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ZEOLITES AS CATALYSTS: A REVIEW OF THE RECENT DEVELOPMENTS

Abstract: *The article presents the latest solutions (period 2015-2023) regarding zeolites and zeolitic materials used as catalysts for chemical reactions. The use of zeolites, among others, was presented and discussed for the purification of gases and sewage, as a raw material for the production of cement, as a component of dressings for hard-to-heal wounds, for blood purification, for the purpose of controlled release of drugs, as molecular sieves, or for the protection of monuments. The use of zeolites as catalysts and the trends in their use for this purpose are discussed with particular emphasis.*

Keywords: *zeolite, application, biomass conversion, biofuels production, pyrolisis procceses, water purification procceses*

Introduction

The first zeolite was discovered in the 18th century, when it was noticed that the mineral stilbite began to release significant amounts of water vapor when heated. This led to the understanding that water could be adsorbed on the surface of the material. Further research has identified many minerals of the zeolite family with many different structural configurations and pore sizes. There are about 70 types of natural zeolites, and more than 260 synthetic zeolites are registered [1]. The most common forms are clinoptilolite, mordenite, phillipsite, chabazite, stilbite, and laumontite, while offretite, paulingite, barrerite and mazite are not very common. Among them, clinoptilolite is the most abundant natural zeolite in nature and is widely used around the world.

Zeolites have found their application in many different fields. One of them is, for example, air-conditioning systems, filtration of drinking water, water and sewage treatment – mainly clinoptilolite filters are used there, which purify water from coarse suspensions and colloidal particles of mineral and organic origin. In combination with chlorination, ozonation and contact coagulation, drinking water is effectively purified. Another use is pool filters. Zeolites can also be used to deactivate radioactive wastewater by adsorption deactivation [1]. The ion-exchange selectivity of clinoptilolite towards cesium, strontium and other radioactive elements greatly facilitates this task. Zeolites also support groundwater treatment plants from radioactive isotopes and heavy metals. They are used during aeration of aquatic organisms with oxygen obtained by air separation. They absorb unpleasant odors and moisture, which is why they are a component of bedding for animal litter boxes. Zeolites were also used to deactivate nuclear waste after the Chernobyl nuclear power plant disaster. It is also worth mentioning that they are used to make very effective heat exchangers used in the power industry [2]. All this indicates a growing interest in zeolites and new innovative ideas for their use.

The purpose of this text is to present, on the basis of examples, the solutions studied in recent years and what the trends look like and what challenges they must meet.

Application of zeolite today

Taking into account all the properties of zeolites, the possibilities of its use are very wide. They are shown in Figure 1.

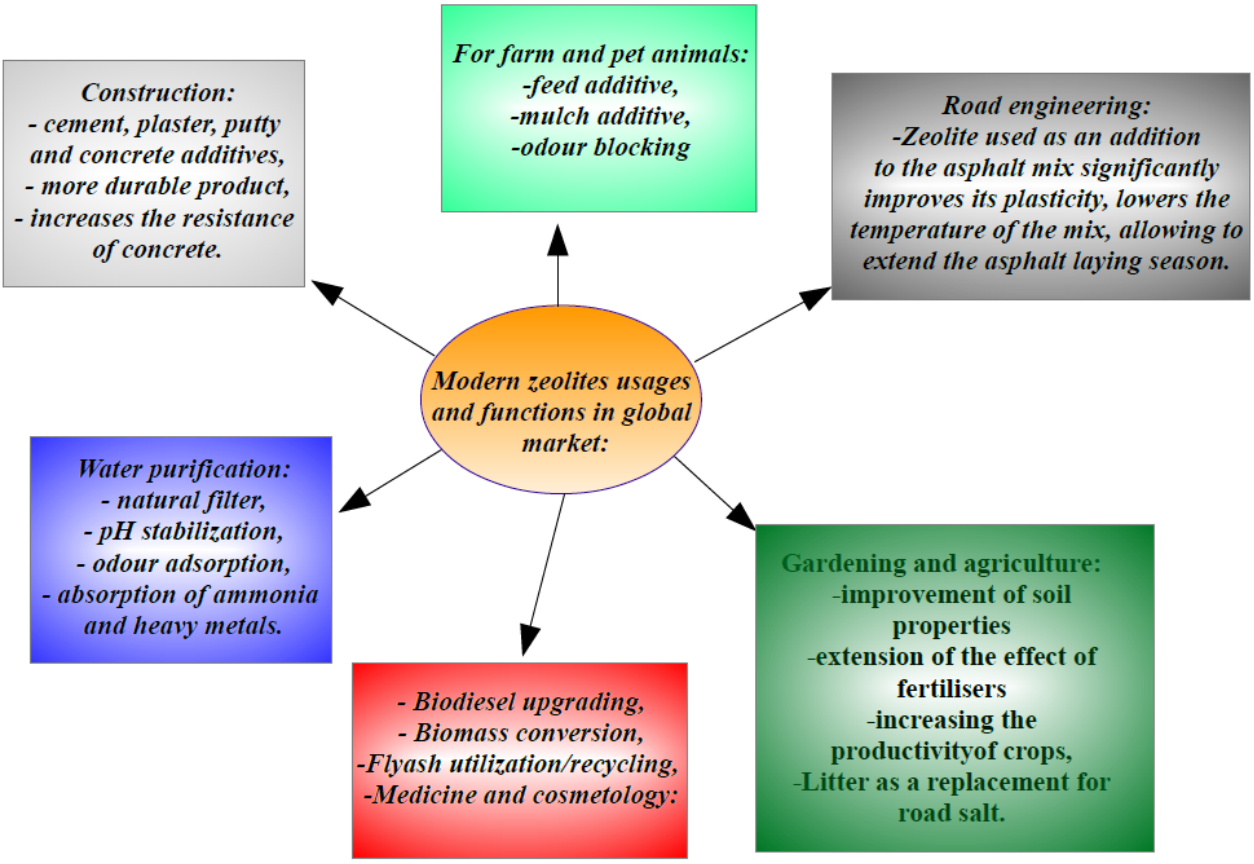

Figure 1. *Modern zeolite usage and various functions in global market*

There are several ways to increase the use of zeolites. The most commonly used zeolite modification techniques include:

- ion exchange in the liquid phase,
- solid phase ion exchange,
- impregnation with salts of metal precursors,
- dealumination,
- incorporation of metals into the structure of the zeolite,
- desilatation,
- deposition of active material from the gas phase [3, 4].

According to economic analyses, the market of zeolites is growing year by year, which shows. Figure 2 with assumed economic projections from 8.5 billion USD for 2022 to even 12.7 billion USD in 2032.

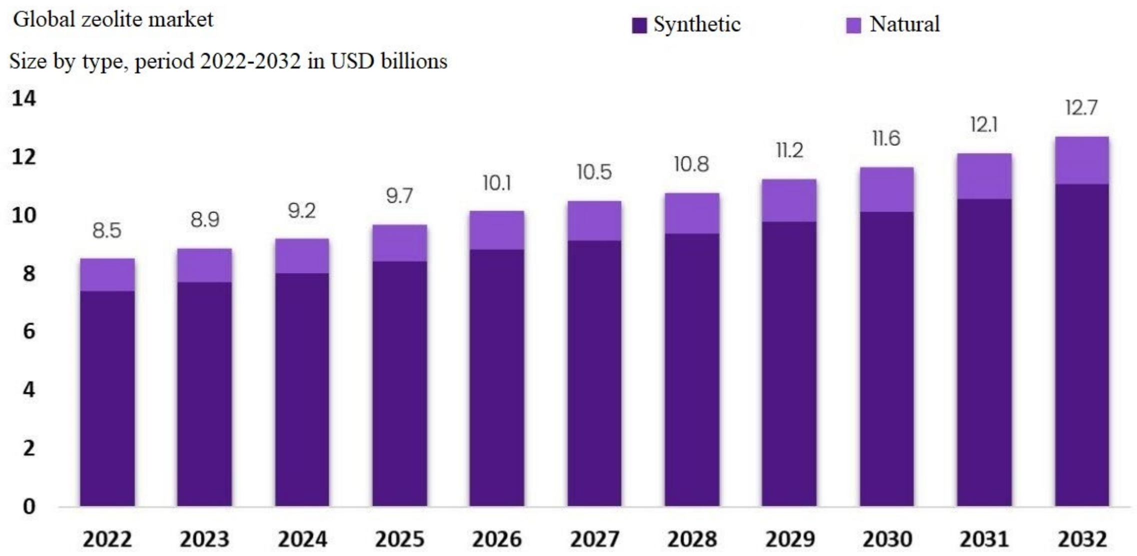

FIGURE 2. *Global zeolite forecast of market size from 2022 to 2032 [5]*

As can be seen in Figure 3, the largest market for zeolites, having nearly half of the total value from 2022, are catalysts. Another over 30% of the value are adsorbents and detergent additives. The use of zeolites for the production of cement, animal feed and other purposes accounts for about 20% of the market. It can be easily assumed that in the future, further and new applications will constitute an increasing proportion of the global market for the trade and production of zeolites.

Examples of modern usage of zeolites in biomass conversion

In response to the growing demand for fossil fuels, the rising cost of production and environmental concerns, the valorization of cheap, widely available and renewable biomass from waste is very beneficial for industrial applications using a zeolite-based catalysis reaction. The amount and variety of biomass waste currently available offers the opportunity to produce industrially useful chemicals and valuable commodities. Such zeolites can be used in various industrial sectors, such as the chemical, pharmaceutical, cosmetic and food sectors. One of the many applications in which the greatest hopes are currently pinned is the synthesis of biogas, which is a promising alternative fuel with low CO_2 emissions and high market potential due to the abundance of organic biomass. Biogas, despite being a renewable form of energy, usually contains 40-45% CO_2, which significantly reduces its calorific value. Many porous materials have been adapted to adsorb gaseous CO_2 from the biogas stream in order to obtain biogas with a biomethane content of 95-97%. Zeolites are therefore one of the promising porous materials that can significantly contribute to the upgrading process through selective adsorption of gaseous CO_2 from biogas [6]. The use of natural material as a catalyst or a substrate for the production of a catalyst not only reduces the costs associated with the production of catalysts, but also makes the process used environmentally friendly. In addition, the use of waste materials reduces the problem of waste disposal. The most abundant by-products of technology include, above all, waste from agriculture, mining and metal production, in particular from the steel industry [7].

In recent years, the use of zeolites in biomass conversion processes has developed significantly [8]. More precise biomass component conversion technologies are gradually replacing traditional biomass cracking processes, comparable to today's oil-based petrochemical industrial activities. As a consequence, lignocellulosic biomass can be transformed into a sustainable feedstock for the production of bulk chemicals and fuels in the coming years. Zeolites have the potential to be used in these types of processes, and their availability and adaptability make them a fascinating prospect to explore. In previous years, several new possibilities for the selective production of zeolite particles were discovered, which are now being studied in great detail, which is also necessary to reduce the overall environmental impact of the chemical industry.

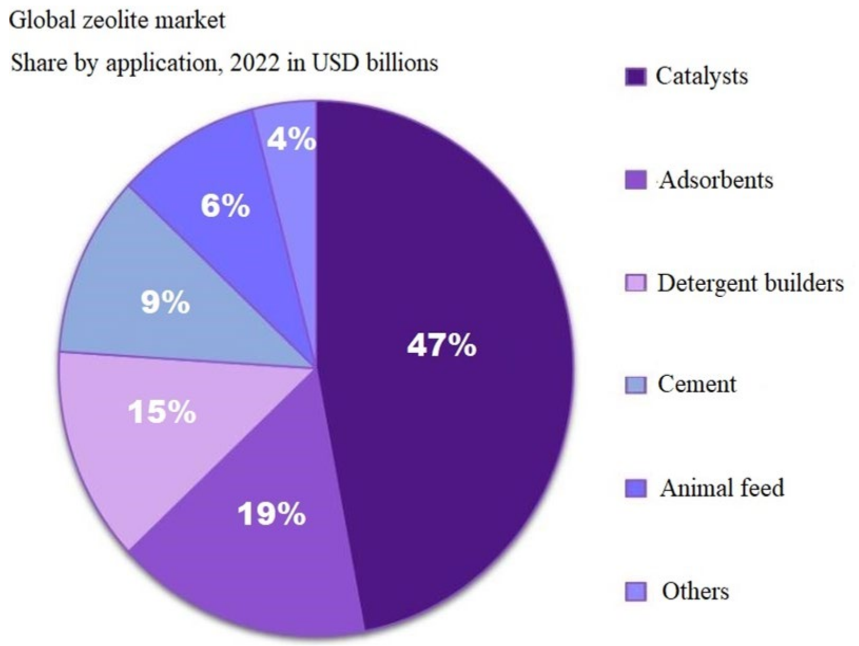

***FIGURE 3.** Global zeolite market divided into biggest usages [5]*

Another popular waste in the transformation of which zeolites can help is fly ash and its use as a substrate for the synthesis of zeolites. Then its transport and storage in appropriate geological structures or mineral sequestration [9]. As it results from the research presented in [10], activation with silver by ion exchange method allows to obtain a zeolite form of the Ag-X type. On the other hand, activation with silver (Ag-X) allowed to obtain more than five times longer time to breakthrough (5% wt. and 10% wt. HgO) compared to the commercially available bromine-modified activated carbon (AC/Br). Determination of the sorption capacity showed that activation with silver did not significantly affect the sorption properties of the zeolite towards CO_2. The results of sorption in dynamic conditions indicate the possibility of using the Ag-X zeolite as a sorbent for gaseous forms of mercury [11].

Examples of zeolites usage in biofuels production

One of the most innovative solutions, presented by the authors of paper [12], is the conversion of oil from the larvae of the Black Soldier Fly (BSF – Black Soldier Fly lat. Hermetia illucens) into hydroxysodalite zeolite (HS) synthesized from waste coal of fly ash (CFA) in the production of biodiesel. The zeolite product obtained after CFA fusion followed by hydrothermal synthesis (F-HS) gave a highly crystalline, mesoporous F-HS zeolite with a significant surface area of 45 m^2/g. The parent F-HS zeolite catalyst gave a high biodiesel yield of 84.10% with good quality and 65% fatty acid methyl ester (FAME) fuel characteristics meeting standard biodiesel specifications. The F-HS zeolite derived from CFA waste showed favorable performance as a heterogeneous catalyst compared to the conventional sodium hydroxide (NaOH) homogeneous catalyst. The zeolite catalyst provided a more cost-effective process using BSF fly oil and was economically comparable to NaOH for every kilogram of biodiesel produced. In addition, this study showed the potential to address the general cost challenge of biodiesel production by developing waste-derived catalysts and BSF worm oil as low-cost alternative feedstocks.

In another case, the catalytic conversion of CO_2 with a surplus of glycerol (GL) produced during the production of biodiesel has attracted much academic and industrial attention, demonstrating the urgent need to develop high-performance catalysts with significant environmental benefits. In studies [13], catalysts based on ETS-10 zeolite with titanium tanosilicate with active metals introduced by impregnation were used to couple CO_2 with GL for the efficient synthesis of glycerol carbonate (GC). The catalytic conversion of GL at 170°C reached 35.0% and a 12.7% higher yield of GC to Co/ETS-10 was obtained with CH_3CN as a dehydrating agent.

Examples of conversion of Fly Ash waste into zeolites

As a result of thermal treatment of waste in incineration plants, large amounts of ashes and slags are generated, which contain significant amounts of heavy metals, dioxins and furans [14]. The issue of such secondary waste has recently gained importance due to the construction of new waste incineration plants in Poland. Such materials should be properly processed and managed. One of the possibilities of using post-process waste from waste incineration plants is the technology of producing zeolites and sorbents. The manufactured products have ion exchange capabilities and can be used in a number of applications. Based on research [15], the following conclusions were formulated:

1. The usefulness of selected post-process waste from the waste incineration plant for the production of zeolites in hydrothermal alkaline activation processes was found.
2. The synthesis of ashes and slags from waste incineration plants in an alkaline environment leads to a change in the morphology of these ashes. One of the mineral components of the synthesis products are zeolites - e.g. Sodalite.
3. In order to improve the efficiency of obtaining zeolites from slags, it is necessary to crush/grind tchem.
4. It is also necessary to carry out detailed studies of pore size and surface area.

Disposal of Municipal Waste Fly Ash (MSWFA) remains a challenging task. Unlike coal fly ash (CFA), which can be used for the synthesis of various types of zeolite-like materials, MSWFA is devoid of silicon and aluminum, which are necessary for the synthesis of zeolites. According to a study by [16] using MSWFA by silicon and aluminum source addition method from various solid wastes to achieve recycling utilization, that the products obtained by both hydrothermal and fusion treatment showed zeolite-like material properties. Compared to the raw materials, the synthetic products showed a higher cation exchange capacity of 1.00 meq/g, suggesting application potential by converting MSWFA into usable materials.

Another solution presented by the authors of paper [17] are fly ash-based geopolymers as stable bifunctional heterogeneous catalysts in Friedel-Crafts acylation reactions. Class C coal fly ash was used as a precursor to reactive, inexpensive and environmentally friendly heterogeneous catalysts based on geopolymers. The developed catalysts showed high reactivity with excellent selectivity towards very demanding Friedel-Crafts acylation of various surfaces. The high reactivity of geopolymer-based catalysts is attributed to the different active sites they possess; Lewis and Brønsted acid sites that are generated within them and the catalytically active Fe_2O_3 compounds present in the original fly ash. This combination of different sites is expected to provide bifunctionality in the catalysis of acid and/or redox catalysed reactions. The metal oxide particles are either encapsulated in the geopolymer matrix or glued to the geopolymer particles, therefore these catalysts are expected to have a high degree of reusability and catalyst lifetime.

According to [18], zeolite, which was synthesized from three different types of waste (i.e. fly ash, sludge and contaminated soil), was then used as a carrier for the preparation of a catalyst for the hydrogenation of nickel to levulinic acid and γ-valerolactone. Under optimal synthesis conditions, the newly synthesized geopolymer zeolite has excellent structure and performance. The characterization results indicate that the composites have a three-dimensional network structure, and the pore structure is homogeneous, mesoporous or microporous. In [19], the results of catalytic hydrogenation show that the yield of γ-valerolactone can reach 94% using the synthesized catalyst, which is comparable to the yield of commercial catalysts and the concentrations of typical contaminating heavy metals Cu, Zn, Pb and Cd in the reaction solution were below the concentration limit emissions (class I standard) after five reaction cycles. In conclusion, the geopolymer type catalyst is cheap and has excellent performance; therefore, it is expected to be widely used in catalysis instead of commercial supports. The authors [20] in their work expect that in the future this material will also be used in various high-value fields, such as electrocatalysis and adsorption.

Examples of zeolites usage in pyrolisis procceses

Bio-waste valorisation is an excellent way to deal with resource depletion and climate change, with benefits for the environment and economic growth. One of the best-known technological ways of converting bio-waste into bio-products is pyrolysis, which is gaining more and more importance as a technology used for the production of alternative fuels and chemicals. This reaction may be carried out using a catalyst.

One of the materials that can support the production of synthetic zeolites considered recently is the pyrolysis of MPFP (Multi-layered Plastic Food Packaging) waste, widely used in food production, which is currently difficult to recycle due to the variety of materials from which individual layers of packaging are made and often it is incinerated instead of being reused [21]. The same applies to plastic waste from scrapped cars, which is mostly not reused. The authors of the paper [22] analyzed the catalytic pyrolysis of a realistic mixture of MPFP multilayer waste, such as plastic food packaging and ZSM-5 zeolite synthesized from them, for the pyrolysis reaction and obtaining final products such as oil and gas. An example of the tested MPFP waste mixture contained 71.9% PET, 25.1% PE and 3.0% PP. Each sample was cut into small pieces of 2-3 mm. The metallization of the film was carried out using a plasma metallization process, resulting in very fine particles that could not be measured in μm. The thermal behavior, kinetic parameters and pyrolysis kinetic model of multi-layer plastic food packaging were determined to show the potential of the process at scale. These experiments used a powdered ZSM-5 zeolite catalyst defined by the MFI crystal structure and loaded with iron(III) oxide. The main characteristics of the catalyst are a pore diameter ranging from 2.5 to 5 nm, a specific surface area of 135 $m^2 g^{-1}$, an average particle size of 82 μm and a SiO_2/Al_2O_3 ratio of 4.07. Thermal decomposition occurred in the range of 350-510°C, with a weight loss of more than 90%. The kinetic study revealed a complex pyrolysis process that consisted of three stages of decomposition, diffusion and Avrami-Erofeev type reaction. The activation energy values determined by the Friedman method increased with the degree of conversion from 127 kJ mol^{-1} at 0.01 to 219 kJ mol^{-1} at 0.95. Catalyst doping lowered the activation energy of the reaction by 44% and 8%, respectively, in the first and second stages, and increased the acidity of the zeolites, thereby increasing the reactivity on the surface of the catalysts. The lower activation energy meant that less energy was required to heat the pyrolysis reactor as the sample's onset temperature was lowered and the ZSM-5 synthetic zeolite was found to be effective in its intended role.

Catalytic pyrolysis of plastic waste using zeolites produced from fly ashes from coal was the subject of work [23]. Residual PFR film was selected as the raw material for pyrolysis. The authors conducted thermal and catalytic pyrolysis experiments, and coal fly ash (CFA) and X zeolite synthesized from CFA (X/CFA) were used as pyrolysis catalysts. The main goal is to study the effect of cheap catalysts on the efficiency and quality of pyrolysis oils. The fusion/hydrothermic NaX/CFA was ion exchanged and then calcined to produce HX/CFA. First, thermogravimetry and differential scanning calorimetry (TG and DSC, respectively). The analyzes performed assessed the effect of catalysts on the PFR degradation temperature and on the energy demand of the process. The pyrolysis run showed that the highest oil yield (44 wt%) was obtained by HX/CFA, while the main products obtained by thermal pyrolysis were wax and tar. In addition, up to 70% of the HX/CFA oil consisted of gasoline-range hydrocarbons. The gases produced had a combustion energy up to 8 times higher than the energy needed for pyrolysis.

Examples of zeolites usage in water purification procceses

Clinoptilolite is one of the most widespread and naturally occurring zeolites. Its availability, low cost, and unique ion-exchange properties make it an excellent candidate for both direct application and various modifications to create new low-cost functional materials for sustainable development. Specific applications where clinoptilolite is already used include water treatment and removal of heavy metal ions, agricultural purposes, storage and conversion of unwanted gaseous emissions to the atmosphere, production of catalysts and photocatalysts, bioactive materials and many others [24]. However, unlike some other zeolites, clinoptilolite is difficult to synthesize [25], therefore most publications refer to this zeolite in its natural form, either directly from the deposit or after various processes have been applied to improve its properties. Among the modification methods used, ion exchange stands out the most.

Studies presented by [26] on zeolite for removing trace metal ions from water showed that natural zeolite in the form of clinoptilolite derived from tuffs can be used as a material for removing heavy metal ions from groundwater in the technology of permeable active barrier. The highest efficiency of removing zinc and cadmium ions (>90%) was obtained at pH = 6÷7 and their initial content in the range of 5÷25 g/m^3. This also confirmed the good efficiency of zeolite as an active material for removing zinc and cadmium ions from water with a slightly acidic pH and not very high (approx. 25 g/m^3) initial amounts of these impurities. The effective action of the zeolite (approx. 99%) was maintained for a time corresponding to 5-6 times the exchange of the volume of the zeolite bed as a permeable active barrier. The author [2] demonstrated the effectiveness of removing both zinc and other metals present in wastewater. For sewage with a zinc concentration of 130 mg/dm^3, in order to reduce the zinc concentration to the standard level of 2 mg/dm^3, it was necessary to dose zeolite in the amount of 50 g/dm^3. It was shown that the use of synthetic zeolites made it possible to obtain concentrations below the normative values for all metals present in the tested wastewater.

Conclusions

Zeolites are an excellent response to the market demand for natural and ecological materials, the use of which can have a real and conscious impact on the condition of the natural environment. As the analysis of the market of zeolites shows, their use is constantly increasing and forecasts predict an annual increase in the value of the zeolite market. As the presented analysis shows, zeolites are materials with almost unlimited applications in many fields, such as industry and environmental protection.

The review of the latest trends and applications presented in the article shows the great importance of the use of zeolites for such purposes as catalysis, biomass conversion, biofuel production and refining, fly ash recycling, hydrogenation of metals to acids or various wastewater treatment methods shows how versatile these minerals are. One of the most important problems was the production of an efficient catalyst for wastewater treatment, which is constantly being developed. The issue of reducing emissions and taking greater care of the natural environment additionally promotes the use of such innovative methods. Nowadays, they can be a cheap alternative to known and energy-intensive technologies known for a long time. The fact that zeolites are constantly developed and modified proves their great potential in many branches of the economy.

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