oxidative dehydrogenation of propane to propylene. Two series of Co all-silica zeolite catalysts were prepared by a two-step post-synthesis method at pH = 2.5 and pH = 3.0–9.0, respectively. This method allows for the incorporation of cobalt ions into SiBEA zeolite via their reaction with silanol groups. The generation of Lewis acid sites without the formation of Brønsted sites was confirmed by NMR and FTIR using pyridine and CO as probe molecules. DR UV-vis spectroscopy showed that, for low Co content (<2 wt.%), cobalt is present in the form of framework pseudo-tetrahedral Co(II) species. For higher Co content (>2 wt.%), both framework pseudo-tetrahedral and extra-framework octahedral Co(II) species are present. The Co Al-containing zeolite beta series prepared on non-dealuminated support shows the presence of only extra-framework octahedral Co(II).

Contribution 11 presents a DFT study on single Brønsted acid sites in zeolite beta modification A, correlating the widely used TPD methods of their identification with the theoretically determined strongest and weakest acid sites. A diverse set of probe molecules, with a wide range of acid strength in their conjugated acids, was applied to determine the heat of their adsorption over protonated zeolite beta samples. The molecules studied were acetonitrile, dimethyl sulfide, dimethyl sulfoxide, isothiazole, pyridine, tetrahydrofuran, and ammonia. It was found that the heat of adsorption of the probe molecules only partially correlated with the acid strength of acid sites. Only some of the strong acid sites were able to be identified, while the weakest acid site was often identified correctly. The authors conclude that the widely used method of studying zeolite acid sites delivers only partially correct results, and conclusions from such TPD studies should be treated with caution.

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