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Editorial

Editorial for Special Issue "New Insights in Stability, Structure and Properties of Porous Materials"

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Porous materials (such as zeolites, clay minerals, and assemblies of oxide nanoparticles) are of great importance for the progress in many technological and environmental fields, such as catalysis, adsorption, separation, and ion exchange, because of their unique pore topologies, tunable structures, and the possibility of introducing active reaction sites.

The major goal of this special issue is to provide a platform for scientists to discuss new insights in the stability, structure, and properties of porous materials, as well as in innovative aspects in their processing and applications. The emphasis is on the relationships between the structure and/or chemical composition and the specific physical properties of these materials, as well as their role in mineralogical, technological, green, and sustainable processes. With this special issue of *Minerals*, we have endeavored to provide an up-to-date selection of high-quality original and review papers concerning the physical, chemical, and structural characterization of porous materials, the synthesis of crystalline phases with pores in the appropriate range, structure–property relationships at ambient conditions but also at high temperatures and/or at high pressures, adsorption, and diffusion of mobile species in porous materials, host/guest interactions and confinement effects, ion exchange, modeling in geological and environmental processes, and new insights in processing and applications. In total, eight fashionable contributions reflect both the diversity and interdisciplinary of modern mineralogy, bridging together experimentalists and computational approaches.

The review presented by Bandura et al. [1] is dedicated to the decontamination strategies available today for the removal of petroleum substances and their derivatives from roads, water, and air. Specifically, this paper presents an overview of recent research papers concerning porous (natural, synthetic, and modified mineral adsorbents) materials used as adsorbents for petroleum pollutants, present in water and spilled on land, occurring as oils, petroleum industry derivatives, and volatile compounds. Environmental pollution with petroleum products has become a major problem worldwide and is a consequence of industrial growth. The development of sustainable methods for the removal of petroleum substances and their derivatives from aquatic and terrestrial environments and from air has therefore become extremely important today.

Advanced technologies and materials dedicated to this purpose are relatively expensive. Among several techniques developed for BTEX (benzene, toluene, ethylbenzene, and xylene) removal from waters, adsorption is one of the most efficient methods, thanks to satisfactory efficiencies (even at low concentrations), easy operation, and low cost [2,3].

Recently, adsorption on hydrophobic zeolites has received the greatest interest in water treatment technology due to their organic contaminant selectivity, thermal and chemical stability, strong mechanical properties, rapid kinetics, and absence of salt and humic substance interference [4–10]. In this issue, the Sarti et al. [11] contribution is dedicated to this topic and is focused on the adsorption of toluene from aqueous solutions onto hydrophobic beta zeolites by combining chromatographic, thermal, and structural techniques. This work highlights the differences in adsorption properties between as-synthesized and calcined beta zeolites, with different SiO_2/Al_2O_3 ratios, toward a water contaminant of great concern such as toluene. The authors demonstrate that the thermal treatment significantly improves the adsorption properties of all selected zeolites especially for the most hydrophobic beta, thus opening new alternatives for the industrial application of this material, mainly in hydrocarbon adsorption processes in the presence of water.

In order for the adsorption process to be cost-effective, the progressive deactivation of saturated sorbents has become an essential task [12–16]. Thermal treatment is the most common regeneration technique, where organic host molecules are decomposed and/or oxidized at high temperature. Consequently, there is a strong interest in understanding the mechanisms behind the thermal regenerative solution, which makes zeolites regenerable materials that are efficiently reusable in the contaminant adsorption process. In this issue, the temperature-induced desorption of methyl *tert*-butyl ether (MTBE) from aqueous solutions onto hydrophobic ZSM-5 zeolite is studied by Rodeghero et al. [17] using in situ synchrotron powder diffraction and chromatographic techniques. Rietveld analysis demonstrated that the desorption process occurred without any significant zeolite crystallinity loss, but with slight deformations in the channel apertures. This kind of information is crucial for understanding the features of both adsorption and desorption processes, thus helping in the design of water treatment appliances based on microporous materials as well as designing and optimizing the regeneration treatment of zeolite.

As reported in this issue by Bundru et al. [18], the regeneration of the exhausted zeolite as well as the recovery of ammonia are feasible processes. Spent exchangers such as NH_4-exchanged synthetic zeolites can be transformed into mullite and amorphous silica by thermal treatments [19–21]. With this perspective, a material containing NH_4-clinoptilolite, derived from a wastewater treatment, has be evaluated as a potential raw material for the ceramic industry. The results of this research are interesting, because they indicate that NH_4-clinoptilolite represents a raw material of interest in the ceramic field, in particular in the production of acid refractory.

The reuse (addition) of the spent zeolitic sorbents containing petroleum waste to produce lightweight aggregates (LWAs) is also discussed by Franus et al. [22]. It is well known that the mineral composition and organic amendments to the substrate can control the physical properties of LWAs. Therefore, Franus et al. [22] hypothesize here that the addition of waste zeolites can modify the structure of the standard clay-based LWAs towards higher porosity, which differs depending on the zeolite used.

As reported by Arletti et al. [23], recent studies on the behavior of both natural and synthetic microporous materials under high pressure (HP) provide important information on their elastic behavior and stability, thus opening new perspectives for technological applications. This paper presents a study, performed by in situ synchrotron X-ray powder diffraction (XRPD), of the HP stability and behavior of the natural zeolite amicite. The investigation aimed in particular to understand the relationships between compressibility and framework/extraframework content as well as the influence of different penetrating or non-penetrating fluids on the compressibility and HP deformation mechanisms of this zeolite.

In the present volume, Krupskaya et al. [24] discuss the mechanism of montmorillonite structural alteration and the modification of bentonites' properties under thermochemical treatment (treatment with inorganic acid solutions at different temperatures, concentrations, and reaction times). The mechanism of montmorillonite transformation under acid solution treatment as well as its influence on bentonite properties are evaluated. The modification of structural and adsorption characteristics with acid treatment can be useful to simulate behavior of the engineered barrier properties for repositories of radioactive and industrial wastes, especially in the case of dealing with liquid radioactive wastes.

The aim of the Steudel et al. [25] study is the characterization of a clay from the Madrid basin, which shows exceptional suitability as adsorbent material in biotechnology processes [26], as adsorbent for mycotoxins [27] as well as in pesticide removal from water [28] for this clay. This last can be also used to bind contaminants from the manufacture of paper [29]. The authors reported that this clay is highly suitable for mining without chemical pretreatment, which reduces environmental burden [29].

Finally, the Due et al. study [30] is focused on volumetric swelling strain and strength reduction of pillars when CO_2 is stored in abandoned coal mines. The volumetric swelling strain is theoretically derived as a function of time by adsorption pressure increasing step by step under unconfined conditions. In connection with the conditions of coal pillars in abandoned coal mines, and a uniaxial loading model is proposed by simplifying the actual condition.

In conclusion, it is my hope that this special issue will serve as a valuable and substantive resource for anyone interested in studies of porous materials, as well as satisfy the curiosity of readers and encourage others to pursue further their interest in relationships between the structure and/or chemical composition and the specific physical properties of these materials, as well as their role in mineralogical, technological, green, and sustainable processes.

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

References

1. Bandura, L.; Woszuk, A.; Kołodyńska, D.; Franus, W. Application of Mineral Sorbents for Removal of Petroleum Substances: A Review. *Minerals* **2017**, *7*, 37. [CrossRef]
2. Gupta, V.K.; Verma, N. Removal of volatile organic compounds by cryogenic condensation followed by adsorption. *Chem. Eng. Sci.* **2002**, *57*, 2679–2696. [CrossRef]
3. Pasti, L.; Rodeghero, E.; Sarti, E.; Bosi, V.; Cavazzini, A.; Bagatin, R.; Martucci, A. Competitive adsorption of VOCs from binary aqueous mixtures on zeolite ZSM-5. *RSC Adv.* **2016**, *6*, 54544–54552.
4. Costa, A.A.; Wilson, W.B.; Wang, H.; Campiglia, A.D.; Dias, J.A.; Dias, S.C.L. Comparison of BEA, USY and ZSM-5 for the quantitative extraction of polycyclic aromatic hydrocarbons from water samples. *Microporous Mesoporous Mater.* **2012**, *149*, 186–192. [CrossRef]
5. Abu-Lail, L.; Bergendahl, J.A.; Thompson, R.W. Adsorption of methyl tertiary butyl ether on granular zeolites: Batch and column studies. *J. Hazard. Mater.* **2010**, *178*, 363–369. [CrossRef] [PubMed]
6. Anderson, M.A. Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites. *Environ. Sci. Technol.* **2000**, *34*, 725–727. [CrossRef]
7. Rossner, A.; Knappe, D.R. MTBE adsorption on alternative adsorbents and packed bed adsorber performance. *Water Res.* **2008**, *42*, 2287–2299. [CrossRef] [PubMed]
8. Pasti, L.; Martucci, A.; Nassi, M.; Cavazzini, A.; Alberti, A.; Bagatin, R. The role of water in DCE adsorption from aqueous solutions onto hydrophobic zeolites. *Microporous Mesoporous Mater.* **2012**, *160*, 182–193. [CrossRef]
9. Pasti, L.; Sarti, E.; Cavazzini, A.; Marchetti, N.; Dondi, F.; Martucci, A. Factors affecting drug adsorption on beta zeolites. *J. Sep. Sci.* **2013**, *36*, 1604–1611. [CrossRef] [PubMed]
10. Braschi, I.; Martucci, A.; Blasioli, S.; Mzini, L.L.; Ciavatta, C.; Cossi, M. Effect of humic monomers on the adsorption of sulfamethoxazole sulfonamide antibiotic into a high silica zeolite Y: An interdisciplinary study. *Chemosphere* **2016**, *155*, 444–452. [CrossRef] [PubMed]
11. Sarti, E.; Chenet, T.; Pasti, L.; Cavazzini, A.; Rodeghero, E.; Martucci, A. Effect of Silica Alumina Ratio and Thermal Treatment of Beta Zeolites on the Adsorption of Toluene from Aqueous Solutions. *Minerals* **2017**, *7*, 22. [CrossRef]
12. Leardini, L.; Martucci, A.; Braschi, I.; Blasioli, S.; Quartieri, S. Regeneration of high-silica zeolites after sulfamethoxazole antibiotic adsorption: A combined in situ high-temperature synchrotron X-ray powder diffraction and thermal degradation study. *Mineral. Mag.* **2014**, *78*, 1141–1160. [CrossRef]
13. Martucci, A.; Rodeghero, E.; Pasti, L.; Bosi, V.; Cruciani, G. Adsorption of 1,2-dichloroethane on ZSM-5 and desorption dynamics by in situ synchrotron powder X-ray diffraction. *Microporous Mesoporous Mater.* **2015**, *215*, 175–182. [CrossRef]
14. Braschi, I.; Blasioli, S.; Buscaroli, E.; Montecchio, D.; Martucci, A. Physicochemical regeneration of high silica zeolite Y used to clean-up water polluted with sulfonamide antibiotics. *J. Environ. Sci.* **2016**, *43*, 302–312. [CrossRef] [PubMed]
15. Guisnet, M.; Ribeiro, F.R. *Deactivation and Regeneration of Zeolite Catalysts*; World Scientific: Singapore, 2011.

16. Wu, Z.; An, Y.; Wang, Z.; Yang, S.; Chen, H.; Zhou, Z.; Mai, S. Study on zeolite enhanced contact-dsorption regeneration-stabilization process for nitrogen removal. *J. Hazard. Mater.* **2008**, *156*, 317–326. [CrossRef] [PubMed]
17. Rodeghero, E.; Pasti, L.; Sarti, E.; Cruciani, G.; Bagatin, R.; Martucci, A. Temperature-Induced Desorption of Methyl *tert*-Butyl Ether Confined on ZSM-5: An In Situ Synchrotron XRD Powder Diffraction Study. *Minerals* **2017**, *7*, 34. [CrossRef]
18. Brundu, A.; Cerri, G.; Sale, E. Thermal Transformation of NH_4-Clinoptilolite to Mullite and Silica Polymorphs. *Minerals* **2017**, *7*, 11. [CrossRef]
19. Matsumoto, T.; Goto, Y.; Urabe, K. Formation process of mullite from NH_4^+-exchanged Zeolite A. *J. Ceram. Soc. Jpn.* **1995**, *103*, 93–95. [CrossRef]
20. Kosanović, C.; Subotić, B.; Smit, I. Thermally induced phase transformations in cation-exchanged zeolites 4A, 13X and synthetic mordenite and their amorphous derivatives obtained by mechanochemical treatment. *Thermochim. Acta* **1998**, *317*, 25–37. [CrossRef]
21. Kosanović, C.; Subotić, B. Preparation of mullite micro-vessels by a combined treatment of zeolite A. *Microporous Mesoporous Mater.* **2003**, *66*, 311–319. [CrossRef]
22. Franus, W.; Jozefaciuk, G.; Bandura, L.; Franus, M. Use of Spent Zeolite Sorbents for the Preparation of Lightweight Aggregates Differing in Microstructure. *Minerals* **2017**, *7*, 25. [CrossRef]
23. Arletti, R.; Giacobbe, C.; Quartieri, S.; Vezzalini, G. The Influence of the Framework and Extraframework Content on the High Pressure Behavior of the GIS Type Zeolites: The Case of Amicite. *Minerals* **2017**, *7*, 18. [CrossRef]
24. Krupskaya, V.; Zakusin, S.; Tyupina, E.; Dorzhieva, O.; Zhukhlistov, A.; Belousov, P.; Timofeeva, M. Experimental Study of Montmorillonite Structure and Transformation of Its Properties under Treatment with Inorganic Acid Solutions. *Minerals* **2017**, *7*, 49. [CrossRef]
25. Steudel, A.; Friedrich, F.; Schuhmann, R.; Ruf, F.; Sohling, U.; Emmerich, K. Characterization of a Fine-Grained Interstratification of Turbostratic Talc and Saponite. *Minerals* **2017**, *7*, 5. [CrossRef]
26. Temme, H.; Sohling, U.; Suck, K.; Ruf, F.; Niemeyer, B. Separation of aromatic alcohols and aromatic ketones by selective adsorption on kerolite-stevensite clay. *Colloids Surf. A* **2011**, *377*, 290–296. [CrossRef]
27. Sohling, U.; Haimerl, A. Use of Stevensite for Mycotoxin Adsorption. Patent WO 2006119967, 17 July 2012.
28. Ureña-Amate, M.D.; Socías-Viciana, M.; González-Pradas, E.; Saifi, M. Effects of ionic strength and temperature on adsorption of atrazine by a heat treated kerolite. *Chemosphere* **2005**, *59*, 69–74. [CrossRef] [PubMed]
29. Sohling, U.; Ruf, F. Stevensite and/or Kerolite Containing Adsorbents for Binding Interfering Substances during the Manufacture of Paper. Patent WO 200702941, 1 March 2007.
30. Du, Q.; Liu, X.; Wang, E.; Wang, S. Strength Reduction of Coal Pillar after CO_2 Sequestration in Abandoned Coal Mines. *Minerals* **2017**, *7*, 26. [CrossRef]