

Recent Applications of Zeolites, Natural Nanostructure Materials

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Introduction

The term Zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this; he called the material Zeolite [1-6].

Natural Zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins [7-8]. Naturally occurring Zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other Zeolites. For this reason, naturally occurring Zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves"[1]. The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process.

This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a Zeolite is controlled by the dimensions of the channels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8-ring" refers to a closed loop that is built from 8 tetrahedral coordinated silicon (or aluminum) atoms and 8 oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many Zeolites are not cylindrical.

Zeolite is a naturally occurring mineral group consisting of over 50 different minerals with varying physical and chemical properties [9]. Made of a special crystalline structure that is porous but remains rigid in the presence of water, Zeolites can be adapted for a variety of uses. Density, cation selectivity, molecular pore size, and strength are only some of the properties

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that can differ depending on the Zeolite. Zeolites are microporous, molecular structure of hydrated aluminosilicates of the alkaline and alkaline-earth metals. The most common Zeolites are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, lamontite, mordenite and phillipsite.[4] More than 150 Zeolites have been synthesized.

Compositionally, Zeolites are similar to clay minerals [1]. More specifically, both are alumino-silicates. They differ, however, in their crystalline structure. Many clay minerals have a layered crystalline structure and are subject to shrinking and swelling as water is absorbed and removed between the layers. In contrast, Zeolites have a rigid, 3-dimensional crystalline structure (similar to a honeycomb) consisting of a network of interconnected tunnels and cages. Water moves freely in and out of these pores but the Zeolite framework remains rigid. Another special aspect of this structure is that the pore and channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve. The porous Zeolite is host to water molecules and ions of potassium and calcium, as well as a variety of other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the "sieving" property.

One important property of Zeolite is the ability to exchange cations. This is the trading of one charged ion for another on the crystal. One measure of this property is the cation exchange capacity (CEC). Zeolites have high CEC's, arising during the formation of the Zeolite from the substitution of an aluminum ion for a silicon ion in a portion of the silicate framework (tetrahedral units that make up the Zeolite crystal).

When developing applications for Zeolites, it is important to remember that not all of these minerals are the same. Some help to assist plant growth while others make excellent filtration media, but the same Zeolite will not necessarily do both well. It is critical to understand how Zeolites differ so that only the appropriate types and source materials are selected for each application.

Variations not only occur between different types of Zeolites but also in the physical and chemical properties of Zeolites of the same group. Source plays a large role in these variations. For instance, Clinoptilolite from one source will not necessarily have the same properties as Clinoptilolite from another distinct source. Environmental conditions during and following the geologic genesis of each source are rarely the same, causing these variations. The types and number of impurities present and the way in which

the Zeolites are cemented together are all dependent on the unique conditions during formation [6].

Clinoptilolite, the most common natural Zeolite, has 16% more void volume and pores as much as 0.2 nm larger than Analcime, another common Zeolite. It is important to know the specific type of Zeolite one is using in order to assure that it is appropriate for one's needs.

Natural and synthetic Zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

One difference between Zeolites worth giving special mention is the composition of exchangeable cations residing in the Zeolite. Exchange sites on natural Zeolites are primarily occupied by 3 major cations: potassium (K), calcium (Ca), and sodium (Na) (other elements such as magnesium (Mg) may also be present). Exchange sites on a particular Zeolite may contain nearly all K, nearly all Na, some Ca or Mg, or a combination of these. It is important to take these differences into account when assessing which Zeolite to use for a particular product. Zeolites dominated by exchangeable K for example, may be well-suited for plant growth applications while those dominated by Na should be approached much more carefully as Na in high concentrations can be detrimental to plants.

While Zeolites have several properties that make them highly useful minerals, they can be chemically modified to make them even more effective. The best example of this is Zeolite used for plant growth applications. By changing the composition of the ion exchange sites and by "loading" the sites with selected nutrient cations, Zeolites can become an excellent plant growth medium. Other enhancements can also be done to modify the properties. Combined with slowly dissolving materials (such as synthetic and/or natural nutrient anions), Most importantly, these nutrients are provided in a slow-release, plant root demand-driven fashion.

Major markets for natural Zeolites are pet litter, animal feed, horticultural applications (soil conditioners and growth media), and wastewater treatment. Synthetic Zeolites applications are catalysts, detergents, and molecular sieves.

2. The application of Zeolites for mercury removal

The main sources of mercury emissions to land, water and air are the processes of ores mining and smelting (in particular Cu and Zn smelting), burning of fossil fuels (mainly coal), industrial production processes (Hg cell chlor-alkali processes for the production of Cl and caustic soda) and consumption related discharges

(including waste incineration) [11]. It was reported that Zeolites are materials that can be used for mercury removal from soils, flue gases [12, 13] and solutions [14, 15]. Zeolites are considered to be, next to clays, ironoxide-coated sands and activated carbons, low-cost sorbents [16, 17]. They are naturally occurring silicate minerals, which can also be produced synthetically. Clinoptilolite is probably the mostly abundant out of more than 40 natural Zeolites [17, 18], making it readily available and inexpensive [17]. Zeolites offer a potential for a variety of industrial uses including molecular sieves, ion-exchangers, adsorbers, catalysts, detergent builders [11, 19, 20], the removal of cations from acid mine drainage and industrial waste waters [21]. Leppert [22] reported that Zeolites, Clinoptilolite in particular, have strong affinity for heavy metal ions. The mechanism of adsorption by Zeolites was found to be ion-exchange. In the three dimensional structure there are large channels containing negatively charged sites resulting from Al^{3+} replacement of Si^{4+} in the O4 tetrahedral-linked by sharing oxygen atoms in rings and cages—cavities occupied by cations which are weakly held in the structure to compensate the charge imbalance [17, 21]. Zeolites contain various types of cationic sites [22]. The overall negative charge of the anions is balanced by cations that occupy the channels within the structure, and can be replaced with heavy metal ions [17]. A wide variation in the cation-exchange capacity of Zeolites was reported because of different nature of various cage structures of Zeolites, natural structural defects, adsorbed ions and their associated gangue minerals [21]. Structural imperfections, a variety of dimensions, degree of hydration, and the presence of clays and other slime particles may lead to differences in properties between Zeolites [21]. Reported sorption capacities of Zeolites are (mg/g): Cd 84.3, Cr(III) 26.0, Hg 150.4, Pb 155.4 [22]. The overall sorption capacity was evaluated as ca. 1.5 meq/g.

3. Color removal from textile dyeing wastewater

The textile industry wastewaters contain colorants originating from dyeing and finishing processes. Important pollutants in the textile effluent are mainly recalcitrant organics, color, toxicants and inhibitory compounds, surfactants, chlorinated compounds (AOX), pH and salts. Dye is the most difficult constituent of the textile wastewater to treat [23]. Azo-reactive dyes are presently the most important compounds, constituting about 60–70% of the total dyes used industrially for coloring [24]. Besides, azo-reactive dyes hydrolyze easily, resulting in a high

portion of unfixed (or hydrolyzed) dyes, which have to be washed off during the dyeing and approximately 50% of the initial dye load is present in the dyeing wastewater [25, 26]. Physico-chemical methods are applied for the treatment of this kind of wastewaters, achieving high dye removal efficiencies [27].

In the biological treatment systems, the recalcitrant nature of azo dyes, together with their toxicity to microorganisms, makes aerobic treatment difficult whereas, a wide range of azo dyes is decolorized anaerobically [28, 29]. On the other hand, adsorption [30-32], oxidation [33, 34] and membrane [35] processes are major technologies that are used for wastewater treatment in the textile industry.

Adsorption is advantageous to other techniques in respect of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [36]. In addition, adsorption is one of the most important unit processes in a wastewater treatment plant and the design of the adsorption column usually requires information from pilot-plant experiments [37, 38]. Most commercial systems currently use activated carbons and organic resins as adsorbents to remove the dye in wastewater because of their excellent adsorption abilities [37, 39]. Several investigators reported studies on cost-effective adsorbents including sepiolite [40, 41], Zeolites [31, 42, 43], waste materials [44, 45] and biomass [46] etc. Natural Zeolite (Clinoptilolite) has a three-dimensional crystal structure and its typical cell formula is given as $Na_6[AlO_2]_6(SiO_2)_3 \cdot 0.24H_2O$ [47]. The three-dimensional crystal structure of Zeolite contains two-dimensional channels [48] which embody some ion exchangeable cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} . These cations can be exchanged with organic and inorganic cations [49]. Zeolites have negative charges that arise due to isomorphous substitution of Al^{3+} for Si^{4+} , and this negative charge is neutralized by exchangeable cations. Several authors have reported that Zeolites are not suitable for the treatment of anionic contaminants and reactive dyes. To enhance the adsorption capacity of Zeolite, the surface of natural mineral was modified using some cationic surfactants in the literature [31, 42].

4. Zeolite as efficient adsorbent for the hydrophobic fraction from wastewater treatment plants effluents

Freshwater is a precious natural resource that is increasingly limiting economic development in many geographical areas [50]. In order to minimize the environmental impact of urban wastewater and at the same time to make possible its reuse for agricultural

irrigation, it is mandatory to devise more efficient and safe urban wastewater treatments [51]. Up to now most of the urban wastewater treatments are based on primary sedimentation and microbiological decontamination combined sometimes with tertiary processes [52]. The current technologies for urban wastewater processing are still far from being completely satisfactory and the total organic carbon (TOC) of the effluents after wastewater treatment is still much higher than the typical values from fresh natural waters [53].

Among the type of chemical compounds widely present in urban wastewater effluents, those having a long alkyl chains are very common since there are used in soaps and detergents [54]. These types of amphiphilic organic compounds can go through the waste water treatment plant without undergoing a complete elimination and will form part of the organic matter present in the effluents of urban wastewater treatment plant (UWTP) [55, 56].

It has been reported that dealuminated large pore Y Zeolites can be very efficient adsorbents for removing fatty compounds from the effluents of conventional UWTPs [57].

5. Selective adsorption of Zeolite towards nitrosamine in organic solution

Reducing environmental carcinogens is one of the applications for Zeolites in life science. Among many harmful constituents present in our environment, nitrosamines are a class of well known carcinogens. They can be found in tobacco smoke, alcoholic beverages and fried meat products. Among the different forms of tobacco uses, the exposure level for tobacco-specific nitrosamines (TSNAs) are reported to be 48 (heavy smokers), 223 (tobacco chewers) and 733 (snuff users) μg per person per day and TSNAs can contribute to the induction of lung cancer, esophagus, nasal and oral mucosa [58, 59]. Some of the volatile nitrosamines are also carcinogenic. The largest contributors to dietary volatile nitrosamines are alcoholic beverages, salted fish and cured meat containing nitrite. Some drugs with amines or N-substituted amides can be nitrosated in human body to generate nitrosamines [60]. Selective removal of nitrosamines from our environment is therefore beneficial.

Zeolites have been used to adsorb different form of nitrosamines [61-63]. In principle, this relies on pore size selection and optimization of electrostatic interaction between the cations of Zeolite and the

oxygen atom in the N–NO group of nitrosamines, with mass transport playing a secondary role [64-66].

6. Measuring trace organic vapors

Quantifying organic vapors of trace concentrations often requires laboratory sample preparation and sophisticated instruments that are inconvenient for mobile applications demanded in many critical areas such as environmental monitoring, public health protection, and large area security defence. In the last several years, the development of compact and sensitive fiber optic chemical sensors (FOCS) has been attracting increasing interests for broad applications ranging from detecting DNA to measuring gas molecules and ions in liquid [67-73]. Different fiber structures and sensing mechanisms may be employed in FOCS among which the recently invented LPFG [74] provides new opportunities to develop refractive index sensors for measuring chemical concentration with high sensitivity [75, 76].

Zeolites are crystalline aluminosilicate materials possessing a unique combination of chemical and optical properties that is ideal for developing various optical chemical sensors [77-80]. The uniform nanometer scale pores with effective diameter from $\sim 3\text{\AA}$ to $>1\text{nm}$ depending on the crystallographic structure and the very large surface-to-mass ratio, normally $400\text{--}1000\text{m}^2/\text{g}$, are suitable for highly efficient selective molecular adsorption. The pore size and structure as well as the surface chemistry of the Zeolites can be finely tuned by isomorphous elementary substitution in the framework, exchange of the extra-framework cation compensators, and chemical deposition of molecular or atomic species in the zeolitic cavity to further improve the selectivity of molecular adsorption [81-84].

Because of their crystalline nature, Zeolites also have excellent thermal, chemical, and mechanical stabilities to function in harsh conditions. The adsorbed analytic molecules are organized and aligned in the nanoscale Zeolite pores due to spatial confinement and guest–host interactions. Loading and unloading sorbate molecules can thus cause optical and structural property changes of the Zeolite that can be effectively examined by various optical methods including refractometry, interferometry, birefringence, light absorption, fluorescence, and spectroscopy [67, 68, 80, 85, 86]. Thereby, Zeolites with multidimensional functions as effective sample concentrator and optical probe have the potential for developing a variety of optical chemical sensors.

However, developing Zeolite-based optical chemical sensors is still in the very early stage because of the difficulties associated with integrating Zeolite with operational optical devices and the lack of fundamental understanding on the optical behavior of Zeolite guest-host systems. Recently, we successfully synthesized highly coherent Silicalite thin films on straight cut end faces of single mode optical fibers [87]. The end face-coated Zeolite-fiber device was used to investigate the relationship between the Zeolite refractive index and organic sorption level by an interferometric method [88, 89].

Silicalite is a hydrophobic material with an effective pore size of ~0.6 nm. It is an excellent adsorbent for a large number of organic molecules including aromatic compounds. The Silicalite refractive index was found to increase from 1.3361 in pure N₂ to 1.4020 in 5353ppm isopropanol vapor in N₂ [89]. This particular range of refractive index is desirable for constructing highly sensitive, film coated LPFG sensors. In this study, we investigate a Silicalite thin film-coated LPFG sensor for highly sensitive detection of organic vapors.

7. Adsorption of paranitrophenol onto Zeolite

Because of the danger of environmental catastrophes as a consequence of the indiscriminate spill of organic pollutants in water streams, a growing public concern in the establishment of limits on the suitable levels of particular contaminants in the environment currently exists.

Phenol is a fundamental structural part for a diversity of industrial organic compounds; consequently, it is between the most widespread dangerous contaminants; since, it is a starting substance for many intermediate products and finished merchandises; as for instance, detergents, adhesives, pesticides, dyes, resins, plasticizers, and additives for rubber chemicals [90]. Thereafter, phenols come from a variety of industrial sources; such as: pesticides, dyes and paper industries, coke and resin manufacturing and textile, plastic, rubber, pharmaceutical, and petroleum production [91].

Because of the toxicity of phenols, their elimination from water is a vital question. Therefore, during the last years has been an increasing interest in the creation of processes for the elimination of these compounds from water. In this sense, different methods, as: oxidation with UV radiation and ozone/hydrogen peroxide [92], UV radiation and hydrogen peroxide [93], membrane filtration [94], reverse osmosis [95], photocatalytic [96] and

sonocatalytic [97] degradation, electrochemical oxidation [98] and adsorption [91, 99-103] have been applied for the elimination of organic products in general and phenolic compounds in particular. However, adsorption is frequently the chosen separation process.

Paranitrophenol (PNP), or 4-nitrophenol (C₆H₅NO₃) is a phenol derived chemical. PNP is a corrosive eye irritant and a potential dermal irritant; as well it is very toxic through the oral way and somewhat toxic, through the dermal route [104-106]. PNP can be discharged to a water flow only at a concentration of: 37.3 mg / l [106]. Consequently, the reduction of the concentration of PNP in wastewaters containing it, by dynamic adsorption in a packed bed reactor, is a worthy task.

The adsorbent that will be tested in the present study, that is, dealuminated Y (DAY) Zeolite, exhibit the FAU framework type [107-110]; to be precise, it is a Y Zeolite, which has been dealuminated [111-112]. The DAY Zeolite will be applied to clean a liquid flow, by the removal of a relatively low concentrated impurity with a packed bed adsorption reactor (PBAR) [113].

8. Adsorption of phenol onto Zeolite

Chlorinated organic compounds are a major source of pollution. These pollutants are now receiving great concern due to ecological and public health concern [114]. Benzene refining plants, oil refineries, coke plants, and plants, which are processing phenols to plastic, all discharge harmful effluents of phenols [115]. Phenols may occur in domestic and industrial wastewater, natural water, and potable water supplies [116]. During the chlorination of water and sewage, phenol is readily transformed into chlorophenols. Over the last century, much research has taken place in the area of adsorption of phenols on activated carbons, which were proved to be very effective in removal of organic pollutants [117-119].

Removal of phenols from water using Zeolite has not been studied extensively [117, 120-123]. Okolo et al. investigated the interaction of phenol/chlorophenols with Na-Y synthetic Zeolites and found that the adsorption capacity of phenol equals 0.8 mmol/g [117]. By dosing phenols vapor into Na-X Zeolite and using ¹H and ²⁹Si MAS NMR spectroscopy, Beutel et al. [122] showed that hydrogen bonding of phenol to the oxygen atoms of Zeolite is not the only interaction between phenol and Na-X Zeolite. Of the same importance is the interaction of aromatic ring of phenol with either Na⁺ cations or oxygen atoms of the Zeolite supercages. Khalid et al. [123] showed that the

adsorption capacity of phenol onto HFAU Zeolites increases in the range 0.1–0.6 mmol/g with an increase of Si/Al ratio from 5 to 500. Khalid et al. concluded that the Si/Al ratio, rather than the pore size of Zeolite, has the predominant effect on the adsorption capacity of phenol.

9. Zeolites as a builder in detergents

Eutrophication of natural water is a serious environmental problem that can cause the death of marine life. The use of STPP (sodium tripolyphosphate) in laundry detergents as a builder is known to be one of the prime sources for phosphate deposition in water [124]. The role of phosphates is to remove calcium and magnesium from water in order to favor the removing, solubilizing, emulsifying and suspending action of surfactants. Because of this harmful effect to the environment, Zeolites have been successfully used as alternative builders in detergents to replace STPP [125]. Among the various Zeolites, Zeolite 4A has been extensively employed as detergent builders [126] and water softeners.

Compared to phosphates, Zeolites can additionally prevent the formation of poorly soluble (partially soluble) inorganic salts, which is a key factor in the formation of textile incrustations. At present, more than 1,000,000 tonnes of Zeolites are used per annum in detergents and cleaning products world-wide [127]. Moreover, Zeolite 4A has found widespread applications in both laboratories and industries. For these purposes, it has been manufactured industrially on a greater scale than any other Zeolite [128].

10. Entrapment of cyclopentadiene in zeolite NaY and its application for solvent-free Diels–Alder reactions in the nanosized confined environment

The Diels–Alder reactions have frequently been employed for the formation of a six-membered carbon skeleton in synthesis of fine chemicals and pharmaceuticals. The rate enhancement of this reaction has been achieved by the use of Lewis acids [129], in solvents such as supercritical CO₂ [130] and ionic liquid [131], and by the application of high pressure [132] or ultrasonic radiation [133]. In 1980, Rideout and Breslow demonstrated the Diels–Alder reactions were dramatically accelerated in water owing to ‘hydrophobic effect’ [134]. Hydrophobic organic substrates tend to assemble in water so as to diminish the hydrocarbon–water interfacial area. Many organic chemists have paid much attention to the Diels–Alder reactions conducted in a hydrophilic, polar environment in terms of acceleration of organic

reactions on exposure to ‘hydrophobic effect’ or ‘internal pressure’ [135]. Olefinic compounds such as ethylene, furan, pyrrole, thiophene, and benzene are known to be adsorbed in hydrophilic zeolites [136]. Accordingly, cyclopentadiene (CPD) molecules possessing a 1,3-diene structure are expected to be similarly entrapped in the hydrophilic zeolite. Shouhei and Onaka [137], as an adsorbent selected zeolite NaY (Si/Al=2.4) composed of interconnected supercages of 1.3 nm in diameter with pore windows of 0.7 nm in diameter. The NaY has a specific surface area of 810 m²/g, a pore volume of 0.34 mL/g, and hydrophilic supercages. CPD vapor in a N₂ flow was passed over NaY. When 3.4 mmol of CPD was adsorbed into 1 g of NaY, the adsorption was saturated. In the saturated state, it was estimated that about 80% of the pore volume of NaY was occupied by the adsorbed CPD molecules, implying that every supercage on average contained five to six CPD molecules. As a control, CPD was also adsorbed on SiO₂ (Silica gel 60; specific surface area: 500 m²/g) adsorbing 2.0 mmol of CPD per gram of silica. By simply putting together with dienophile reagents, the entrapped CPD showed the greater reactivity for the Diels–Alder reactions in the nanosized cages of NaY than in an organic or aqueous solution.

11. Heterogeneous Suzuki reactions catalyzed by Pd(0)–Y zeolite

The Pd-catalyzed cross-coupling of aryl halides with aryl boronic acids, that is the Suzuki reaction, is recognized as being one of the most powerful and popular methods for the construction of unsymmetrical biaryls, which are widely used for the synthesis of valuable organic compounds such as pharmaceuticals and agrochemicals [138]. The particular merits of this reaction are that the reaction can be performed under mild conditions in aqueous solutions and that it tolerates a broad range of functional groups.

Many Pd complexes have been investigated in homogeneous systems in the Suzuki reaction of aryl halides. However, palladium reagents tend to be expensive and sometimes difficult to manipulate, recover, and reuse. One method to construct a recoverable and reusable catalyst is to immobilize the active palladium species on a solid material. Several types of solid materials have been used to support palladium species. Artok and Bulut [139], tested the Pd (II) exchanged NaY zeolite in Suzuki reactions of activated and unactivated bromobenzenes, and an activated chlorobenzene [140]. They found that the

catalyst displayed high activity for bromobenzenes in an N,N-dimethylformamide (DMF) / water (1:1) mixture, almost quantitative coupling yields being obtained at room temperature, and was moderately active for 4-chlorobenzotrifluoride at relatively higher temperatures. They have found that aryl bromides, in general, can be coupled with arylboronic acids in excellent yields using a Pd (0)-loaded NaY zeolite under mild conditions. However, the reactions occurred on the external surface of the catalyst. The catalyst can be reused subsequent to regeneration.

12. Sonogashira cross-coupling reactions catalysed by heterogeneous copper-free Pd-zeolites

The Sonogashira cross-coupling of aryl halides and terminal alkynes or arylenes is a useful tool for the synthesis of alkyl-aryl and diaryl-substituted acetylenes [141]. Functionalised alkynes are important building blocks for the synthesis of biologically active molecules and, surprisingly, are common structural features of natural products that have been isolated from plants and marine organisms, or synthetic drugs [141,142]. Therefore, the Sonogashira reaction is frequently used as a key step in the synthesis of pharmaceuticals, such as the enediyne antibiotics or the contraceptive pill [143].

Generally the Sonogashira reaction is carried out in an organic solvent such as toluene, THF or DMF, using at least a stoichiometric amount of base, and a Pd (0)/Cu(I) catalytic system [144]. To extend the Sonogashira reaction for fine chemical applications, numerous studies have been reported in the literature over the last 10 years including the use of a phase transfer agent [145], reaction in aqueous media or without solvent [146], reaction in ionic liquids [147], copper-free versions [148], and the use of promoters such as Zn, Mg, Sn and R₄NI [149]. The most important improvement concerned the elimination of CuI, which is used as the co-catalyst since it can induce homocoupling reactions of terminal alkynes to diynes in the presence of oxygen (Glaser-type reactions) [150].

The intensive application of the Sonogashira reaction in the chemical industry depends on the development of new, stable heterogeneous copper-free palladium catalysts. With this aim, the use of palladium supported on metal oxides appears to be the most appropriate heterogeneous catalyst to perform this cross-coupling reaction on a large scale.

Djakovitch and Rollet [151], describes the remarkable catalytic activity of Pd-modified zeolites for the Sonogashira cross-coupling reaction of aryl iodides

and bromides with phenylacetylene. They established that the heterogeneous [Pd(NH₃)₄]-NaY catalyst is an efficient, stable and recyclable catalyst for the copper-free Sonogashira cross-coupling of aryl halides with terminal alkynes.

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