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USE OF ALUMINOSILICATES SUCH AS ACID - ACTIVATED CLAYS AS SOLID CATALYSTS FOR THE REACTIVITY OF THE VARIOUS CARBONYL COMPOUNDS IN HETEROCYCLIC SYNTHESIS

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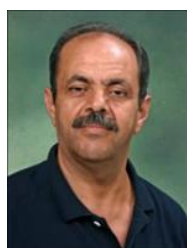
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46

Abstract

The heterocyclic compounds, in particular the heterocycles containing five, six and seven members, are the the most abundant of which are an incredibly diverse and large class of ubiquitous molecules that occur in a variety of synthetic drugs, bioactive natural products, pharmaceuticals and agrochemicals. Due to the glorious past and impressive present of biologically active heterocyclic scaffolding, these skeletons have long been the subject of immense interest. Therefore, substantial efforts have been made development of new and innovative synthesis strategies for the synthesis of these heterocycles involving use of different metallic catalysts, organic and inorganic reagents, etc. Among the different types of metals catalysts used, iron-based catalysts are among the cheapest and most readily available. In recent times, several new an innovative synthesis catalyzed by catalysts based on aluminosilicates, heterocycles of diversity at the forefront of the literature by the scientific community. This review highlights advances produced up to now by solid catalysts based on aluminosilicates such as clays activated by acids, zeolites, montomorillonite K10 ... for the synthesis of different assemblies of small heterocycles covering these last years.

Introduction

Heterocyclic skeleton is a "privileged" structural motif in innumerable natural products and synthetic compounds often exhibiting relevant biological properties [1]. More specifically, nitrogen heterocycles are abundant in nature existing as part of vitamins, hormones, antibiotics, and alkaloids.

Among the synthetic drugs commercialized in more than 100 different countries and containing a heterocyclic core are *Atorvastatin* (Lipitor$^{®}$, (1)) [2], and *Azoxystrobin* (Amistar$^{®}$, (2)) [3] considered as a blockbuster blood choles- terol reducer preventing the cardiovascular diseases and a broad-spectrum fungicide, respectively (Figure 1).

In this sense, the studies concerning the synthesis, properties, and applications of the heterocyclic compounds constitute an important issue in organic synthesis. In fact, the heterocyclic chemistry is nowadays considered as a subdiscipline of organic chemistry [4-7].

Heterocycles are a class of compounds especially relevant in the life processes through their enzymatic functions and the hereditary information transfer; they also find applications in medicine, agriculture and industry, and in dif- ferent areas of the chemistry.

Heterocyclic compounds are often used in nanochemistry, molecular devices and sen- sors, combinatorial and supramolecular chemistry, and also in catalysis [8]. Furthermore, an important type of ionic liquids (ILs) useful in the pharmaceutical industry, which can act both as green solvents and catalysts, are composed of heterocyclic compounds [9,10].

Some porous materials such as zeolites or even metal-organic frameworks (MOFs) constructed from heterocyclic scaffolds and interestingly with important nanotechnological applications, are useful also as catalytic systems [11,12]. Considering that the heterocycles are frameworks of biologically active compounds and more than 70% of all phar- maceuticals

contain at least one heterocyclic ring, the development of new and more efficient and selective catalytic systems involved in the synthesis of heterocyclic compounds is a challenge with capital importance for the pharma- ceutical industry. From an economic point of view and also with environmental concerns, the catalysis is one of the key technologies used in chemical industry.

To this end, the heterogeneous catalysis over the homogeneous one hold a preferential place because of the highest thermal stability of the catalysts, easy separation of those, and also cleaner and easier isolation process of the products, resulting in lower operating costs.

However, the main disadvantage of using heterogeneous catalysis is the lower selectivity of the processes due to the presence of multiple active sites. Under this background, this chapter is aimed to offer an up-to-date of the most recent advances in the synthesis of biologically active heterocycles or related compounds by using porous catalytic systems.
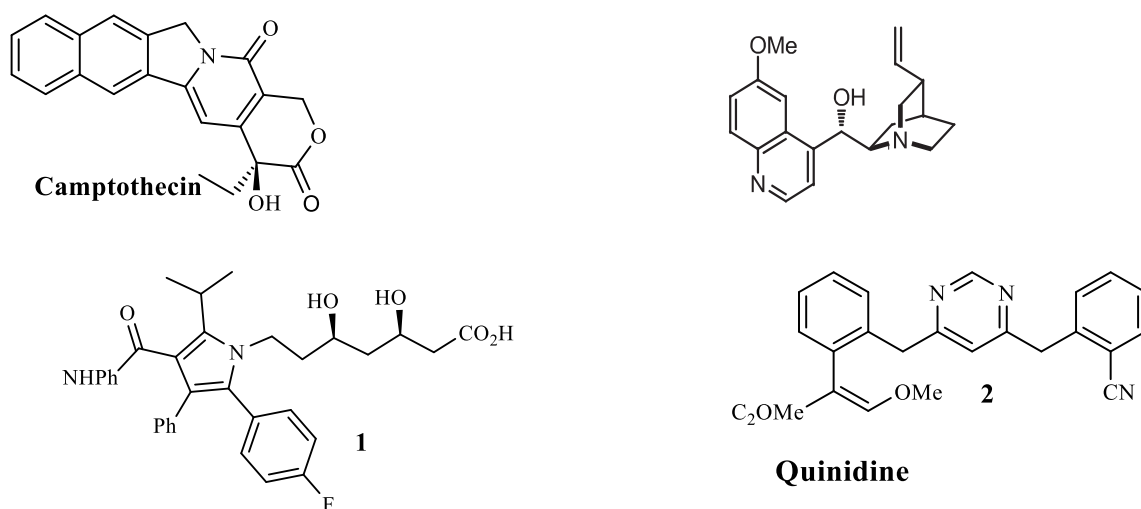

Figure 1. Heterocyclic natural products: Camptothecin and Quinidine. Synthetic compounds: Atorvastatin and Azoxystrobin.

Porous catalytic system

The development of more active and selective novel catalytic materials for efficiently carrying out chemical processes under environment-friendly conditions is an urgent present-day need and a challenging scientific tar- get. Hence, this section particularly summarizes the most relevant characteristics of the porous catalytic systems involved in the synthesis of bioactive heterocyclic compounds. Some of the porous systems used in catalysis include zeolites, mesoporous silicas, clays, MOFs, and porous carbons.

From the point of view of catalytic activity and in terms of selectivity and waste production, zeolites are the most traditional microporous catalysts with clear advantages over the conventionally used homogeneous acid catalysts. Zeolites find applications in the petrochemical and fine chemical industries, and also in gas separation, purification, and ion exchange [13-15]. In addition, zeolites are used in pharmaceutical industry, sensing microsystems, nanotech- nology, the intensification process, and green chemistry.

The main limitation of using microporous zeolites in catalysis is their small pore size which faces difficulty in offer- ing catalytic activity to large molecules. That is why, the mesoporous

48

zeolitic materials emerge as alternative materials; the development of the mesoporous silicas has experienced an impressive progress since the discovery of MCM-41 by scientists of Mobil Corporation in 1992 [16]. Their well-defined surface chemical properties, high surface areas, and nar- row pore-size distributions make them interesting and efficient catalysts for the transformation of bulky substrates [17]. The mesoporous silicas have emerged as an exciting type of materials with technological applications not only in the fields of catalysis, adsorption and gas separation, and as biomolecules immobilizing supports but also as tem- plates for the synthesis of other porous materials-thanks to their porous and morphological characteristics. The investigation on the modified mesoporous silicas is an extensive research field considered as a hot topic of current interest in nanotechnology.

As a result, several reviews focused on the structural characteristics and properties of mesoporous zeolitic materials have been reported in recent times [18].

Naturally occurring clay minerals are composed of crystalline aluminosilicate layers containing hydrated ions occupying the interlamellar space; in order to compensate the negatively charged aluminosilicate layers, cations should necessarily exist within the interlayer space. In general, clay minerals show unique physicochemical proper- ties such as large surface areas, ion exchanging, swelling, and active broken-edge $M-O-$ bonds. These intrinsic prop- erties can be altered by replacing interlamellar cations by other molecules or complexes, by increasing the interlayer space, and even by covalently anchoring molecules to layer atoms leading to nanohybrid materials making them useful materials in adsorption and also in green catalysis. In fact, the area involving clay-based catalysts is now a hot topic as also reflected in recent times by the appearance of a good number of reviews in this direction [19-21].

Finally, the porous carbon materials are especially relevant from an economic and technological point of view. There is a wide collection of carbon materials with different origin, chemical and textural properties, and therefore, useful in different applied fields. Microporosity is an intrinsic characteristic of carbon materials, and such property is generated during carbonization by releasing of gases formed from the heteroatoms present in any carbon precursor (mainly H,O, N, S). The precursors and experimental conditions to prepare mesoporous carbons should be carefully fitted. This type of carbons show high interest in catalysis, medical applications and drug delivery, immobilization of biomolecules to develop biosensors, or decontamination of big molecular size pollutants.

A. SYNTHESIS OF BIOACTIVE HETEROCYCLES CATALYZED BY POROUS MATERIALS

A huge number of heterocyclic compounds differing in the size and number of their rings and in the type, number, and positions of heteroatoms are known. Several heterocycles even unsubstituted ones exhibit biological properties. In fact, the pharmacophore in many synthetic drugs is constituted by a heterocyclic core. Heterocyclic compounds can also act as prodrugs or even as isosteric replacements of functional groups.

This article is aimed to offer an update of the most relevant and interesting catalytic processes involving zeolites, clays, mesoporous materials, particularly functionalized mesoporous silicates and metallosilicates, MOFs, and car- bon materials in the synthesis of bioactive heterocycles and related compounds.

49

1. O-Containing Heterocyclic Compounds

Oxygen heterocycles are present in many natural products such as tannins and polyphenols found in fruits, vegetables, teas, and red wines exhibiting healthy effects in living organisms. In addition, this type of heterocyclic rings is also contained in several medicinal agents. Thus, *O*-heterocycles have appeared as important building blocks in organic synthesis.

1.1. Five-Membered Ring Heterocycles

This section summarizes the most studied organic reactions catalyzed by zeolites and mesoporous aluminosilicates useful in the synthesis of flavoring compounds, in perfumery, and other industrial fields. Acetalization reactions of aldehydes / ketones and the intramolecular hydroalkylation of unsaturated alcohols or tandem reactions such as Claisen rearrangement and subsequent intramolecular hydroxyalkylation of olefins are some of the noted reactions.

It is well known that acetalization reaction is an important synthetic protocol useful not only for the carbonyl group protection when working within multifunctional organic molecules, but also for the synthesis of fragrances and related compounds [22]. Acetalization of phenyl acetaldehyde and vanillin with glycols catalyzed by zeolites afforded hyacinth, vanilla, and blossom orange fragrances in good yields [23]. Compounds 3-5 are flavoring compounds with hya- cinth and vanilla scent fragrances.
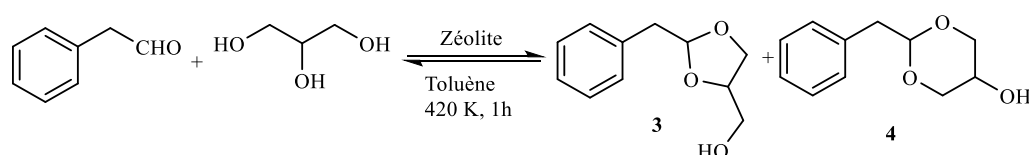
Zeolite	Yield to **3** (%)	Yield to **4** (%)
USY-2	58	35
Beta-2	61	31
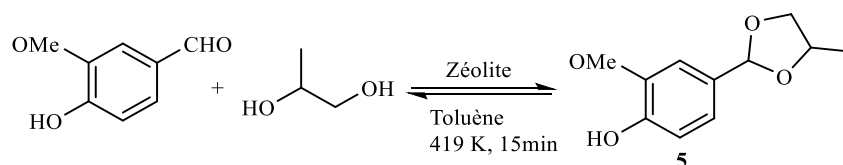
| Zeolite	Yield to **5** (%)
USY-2	81
Beta-2	88
Beta-2	87
Mordenite	67
ITQ-2(II)	89

Scheme 1. Acetalization of (a) phenyl acetaldehyde and (b) vanillin with glycols.

However, Acetalization of larger aldehydes such as 2-acetonaphthone with propylene glycol in the presence of microporous zeolites did not go well. Then dioxolane was selectively

obtained in the presence of ITQ-2, a delaminated zeolite with a very large and structured external surface.
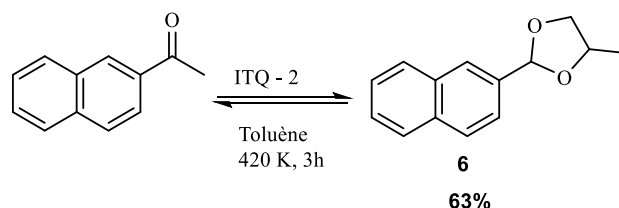
**Scheme 2.** Synthesis of 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane.

The hydrophobic characteristics of the catalysts are as important as the concentration of their catalytically active acid sites. Zeolites were intrinsically more active than the delaminated and mesoporous materials in the acetalization of small size car- bonyl compounds. However, the use of substrates within larger sizes decreased the rate of diffusion of reactants due to geometrical constraints.

USY-3 and BEA-1−3D zeolites were effective and selective microporous catalysts for the synthesis of fructone 7, a flavoring material prepared by acetalization of ethyl acetoacetate with ethylene glycol [24]. Shimizu et al. [25] reported the acetalization of carbonyl compounds with ethylene glycol catalyzed by SO_3H-FSM, propyl-sulfonic acid-functionalized FSM-16 mesoporous silica prepared by a conventional postsynthetic method.

| Zéolite	Yield to **7** (%)	Selectivity to **7**
BEA-1	91	95
USY-3	96	97
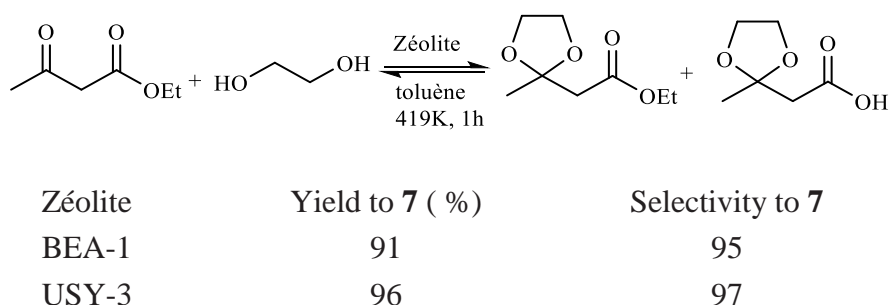
Scheme 3. Synthesis of fructone.

A simple and clean synthesis of dioxolanes has also been reported in the presence of Tunisian clay. The acid treatment of this clay gives rise to Brönsted acid sites which promote synthesis [26]. The surface acidity of clay is considered to be a determining factor in its catalytic activity. This strategy presents an interesting alternative for conventional acetalization reactions. In addition, a range of carbonyl compounds have been considered via acetalization in the presence of silica and alumina [27].


R = Ph-CH=CH$_2$, p-OMe-C$_6$H$_4$, p-NO$_2$-C$_6$H$_4$

51
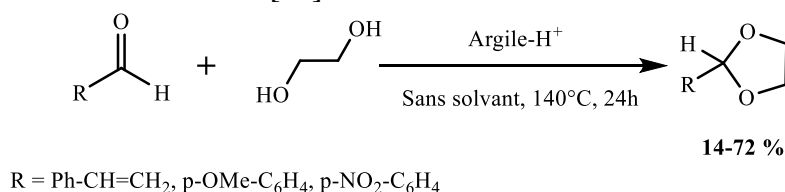
Scheme 4. Acetalization of aldehydes with ethylene glycol.

Reusable, non-polluting catalysts such as titanium-bridged clays (Mont-Ti^{4+}) are effectively used for the selective Acetalization of a variety of carbonyl compounds with ethylene glycol [28].
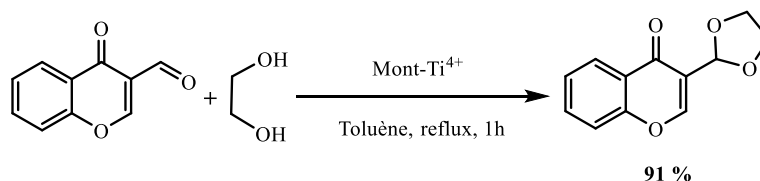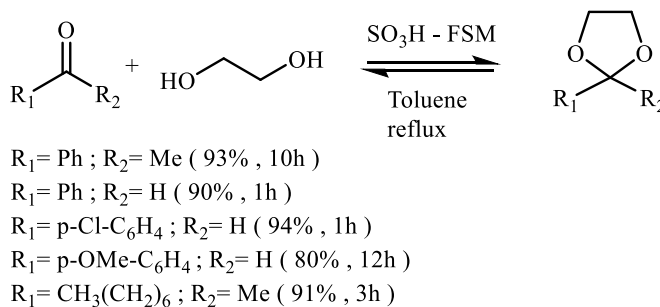
Scheme 5. Acetalization in the presence of Montmorillonite-Ti^{4+}.

Previous work has been done to improve the catalytic activity of Tunisian clays. In this context, clays bridged by metals such as zirconium, cerium and aluminum or a mixture of these metals have also shown great selectivity in the synthesis of 2,2-dimethyl-1,3-dioxolane with yields satisfactory which depend on the nature and the acidity of the clays used and the reaction time [29].
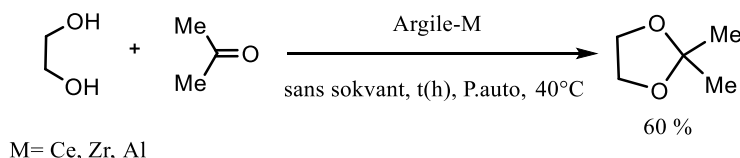
**Scheme 6.** Acetalization of acetone catalyzed by bridged clays.

The corresponding 1,3-dioxolanes were obtained with higher rate and yield than when other traditional porous materials such as zeolites or clays were used. This is probably because both the reactants can easily access the strong Brønsted acid sites with relatively low hydrophilicity in the mesopores. SO$_3$H-FSM was reported to be a reusable catalyst without appreciable loss of catalytic activity.

R$_1$= Ph ; R$_2$= Me (93% , 10h)
R$_1$= Ph ; R$_2$= H (90% , 1h)
R$_1$= p-Cl-C$_6$H$_4$; R$_2$= H (94% , 1h)
R$_1$= p-OMe-C$_6$H$_4$; R$_2$= H (80% , 12h)
R$_1$= CH$_3$(CH$_2$)$_6$; R$_2$= Me (91% , 3h)

Scheme 7. Acetalization of carbonyl compounds from different carbonyl compounds and ethylene glycol.

More recently, Pérez-Mayoral et al. reported the acetalation/ketalation of carbonyl compounds catalyzed by acid- or basic-aluminated mesoporous SBA-15 under solvent-free conditions and

52

thermal activation in the presence of ethanol and/or triethyl orthoformate [30]. The procedure therein reported was applied to the preparation of key intermediate compounds in the synthesis of a pH indicator **8** for Proton Magnetic Resonance Spectroscopic Imaging.
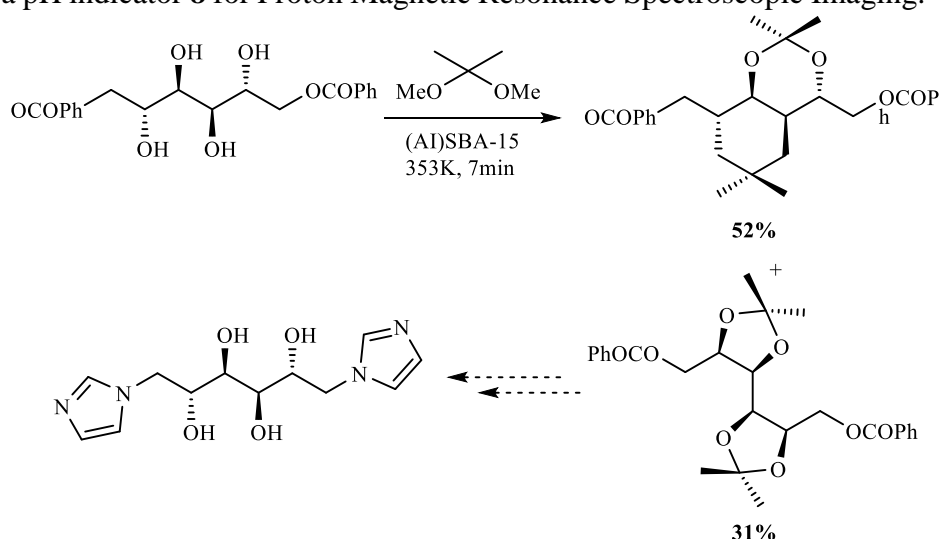
Scheme 8. Synthesis of intermediate for the preparation of the pH indicator **8** for proton magnetic resonance spectroscopic imaging.
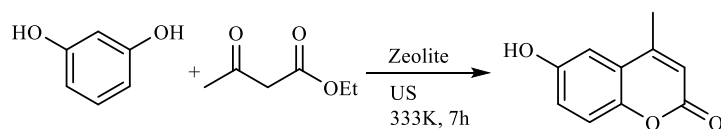
1.2. Six-Membered Ring Heterocycles

Many six-membered oxygen heterocycles are distributed in nature such as coumarins, and chromenes, flavones, and xanthene derivatives. The most relevant and environment-friendly methodologies to prepare these heterocyclic compounds are revised in the subsequent sections.

1,2-Benzopyrones, known as coumarins, display a broad range of biological and pharmacological properties such as analgesic, antimicrobial, vasodilator, anti-inflammatory, antioxidant, and even anticancer and anti-HIV [31].

Pechmann reaction is one of the simplest and useful synthetic methodologies to prepare coumarins consisting of the condensation of phenols with β-ketoesters in the presence of acid catalysts.

Hymecromone is an interesting coumarin commercialized as laser dye, biliary antispasmodic, and also as starting material for the production of insecticides [32-34].

For its useful application, different porous catalytic sys- tems for the preparation of have been extensively investigated. Gutiérrez-Sánchez et al. prepared by Pechmann reaction between resorcinol and ethyl acetoacetate, in the presence of acid zeolites, under solvent-free conditions and ultrasound irradiation at moderate reaction temperatures [35].


53

Dintzner et al have demonstrated the utility of montmorillonitic clays in the Diels-Alder reaction of 2,3-dimethyl-1,3-butadiene with ortho-bromobenzaldehyde. The desired product is obtained with a good yield and a high conversion [36].
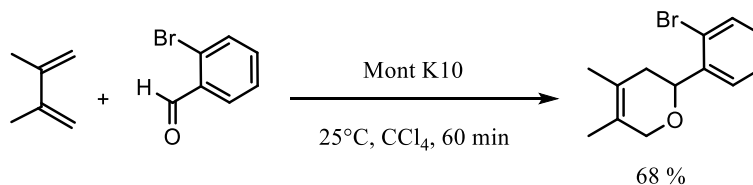
Scheme 10. Hetero-Diels-Alder reaction.

MCM-41 functionalized with ammonium quaternary salt, MCM-41OH, prepared by grafting to the pure silica MCM-41, are useful catalysts capable of promoting Knoevenagel condensations and Michael additions under mild conditions [37,38].
The reported methodology was used for the selective synthesis of chromenes from salicylaldehyde and diethyl 2-pentenedicarboxylate.
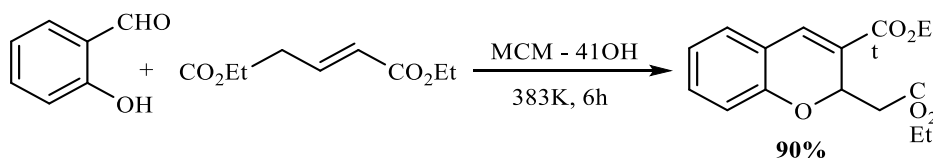
Scheme 11. Selective synthesis of chromenes from salicylaldehyde and diethyl-2-pentenedicarboxylate.

## 2. N-Containing Heterocycles Compounds

Nitrogen heterocycles are a class of naturally occurring compounds essential to life since their structural units are present in many natural products such as vitamins, hormones, antibiotics, and alkaloids and also in many pharmaceu- ticals and herbicides among other synthetic compounds, exhibiting a broad range of biological activities [39].
In this section, the most relevant biologically active *N*-containing heterocycles which are synthesized by using porous catalytic systems are revised.
Five-membered ring heterocyclic compounds containing nitrogen are one of the most common heterocycles. In fact, the synthesis of a great variety of that such as pyrrole, pyrazole, imidazole, triazole, tetrazole, lactams, and imides involving porous catalytic systems have been investigated.

2.1. Pyrrole and Related Compounds

54

Pyrrole containing heterocyclic derivatives have been reported as having important biological activities such as COX-1/COX-2 inhibitors and cytotoxic activity against a variety of marine and human tumor models [40]. Indole is an important heterocyclic system which is built into proteins of amino acid tryptophan. It is also the source of drugs like indomethacin and also the skeleton of indole alkaloids, biologically active compounds from plants. The indole nucleus is a biologically accepted pharmacophore in medicinal compounds possessing wide spectrum of biological activities; anti-inflammatory and analgesic, antifungal, antimicrobial, antiviral, insecticidal, antitubercular, opioid antagonist, antidepressant, anticonvulsant, anticancer, among others [41].
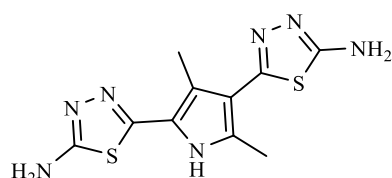

Antifungal pyrrole derivative
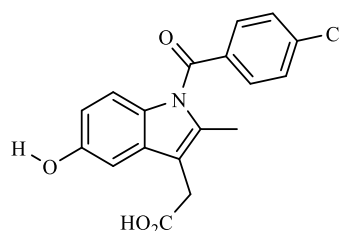
Indomethacin

Figure 2. Antifungal compound, pyrrole derivative highly active against Aspergillus Niger. Indomethacin, an indole derivative with analgesic and anti-inflammatory activity.

Reddy et al. synthesized 5-hydroxyindole derivatives via the Nenitzescu reaction by coupling of aniline, ethyl acetoacetate, and *p*-benzoquinone, in 1,2-dichloroethane, using montmorillonite KSF clay as catalyst [42]. The reaction was also performed using acyclic and cyclic 1,3-diketones and with aryl and alkyl amines. Among several catalysts tested in this reaction, montmorillonite KSF clay proved to be the best catalyst leading to the highest yields in a shorter reaction time.
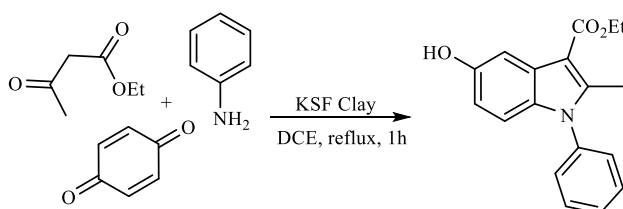

Reaction Conditions	Yield (%)
Cellulose-SO$_3$H, reflux, 3h	65
p-TSA/CH$_3$CN, reflux, 2h	70
Acid carbon/ EtOH, 3h	52
Montmorillonite/ DCE, 1h	95
PMA/SiO$_2$, neat, 3h	35

55

Scheme 12. Three-component coupling reaction for the synthesis of 5-hydroxyindole.

Commercial montmorillonite K10 is effective in the condensation reaction.
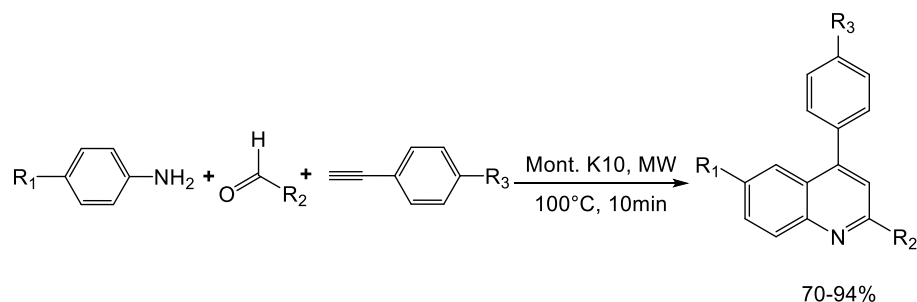
Scheme 13. Synthesis of quinolines in the presence of montmorillonite K10.
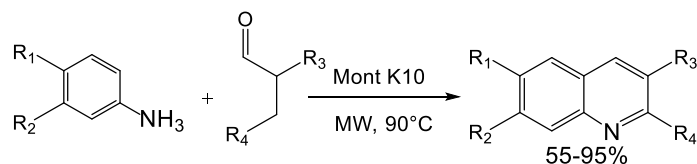
Scheme 14. Addition of aniline to cinnamaldehyde.

2.2. Imidazole and pyrazole

Imidazole, a well-known five-membered heterocyclic compound, is a major source of interest for a variety of medici- nal agents. Imidazole derivatives show various pharmacological activities such as antiviral, anti-inflammatory, analge- sic, antidepressant, antifungal, antibacterial, anticancer, antitubercular, and antileishmanial activities [43,44].
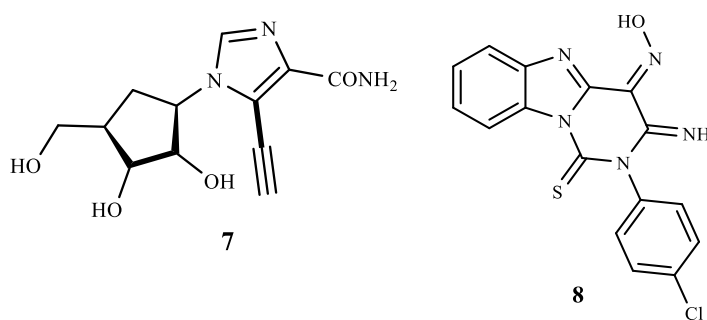

Figure 3. 5-Alkynyl-1-beta-D-ribofuranosylimidazole-4-carboxamide **7** known as EICAR with broad-spectrum antiviral agent and pyrimido[1,6-a]benzimidazole derivative **8** as potent anti-inflammatory–antimicrobial agent with analgesic activity.

Heravi et al. studied the synthesis of 2,4,5-trisubstituted imidazoles through three-components coupling of 1,2-diketone/1,2-hydroxyketone, aromatic aldehydes, and ammonium acetate using MCM-41 as catalyst under solvent-free conditions [45]. MCM-41 efficiently catalyzes the reaction affording the desired product in good yields in a relatively short time.
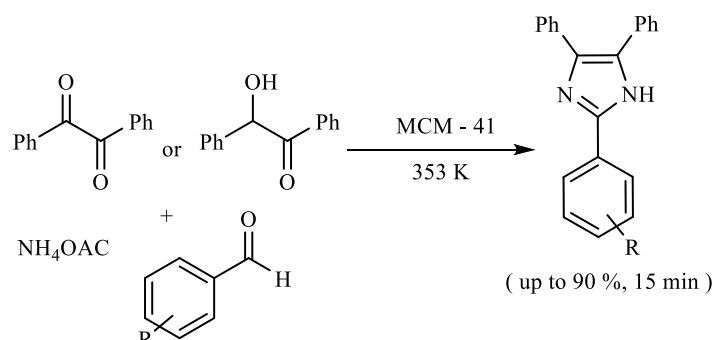
Scheme 15. Synthesis of 2,4,5-triaryl-1H-imidazoles from benzoin or benzil, ammonium acetate, and aromatic aldehydes using MCM-41 as catalyst.

A series of imidazopyridine derivatives have been efficiently synthesized via intramolecular cyclization of the (2-aminopyridin-3-yl) acetamides. The reactions were catalyzed by clay bridged with Al^{3+} ions. It is important to note that this catalyst is reused at least five times without losing its activity [46].
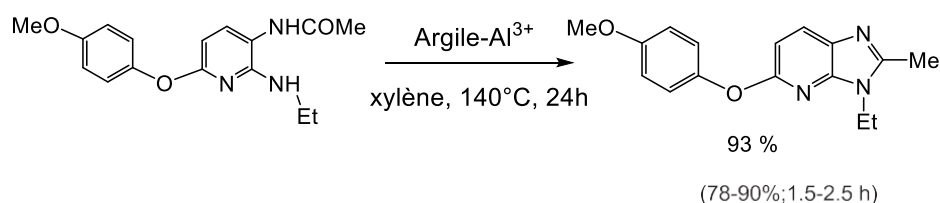
**Scheme 16.** Synthesis of 3-ethyl-3-methyl-3H-imidazo [4,5-b] pyridine.

Pyrazole and its derivatives have displayed broad spectrum of pharmacological and biological activities such as antimicrobial, antitumor, antiviral, antidepressant, anticonvulsant, antihyperglycemic, and enzymes inhibitory activities [47].

Nikpassand et al. performed the synthesis of 1,5-diarylpyrazoles using Baylis - Hillman adducts over HY zeolites [48]. HY zeolite is characterized by containing a framework system of supercages, which are connected by a 3D array of large-diameter channels allowing a much easier diffusion of reactants and prod- ucts. In this work, the Baylis–Hillman adducts were synthesized and converted to the related 1,5-diarylpyrazoles, using 1,2-dichloroethane as solvent, over HY zeolites (Si/Al 2.54) in relatively short reaction times.

57
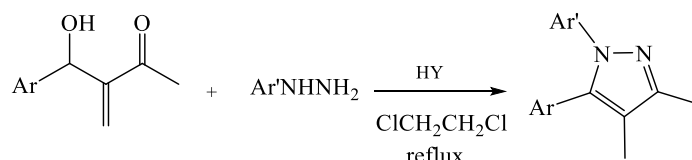
Scheme 17. Synthesis of 1,5-diarylpyrazoles over HY zeolite catalyst.

Matos et al. proposed for the first time (Cs)Al-SBA-15 and DEAPTS/ MCM-41 mesoporous materials (where DEAPTS is diethylamino propyl) as efficient basic catalysts in the alkylation of pyrazole and diethyl iminodiacetate with various reactive alkyl bromides under conventional thermal activation [49]. The alkylation of pyrazole catalyzed by both (Cs)Al-SBA-15 and DEAPTS/MCM-41 catalysts in the presence of a solvent (acetonitrile or dimethylformamide (DMF)) afforded selectively *N*-alkylpyrazole with high value of conversation.
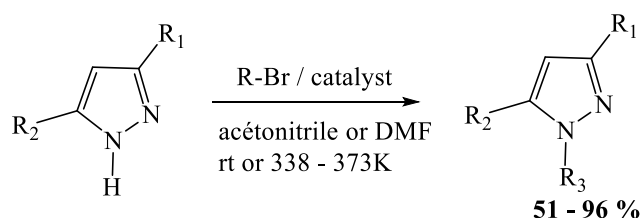
Scheme 18. Alkylation of pyrazole ring with different reactive alkyl bromides.

2.3. Synthesis of Triazole

N-substituted triazole derivatives have shown a huge number of biological activities such as antibacterial, anti- fungal, anti-inflammatory, analgesic, anticonvulsant, anticancer, antitumor, antiviral, antileishmanial, potassium channel activators, antiplatelet, and antioxidant activities [50]. In particular, the 1,2,4-triazole nucleus has been incorporated into a wide variety of therapeutically important agents such as ribavirin with antiviral, riza- triptan as antimigraine, vorozole, letrozole, and anastrozole showing antitumor activity, and posaconazole, flucon-azole, and itraconazole, as efficient antifungal drugs.
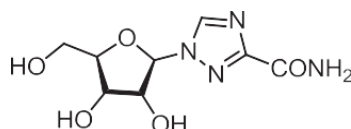

Figure 4. Ribavirin, a triazole derivative exhibiting antiviral activity.

Montmorillonite K-10 or kaolin clays were used as catalysts in the synthesis of 5-substituted 1*H*-tetrazoles [51]. The reaction was carried out using a series of aromatic nitriles with sodium azide, in water or DMF as solvent, at 373-403 K. The reaction was activated under conventional heating or ultrasonic irradiation. The authors found that using nitriles with electron-withdrawing groups resulted in both higher yields (up to 96%) and lower reaction times (from 2 to 24 h).

$$R\text{-}CN \; + \; NaN_3 \xrightarrow[\substack{H_2O \text{ or DMF} \\ reflux, \; 24h}]{Mont \; K\text{-}10}$$

(10 - 96 %)
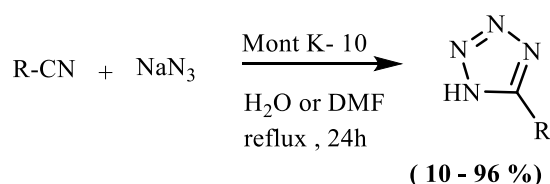
Scheme 19. Synthesis of 5-substituted 1H-tetrazoles using montmorillonite K-10 and kaolin as catalysts.

Conclusion

Nowadays, academic research labs and also the pharmaceutical companies are called to implement and optimize useful synthetic procedures which minimize the generation of chemical wastes because of the environmental concerns. The het- erogeneous catalysis together with other chemical technologies is involved in the design of new and environment-friendly methodologies for the green synthesis of target organic compounds. In particular, the C–C and C–heteroatom bond form- ing reactions are frequently used in the synthesis of highly valuable products including heterocyclic compounds.

Under this purview, clays, zeolites and other zeolitic materials such as mesoporous silicas or MOFs are currently consid- ered interesting porous catalytic systems, clays and carbons being cheaper alternatives to those.

Clays and zeolites are probably the most traditional inorganic solids involved in the synthesis of interesting heterocyclic compounds among others. Their high catalytic activity makes them potentially valuable catalysts for a great variety of chemical processes competing with other porous catalytic systems. Remarkably, the potential of all the mentioned porous catalytic systems in different catalyzed organic transformations relies on their extremely versatile properties such as the compositional variability and their confinement of dimensions.

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