

Perspective

# Investigation of the Acid/Basic Sites of Zeolite Trough Some Catalysed Nucleophilic Reactions

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**Abstract:** Zeolites, both natural and synthetic, are certainly some of the most versatile minerals for their applications. Since the 1940s, they have been used in the chemical industry as catalysts, adsorbents and ion exchanger extensively, and the development of their practical usage is expected to continue upon years. Their versatility is the result of the combination of peculiar and indispensable properties, each of which can be found in other material as a single property, but seldom all of them are found in combination. However, despite the success of their employment, the mechanisms of many important catalytic processes involving zeolites remained elusive. In particular, the comprehension of the structure–property relationships for emerging applications are highly required. In this perspective article we focus on the role of zeolites as solid acid-base catalysts. We go deeply into the structural properties of the LTA kind (Zeolite-Na A 4 Ångstrom) that was successfully employed as basic catalyst for several nucleophilic substitution reactions.

**Keywords:** zeolites; green solid catalysts; basic catalysts; nucleophilic substitution reactions



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## 1. Introduction

### *Zeolites as Emerging Green Catalysts*

In the recent past, we have witnessed a growing phenomenon of interest in the employment of inorganic solid material as catalysts for organic reactions. It can certainly be claimed that the future of synthetic organic chemistry leans on the heterogeneous systems in general, due to specific and undoubted advantages of employing solid surfaces as reaction sites. This approach can ensure more environmentally acceptable procedure for the preparation of organic molecules. In fact, the synthesis of hydrocarbon and fine chemicals in general requires various successive steps, most of them are carried out in homogeneous phase, using acid catalysts, such as H<sub>2</sub>SO<sub>4</sub> or AlCl<sub>3</sub> for example. The neutralization of these acids, which are not reusable, generates large amounts of salts. Such polluting technologies are strongly required to be substituted with a cleaner approach that could consist of employing solid catalysts. Indeed, these offer the advantage of being easily recovered from the reaction mixtures, as well as easily employed in a set-up of continuous processes [1].

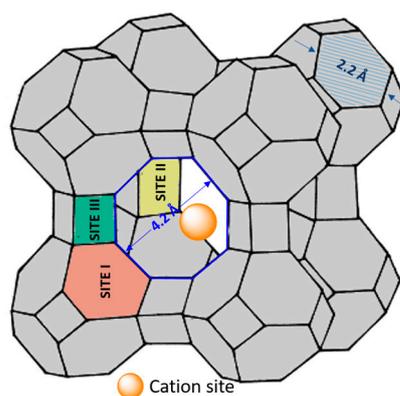
Zeolites, with their selective shape and versatility in tailoring properties, such as the acidity and porosity, constitute one of such solids [2,3].

They are commercially available and can provide environmentally friendly alternatives to liquid acid/base catalysts, being recoverably in order to be reused. In addition, their properties can be fine-tuned for specific transformation, for example by exchanging metal-cations [4,5].

The zeolite structure consists of a host framework and extra-framework region. In detail, tetrahedra (TO<sub>4</sub>; T = Si and Al, among others), connected via shared oxygen vertices, generate cages and channels. Depending on the ways in which these link together, diverse

types of tetrahedral frameworks are generated. Concerning the extra-framework species present in zeolites, they are commonly alkali ions or amines, which are introduced in the host frameworks during the formation of zeolites. All the extra-framework species can be substituted, upon ion exchange, in order to produce well-defined micropores that allow guest molecules to diffuse in [6,7].

LTA Zeolite (Linde Type A) is widely used as an adsorbent for various chemical separations in the chemical industries. Zeolite A-Na  $4\text{\AA}$  (molecular sieve Type  $4\text{\AA}$ ) has the following unit cell formula:  $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}\cdot n\text{H}_2\text{O}$  [8,9]. The sodium ions can easily be replaced by potassium or other alkali ions in order to obtain adsorbent material characterized by peculiar properties, required for several applications [10]. During the adsorption phenomenon, only molecules with a diameter of  $4.2\text{\AA}$  can diffuse through the eight-ring cavity [11]. The cations occupying Site II occlude to some extent the window opening. In consequence of this, only those molecules having the diameter  $<4\text{\AA}$  can reach the inner region of the zeolite cavity. In the case where Na ions are partially replaced (ionic radius  $1/4\ 0:93\text{\AA}$ ) with K ions (ionic radius  $1/4\ 1:33\text{\AA}$ ), molecular sieve Type  $3\text{\AA}$  is obtained, and it is characterized by a pore diameter that is further reduced to  $3\text{\AA}$ . The obtained molecular sieves ( $3\text{\AA}$ ) have been largely applied in the petrochemical industry to eliminate water molecules from gases, such as ethylene and propylene, which are totally prevented from penetrating the zeolite crystal structure (Figure 1) [10,12–14].



**Figure 1.** The structure of zeolite Na-LTA.

Benefiting from modern progress in synthetic strategies, zeolites have been successfully employed in chemical industries for decades [5]. The potential of this old solid material has been shown to have shiny vitality, spanning the traditional industrial applications as well as the recent emerging synthetic fields, such as environmentally sustainable and energy-efficient synthetic processes [15–17].

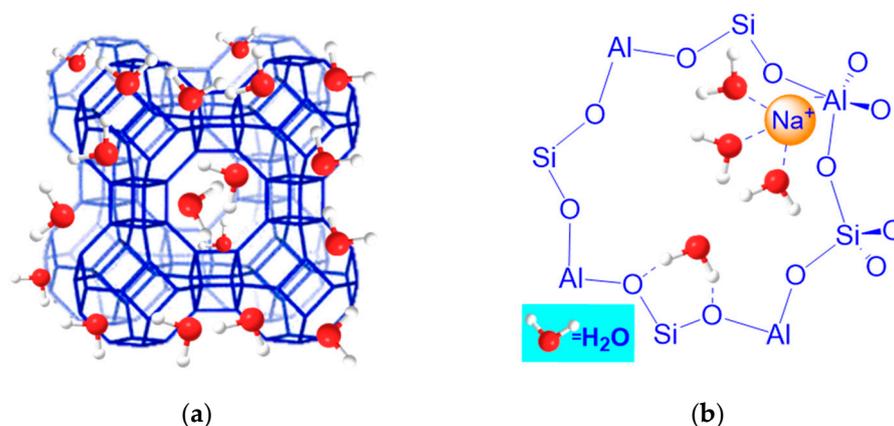
## 2. Discussion

### 2.1. Heat Treatment of Zeolites and a Consequent Dehydration and Activation Process

For many applications, such as ion exchange, adsorption and catalysis, zeolites must be activated by heating [10]. This involves dehydration of the minerals and consequently creates a large number of vacant volumes, in which the so-called “molecular sieve” is generated, and the zeolite can act as an adsorbent. Molecular sieves only allow the entry of molecules with a particular size (less than or equal to the cavities’ size) through channel openings, while the access of molecules with sizes larger than that of the pores is forbidden. After dehydration, liquid or gas molecules, small enough to enter the openings of the channels, are adsorbed and captured in the internal area of the zeolite, while larger-size molecules remain excluded.

The exact nature of the water in zeolites has been a debate for many years. Essentially, three types of water may be recognized: (1)  $\text{H}_2\text{O}$  molecules with crystal-water-like bonds; (2)  $\text{H}_2\text{O}$  bound to the lattice by OH bonds; and (3) typical zeolite  $\text{H}_2\text{O}$  molecules, which are adsorbed internally and freely move into and out of the lattice because they are not

coordinated in fixed positions. In addition, in the case of Zeolite A, key roles are also played by the Brønsted basicity of Al-O-Si framework oxygens that can tightly bind the water molecules via hydrogen bonding. This is in accordance with what was found for water during a dehydration process [18,19]: it is bound at different levels of energy depending on its location in the lattice and on the type of cation with which it is coordinated (Figure 2).



**Figure 2.** H<sub>2</sub>O molecules in Zeolite-Na A cages and channels (a) LTA-type Zeolite 3D print model (b) LTA-type Zeolite molecular model.

### 2.2. Basicity of the Lattice Oxygen Bridging Al and Si: Distribution of Aluminum in the Tetrahedra of Zeolite Crystal

We previously discussed the acid–base sites of zeolites that originate from the different valence of the two ions Al<sup>+3</sup> and Si<sup>+4</sup> present in the crystal structure, so that (AlO<sub>4</sub>) tetrahedrons have a net negative charge that needs to be balanced by cations or protons. In the latter case, the zeolite is considered a solid acid that can offer heterogeneous catalysis thanks to the Brønsted acidity of bridging Si-(OH)-Al sites. However, basic sites are paired with Brønsted acid sites, which means the negative lattice oxygens are characterized by a certain basicity/nucleophilicity in cationic zeolite. After all, the basicity of the zeolites is proved by spectroscopic studies that were performed to assess this behavior, and its origin is related to the presence of Al<sup>+3</sup> ions in the crystal structure [20,21].

Regarding this last issue, we intend to discuss the presence and the structural organization of aluminum in the tetrahedral centers of the zeolite. The distribution of this ion is restricted by crystal structure rules other than the Pauling electrostatic valence rule. This concerns the electrostatic strength of a crystal structure ionic bond that depends on the ratio between the cation charge and its coordination number. In other words, cations characterized by a low charge should not expand their coordination geometry, since it would lead to a weaker ionic strength and, consequently, to an instable structure. However, concerning two tetrahedra linked by an oxygen bridge, in the case where one of the two centers is occupied by aluminum, the second one can accommodate silicon or a smaller ion characterized by a higher electrovalence, such as four or more. Most importantly, in the case where two aluminum ions are bound to the same oxygen anion, it is required that one of them has a coordination number larger than four. The Pauling electrostatic valence rule is not formulated to elucidate the reasons why an oxygen bridge between aluminum tetrahedrons is not allowed, and an expanded coordination geometry is required for one of the two aluminums. This leads to an unfavorable radius ratio and, therefore, an instable configuration [22].

The third rule of Pauling can clarify this geometrical restriction since it underlines that polyhedrals, around cations with high valence and small coordination number, tend to not share anions, such as oxygen, with each other in order to avoid destabilization. In principle, this rule considers the repulsive interaction between the central cations of the polyhedra. When the bonding is largely ionic in a crystal, the crystal is likely to assume a structure that keeps the cations as far apart as possible [23,24].

Generally, anions are commonly shared, so cations cannot be far apart, and instability is generated to a certain extent, especially in the case of large ionic strength of the bonds.

Instead, structures characterized by higher coordination numbers allow the minimization of this effect, and the sharing of elements, such as bridging oxygens, is allowed to a certain extent. This behavior can also be explained in terms of a radius dimension that easily accommodates cations in the anion polyhedra, so that in the case where two coordination numbers are possible, the higher one is preferred. These enhanced coordination numbers are responsible for the stability of the bridging oxygen, and the electrostatic valence becomes negligible. In fact, the neutrality is still maintained.

According to this concept, for an oxygen bridge between two aluminum ions, the stability is reached only when at least one ion has a geometry corresponding to an enhanced coordination number (five or six). However, the lack of accordance between the third Pauling rule and the electrostatic valence rule for cation sharing in an anion polyhedral is apparent. In fact, it is worth mentioning that in polyhedra with an enhanced coordination number the central atom cation has a certain ability to move, so that it does not contact simultaneously the closest anions. In consequence of this, the cation with an enhanced coordination number, suffering from repulsion from the other cation, can increase its distance from the bridge anion, with a consequent weakening of the electrostatic bond. It is worth remembering that the Pauling electrostatic valence rule allows exceptions for anions shared by polyhedra with an enhanced coordination number, considering the instability created by the radius ratio upon the stability of structures, accounting, indeed, for the third Pauling rule. The consequence of this is that the polyhedra with the lowest coordination number result in instability, although they are formally allowed when respecting the electrostatic valence rule.

Therefore, it is fully understandable that the substitution of aluminum for silicon in tetrahedra cannot be entirely random or allowed to an infinite extent. In the case of 50% substitution, Lowenstein formulated a theoretical rule, according to which the maximum amount of silicon that can be substituted by aluminum is 50%, with rigorous alternation between silicon and aluminum tetrahedra becoming necessary [22].

### 2.3. Nucleophilic Substitution Reactions Catalyzed by Zeolite A: INSIGHT into the Basic Active Sites

Chemoselective and for some procedures stereoselective nucleophilic substitution reactions were recently performed by employing the weak lattice basicity of Na-Zeolite A as a mild solid catalyst. For all reactions, a standardized procedure to activate the zeolites was employed, and this allowed for obtaining the final modified peptide molecules in high yield.

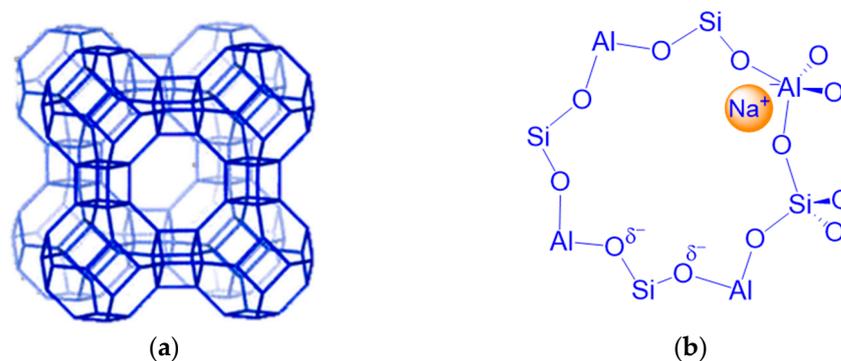
The Brønsted basic sites of zeolites originated from the framework oxygens bridging the silicon and the aluminum (Si-O-Al) that were in proximity of the zeolite pore edge on its external surface. It must be also considered that there are undeniable restrictions to the circulation through the zeolitic micropores since they are accessible only to molecules characterized by a dimension smaller than the pore size (4 Å diameter). These considerations allowed the hypothesis that for the reported chemical reactions, the basic catalysis takes place on the surface of the zeolite. In this regard, FT-IR investigation performed on molecules adsorbed on the zeolite, upon previously treatment for the chemoselective S-functionalization, proved to be a useful technology to confirm that the basic catalysis takes place at the external surface of the zeolites [25].

The origin of the basic sites is extensively discussed as inferable to the presence of Al ions. In major details, the basicity of lattice  $(\text{AlO}_4)^-$  oxygen was investigated by the  $\text{CO}_2$ -probe IR spectroscopy technique. This was also proved to be affected by the environment of the central Al ions in the framework of the zeolites, which means the number of basic sites is strictly correlated to the zeolite topology. However, the most relevant result of this IR spectroscopic analysis concerns the fact that only chemical adsorption of  $\text{CO}_2$  was detected, while carbonate species were not found in any spectrum. This allowed the

conclusion that the transformation of CO<sub>2</sub> to carbonate did not take place, as it usually does on strong solid base catalysts, such as MgO, CaO [20]. This phenomenon was explained in terms of moderate basicity of lattice (AlO<sub>4</sub>)<sup>-</sup> oxygen atoms, which represents the prerequisite for the chemoselective and, in some case, stereoselective catalytic activity provided to promote nucleophilic substitution reaction [8].

In addition, it was recently demonstrated that the activity, selectivity, and stability of zeolites as catalysts are tightly dependent on their Si/Al ratios and Al distribution in the framework. It was also underlined the great importance of being able to control these parameters, since they take into account of the zeolite efficiency [9].

The activation procedure of the zeolites is a peculiar key step of the catalyzed nucleophilic substitution reaction herein reported. This is performed by heating the zeolites at 280 °C and at low pressure ( $2.5 \times 10^{-4}$  Bar). This step is responsible for the efficiency of the nucleophilic reaction, so the high yield of the final substituted product is guaranteed only if the dehydration process is fully successful. To this aim, a high vacuum, besides the high temperature for the heating, is strictly required. It is worth remembering that in Zeolite A, the framework oxygen bridging the two cations, aluminium and silicon, is involved in a hydrogen bond with water, which means that a certain energy characterizes this interaction. It is reasonable to hypothesize that the removal of this type of water molecule is crucial for the execution of the nucleophilic substitution. In this regard, it was observed that a not entirely efficient dehydration process is associated with the failure of the substitution reaction [25]. It can be inferred from the energy associated with the electrostatic strength of the hydrogen bond of the water with the Al-O-Si oxygen framework (Figure 3 that might be the type of water leaving the zeolite lastly.



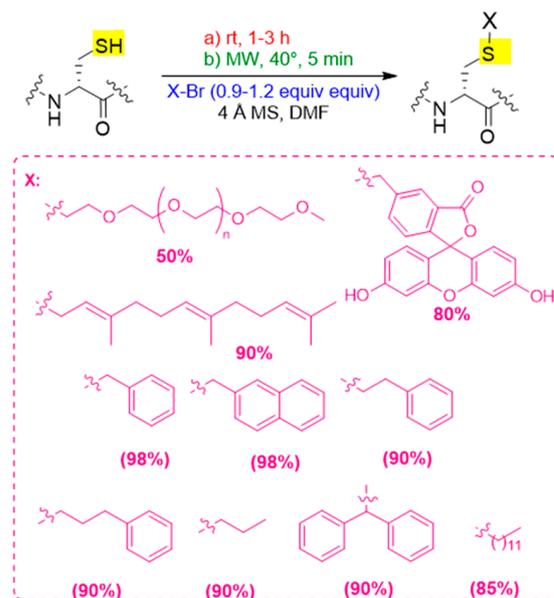
**Figure 3.** Zeolite cages and channels after removal of water molecules through a dehydration process. (a) LTA-type Zeolite 3D print model (b) LTA-type Zeolite molecular model.

We also observed that the percentage of Al present in the Zeolite A, employed for the nucleophilic substitution catalysis under consideration, has a value (50%) that guarantees the maximum number of efficient lattice basic Al-O-Si sites. Indeed, this was already underlined before, only in this case a fully tetrahedral coordination around both cations (Si and Al) ensures a stable geometry of the crystal, characterized by significant ionic bonds in Al-O-Si, accordingly to the Lowenstein law. In other words, the negative charge localized on the lattice oxygen can efficiently assist the basic catalysis.

### 3. Nucleophilic Substitution Reactions Promoted by the Basic Catalysis of Zeolite-Na 4Å Solution and Solid-Phase Thio-Substitution of Peptide Molecules with Different Moieties

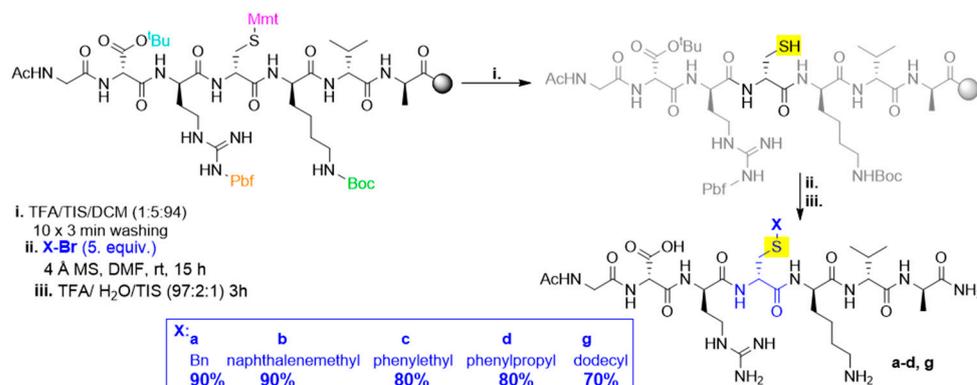
A cysteine thiol group of a peptide molecule was chosen as the nucleophile, due to its peculiar reactivity even at pH values below 9. Cysteine is, among the twenty natural amino acids, one of the most employed functional groups to introduce substituents in peptides. The chemical protocol was confirmed to be highly chemoselective and efficient. The reactions were performed following two protocols. First, the reaction was executed at room temperature in the presence of activated Zeolite-Na A, by using around one equivalent of the alkyl halide, DMF as the solvent, argon atmosphere and a variable reaction

time ( $t = 1\text{--}3$  h). Next, the same protocol was performed under microwave irradiation ( $T = 40\text{ }^\circ\text{C}$ ;  $t = 5$  min), thus reducing the reaction time. Different alkyl substituents were introduced along with useful functional groups, such as a fluorescent probe 5-(bromo-methyl) fluorescein, a polyethylene glycol and a farnesyl group. This latter is a typical post-translational modification of a protein belonging to the RAS family (Scheme 1) [8,25].



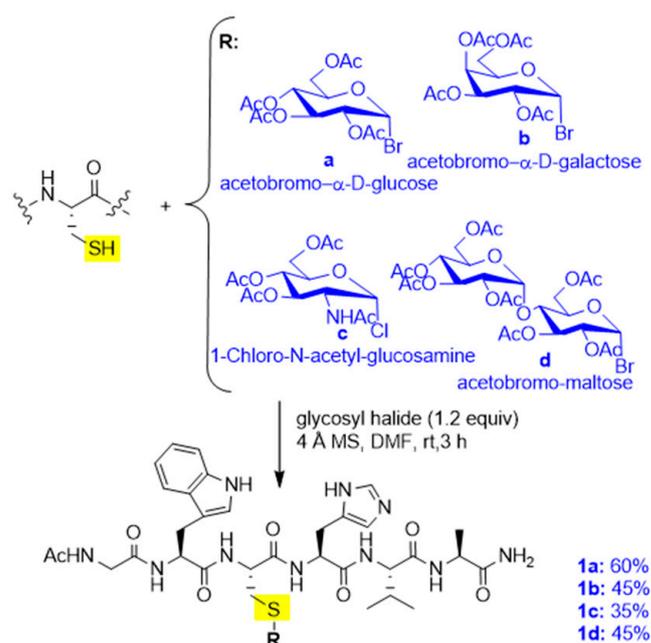
**Scheme 1.** Solution-Phase Approach for thio-substitution reactions catalyzed by activated basic Zeolite-Na A (4 Å MS) [26–28].

The developed protocol to introduce functionalities via thio-substitution reaction catalyzed by the basic Zeolite-Na A was also implemented in solid phase (Scheme 2). This approach allowed the direct modification of a peptidyl resin, thus making the strategy a common solid-phase peptide synthesis step. In this case, the substituents are introduced on a cysteine thiol-group of a peptide sequence still anchored to the resin support. It was necessary to selectively free the cysteine side chain from its super-labile protecting group (Mmt = 4-methoxytrityl) in acidic conditions. The protocol was applied only at room temperature, as previously describe, prolonging the reaction time to 15 h. One of the major advantages of this solid-solid phase protocol consist in avoiding the formation of a S-S dimer of the peptide sequence, in case the S-functionalization results incomplete or totally failed. Indeed, this side reaction can occur on peptides that react in solution, never on peptides anchored on resin.



**Scheme 2.** Solid-Phase Approach for thio-substitution reactions catalyzed by activated basic Zeolite-Na A (4 Å MS) [29].

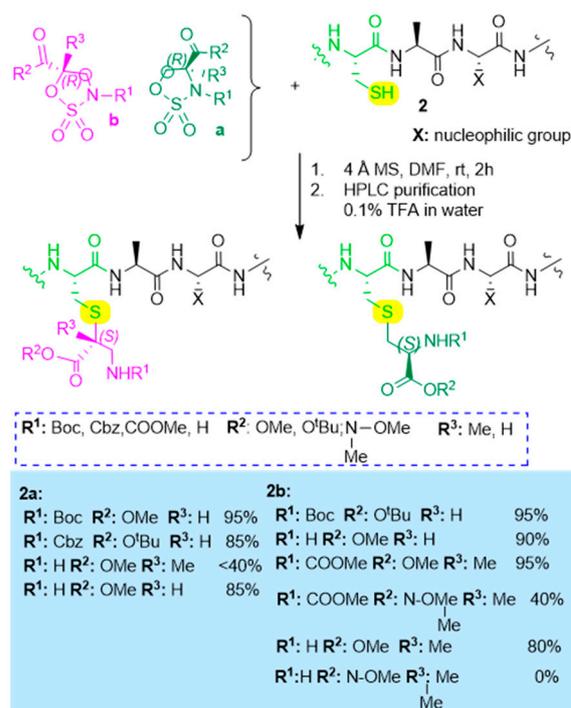
Next, the same protocol was employed to prepare glycopeptides, through the nucleophilic attack of a cysteine thiol group on several  $\alpha$ -D-monosaccharides and disaccharides that are commercialized at affordable prices. The reaction was performed at room temperature for 2 h under the basic catalysis of Zeolite-Na A, following the previously reported conditions. The substitution mechanism  $S_N2$  allowed the preparation of  $S$ - $\beta$ -linked peptides (Scheme 3). The synthetic strategy provided the great advantage of being chemo and stereoselective and easy to perform. For instance, it was recently used by other researchers to prepare  $S$ -glycosyl amino acid building blocks [30].



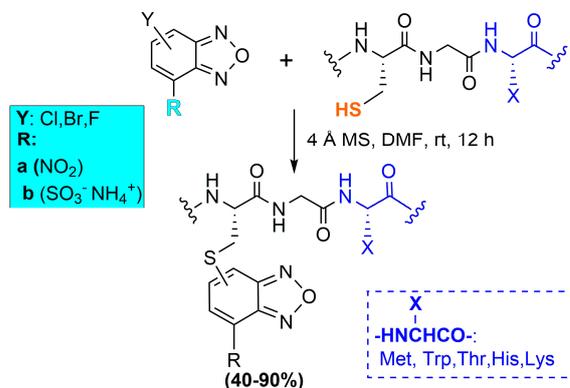
**Scheme 3.** Thio-glycosylation of peptide sequences catalyzed by activated basic Zeolite-Na A (4 Å MS) [31].

The nucleophilic substitution strategy catalyzed by Zeolite-Na A was efficiently employed also to synthesize lanthionine-containing peptides, which are precursors of the synthetic lantibiotics that are currently considered a hot topic. The mechanism involved a stereoselective ring-opening nucleophilic reaction performed via thio-alkylation on cyclic amino acid derivative sulfamidates, under the basic catalytic assistance of Zeolite-Na. The reaction conditions are quite mild and compatible with a wide range of protecting groups of the sulfamidate derivatives (activated Zeolite-Na A, DMF as the solvent and argon atmosphere for 2 h under stirring). Different lanthipeptides were prepared with the aim of obtaining the active portion of the natural lantibiotics (Scheme 4) [32,33].

The proposed strategy was successfully applied to perform the thio-substitution reaction on benzofurazan derivatives, via nucleophilic attack promoted by the basic catalysis of Zeolite-Na A. The reaction conditions for this reaction were not changed, even though the substrates where the nucleophilic substitutions were performed were quite peculiar; they were highly conjugated halo-derivatives. This result confirmed the versatility of using Zeolite-Na A as the basic catalyst, in addition to the high efficiency already confirmed by the different types of nucleophilic attacks performed to prepare different modified peptides (Scheme 5).



**Scheme 4.** Stereoselective thio-substitution performed on cyclic sulfamidates catalyzed by activated basic Zeolite-Na A (4 Å MS).



**Scheme 5.** Thio-substitution performed on halogen-sulfo/nitro-benzofurazans catalyzed by activated basic Zeolite-Na A (4 Å MS) [34].

#### 4. Conclusions

In this perspective article, we analyzed the basic properties of Zeolite-Na A as they are related to the structure of the crystal mineral under investigation. The final aim was to gain insights on the mechanism of the provided basic catalysis. In fact, this could help in widening the application of the LTA type of Zeolite for the ever-growing chemical fields.

Although hydrocarbon transformation can be considered the major application field for the use of zeolites as efficient catalysts, the nucleophilic substitution reactions herein analyzed proved the high chemoselectivity exhibited by zeolites in organic reactions. This requisite is of primary importance for those chemical reactions involving complex transformations of molecules with several functional groups. In addition, the mild conditions represent another fundamental requirement since they avoid undesired degradation of the organic molecules. These remarkable properties set forth zeolites as cleaner and more efficient catalysts to produce fuels and chemicals. Therefore, considering their unique and selective shape, tunable acid/ base properties, high thermal stability and low production

cost, zeolites continue to attract a great deal of interest for applications as a solid green catalyst of organic reactions.

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