



## A NOVEL APPROACH FOR THE MICROWAVE-ASSISTED SYNTHESIS OF 5-SUBSTITUTED 1H-TETRAZOLES CATALYZED BY MICRO AND MESOPOROUS MATERIALS

Farah Belalia<sup>a</sup>, Nabila Bouchiba<sup>b</sup>, Mohamed El Hadi Benhalouche<sup>a</sup>, and Mohammed Hamadouche<sup>a\*</sup>

<sup>a</sup> *Laboratoire de Chimie Fine, Université Oran1 Ahmed Ben Bella, BP 1524 El M'naouer, Oran 31000, Algérie.*

<sup>b</sup> *Laboratoire de Chimie des Matériaux, Université Oran1 Ahmed Ben Bella, BP 1524 El M'naouer, Oran 31000, Algérie.*

\*E-mail:hamadouche.mohammed@univ-oran1.dz

**ABSTRACT:** A variety of 5-substitued-1H-tetrazoles were prepared under microwave irradiation by addition of sodium azide to nitriles in equimolar quantity. The reaction was catalyzed by porous materials H-Y and Al-MCM-41. Products were obtained in short time with moderate to excellent yield (up to 96%). The reusability and stability of catalyst made this protocol safe, eco-friendly and suitable for 1,3-dipolar cycloaddition.

**KEYWORDS :** Porous materials, zeolite H-Y, Al-MCM-41, 5-substitued-1H-Tetrazoles, Heterogeneous catalysis, Microwave irradiation.

### INTRODUCTION:

Nitrogen compounds containing tetrazole moiety are an important structural unit found in many scopes with interesting pharmaceutical<sup>i</sup>, agriculture<sup>ii</sup> and photographic activities<sup>iii</sup>.

Due to their broad applications, several methods were developed to access tetrazoles scaffold. Generally, 5-substitued -1H-tetrazoles are prepared by the addition of azides to nitriles<sup>iv</sup> conversion of amides<sup>v</sup>, aldehydes<sup>vi</sup>, acid chloride<sup>vii</sup>, amine<sup>viii</sup> and one-pot conversion of arylbromide<sup>ix</sup>.

Many sources in the literature describe different synthetic methods for accessing this class of molecules in the presence of homogeneous catalysts such as Pd/(OAc)<sub>2</sub> / ZnBr<sub>2</sub><sup>ix</sup>, Zn(OTF)<sub>2</sub><sup>x</sup>, AlCl<sub>3</sub><sup>xi</sup> and Pd(PPh<sub>3</sub>)<sub>4</sub><sup>xii</sup> and heterogeneous catalytic systems using zinc hydroxyapatite<sup>xiii</sup>, Cu<sub>2</sub>O<sup>xiv</sup>, CdCl<sub>2</sub><sup>xv</sup>, ZnS nanospheres<sup>xvi</sup>, zeolite encapsulated cobalt CoY<sup>xvii</sup>, phosphomolybdic acid<sup>xviii</sup>. Other metals in DMF for example scandium<sup>xix</sup>, bismuth<sup>xx</sup> and ZnClN<sub>3</sub><sup>xxi</sup> were reported.

The drawbacks of these metal-based catalysts are the large excess of sodium azide, high temperature, longer reaction time, and use of strong Lewis acids.

The development of catalytic synthetic methods for the tetrazoles still remains an active research area<sup>xxii</sup>.

Actually, the main challenge is to reduce environmental impact and keep efficiency of synthetic methods.

In the last decades, there has been a tremendous interest in various chemical transformations performed under the heterogeneous catalysis<sup>xxiii</sup>.

The porous materials such as zeolites and MCM present an interesting alternative to classical methods. Since the first utilization in 1960 for cracking reaction<sup>xxiv, xxv</sup>, zeolites found broad applications in water treatment<sup>xxvi</sup>, filtration, drying and environmental sciences<sup>xxvii</sup> due to their unique physical and chemical properties, such as regular pore shape tunable pore size and good thermal stability.

As catalyst, porous materials are low-waste compared to lewis-acids. The presence of acidic sites promotes synthesis reaction of cycloaddition<sup>xxviii</sup>, cumene<sup>xxix</sup> and recently caprolactam<sup>xxx</sup>. These advantages coupled with microwave heating increase energetic efficiency and rapidity of reaction.

In this work, various tetrazoles were prepared under microwave irradiation using micro and mesoporous materials as catalysts.

## **EXPERIMENTAL:**

### **REAGENTS:**

Sodium aluminate (50.38% Al<sub>2</sub>O<sub>3</sub>; 36.70% Na<sub>2</sub>O<sub>3</sub>; 13.63% H<sub>2</sub>O; Aldrich) was used as the aluminium source, Zeosil 175MP (84.96% SiO<sub>2</sub>; 0.31% Al<sub>2</sub>O<sub>3</sub>; 0.93% Na<sub>2</sub>O<sub>3</sub>; 13.78% H<sub>2</sub>O; Rhône Poulenc) as a silica source, Sodium hydroxide; Prolabo and the demineralised water was used as a solvent.

### **CATALYST PREPARATION:**

#### **GENERAL PROCEDURE FOR ZEOLITE Y SYNTHESIS STARTING MATERIALS:**

The Na-Y zeolite gel was prepared from an alkaline solution containing sodium hydroxide and sodium aluminate<sup>xxxi</sup>. After 1h stirring, the silica is added slowly. The reaction mixture thus formed was homogenized for 2h at room temperature and then the hydrogel formed was transferred into autoclave for the crystallization at 100 °C during 48 hours. The product was washed several times with demineralised water, filtered and dried at 60°C overnight. The molar composition of the initial gel is the following : 5Na<sub>2</sub>O ; 10SiO<sub>2</sub> ; Al<sub>2</sub>O<sub>3</sub> ; 160H<sub>2</sub>O.

#### **GENERAL PROCEDURE FOR AL-MCM-41 SYNTHESIS STARTING MATERIALS**

Sodium aluminate (54% Al<sub>2</sub>O<sub>3</sub> 36.70% Na<sub>2</sub>O<sub>3</sub> 13.63% H<sub>2</sub>O; Aldrich) was used as the aluminium source, (Tetraethylorthosilicate TEOS 98%, Alfa Aesar) as a silica source, cetyltrimethylammonium bromide (CTABr, Biochem) as a surfactant, tetramethylammonium hydroxide (TMAOH.5H<sub>2</sub>O, 98%, Alfa Aesar) was used as a base and the demineralised water was used as a solvent.

For the synthesis of the mesoporous Al-MCM-41<sup>xxxii</sup>, we chose the following molar composition of the starting gel: 1 SiO<sub>2</sub>; 0,25 CTAB; 0,2 TMAOH; 0,012 Al<sub>2</sub>O<sub>3</sub>; 40 H<sub>2</sub>O, and we prepared then three solutions : the first solution contains the CTABr as surfactant. The second solution contains the TEOS as source of silica and the third solution contains TMAOH, as source of aluminium.

After total dissolution of sodium aluminate in the TMAOH solution, the second solution was added in small amounts. After vigorous agitation, the reaction mixture was poured drip to drip into the CTABr solution. The reaction mixture thus formed was homogenized under stirring for 2h at room temperature and then was heated at 100°C for 48 h for crystallization. The solids obtained are filtered, washed several times in demineralised water, dried for 24 hours at 100°C and calcined at 550°C in air for 6h.

### GENERAL PROCEDURE FOR TETRAZOLES SYNTHESIS:

Catalyst (20 mg) was added to a mixture of benzonitrile (1mmol) and sodium azide (1,5mmol) in solvent (2 mL), irradiated in a microwave reactor. After completion of the reaction (as indicated by TLC), 10 mL of ethyl acetate was added, the catalyst was removed by filtration, and the filtrate was washed with distilled water. The organic layer was treated with 6N HCl (10 mL), the resultant organic layer was separated, and the aqueous layer was again extracted with ethyl acetate (10 mL). The combined organic layers were washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get the corresponding tetrazole.

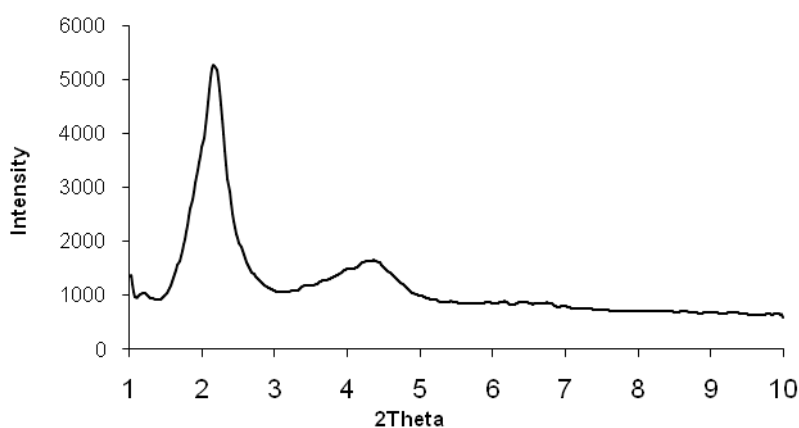
### RESULTS AND DISCUSSION:

#### CHARACTERIZATION OF THE CATALYSTS:

The materials were determined by X-ray diffraction (XRD) patterns using a Bruker AXS D8 diffractometer (Cu-K $\alpha$  radiation). N<sub>2</sub> gas sorption measurements were performed at -196 °C with a Micromeritics ASAP 2010 volumetric instrument. For the N<sub>2</sub> adsorption–desorption, the sample was degassed under vacuum at 80 °C over 24 hours prior to adsorption. The surface area was calculated by the Brunauer–Emmet–Teller (BET) method<sup>xxxiii</sup>. The surface morphology of the materials were observed by Hitachi S4500 microscope. The functional groups of the catalysts were analyzed by infrared spectroscopy FTIR in the range of 4000-360 cm<sup>-1</sup> using Bruker Alpha Platinum-ATR spectrometer.

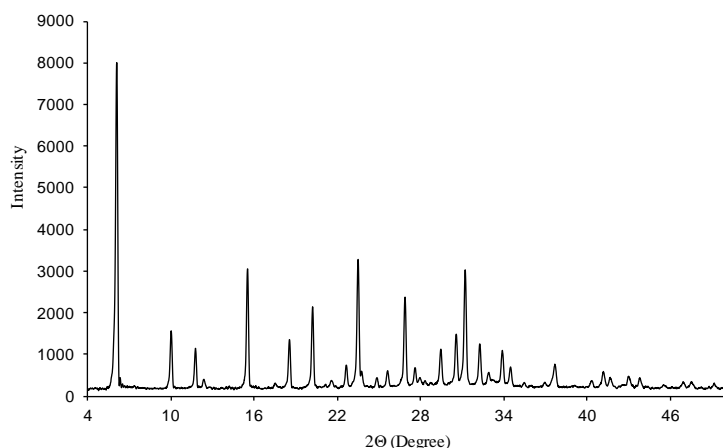
#### X-RAY DIFFRACTION ANALYSIS

The diffraction patterns of the synthesized Al-MCM-41 and zeolite Y catalysts are given in **Figure 1** and **Figure 2** respectively.



**Figure 1:** XRD pattern of synthesized Al-MCM-41

The main peaks of the XRD pattern is compatible with the characteristic peaks of the hexagonal structure of the mesoporous material MCM-41<sup>xxxiv, xxxv</sup>. The Al-MCM-41 material has a strong, widened peak, at 2theta = 2.04 due to (1 0 0) reflection. This suggests the more disordered arrangement of channels for the Al-MCM-41, while keeping a very regular hexagonal structure.

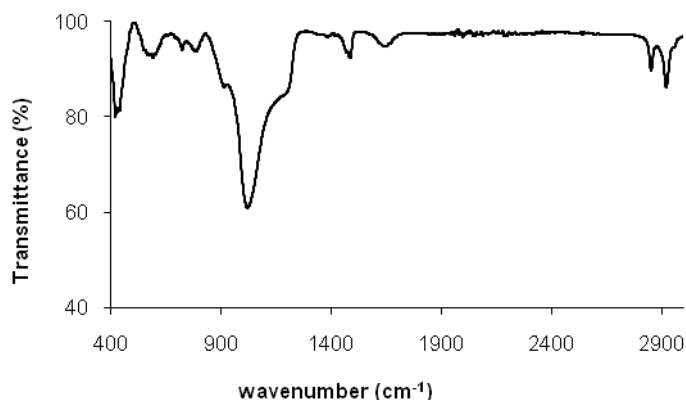


**Figure 2:** XRD pattern of synthesized Zeolite Y

All peaks observed can be assigned to Y zeolite structure characterized by  $2\theta$  of standard type equals to 6.3, 15.8 and 23.7 degree which corresponds to the reflections (1 1 1), (3 3 1) and (5 3 3) respectively. The X-ray diffractogram shown in **Figure 2** confirms that the resulting material is a pure Faujasite Na-Y Zeolite.

#### FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The Infra-Red spectra of the no calcined Al-MCM-41 catalyst (**Figure 3**) is consistent with that of the literature<sup>xxxvi, xxxvii</sup>.

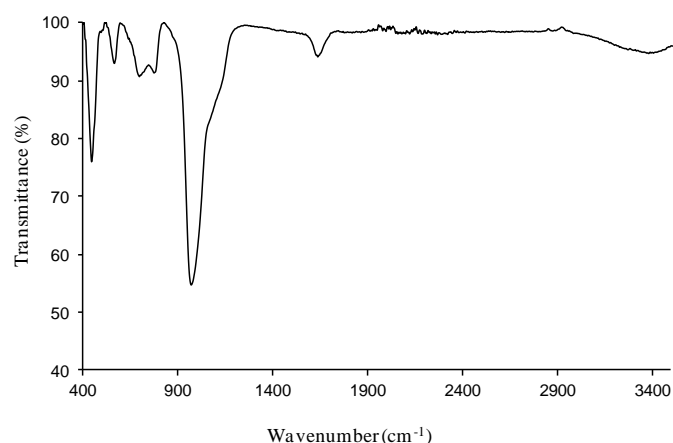


**Figure 3:** FT-IR spectra of no calcined Al-MCM-41 mesoporous materials

The symmetric stretching of the T-O-T groups (T is Al or Si) are observed around  $435\text{ cm}^{-1}$ . The peaks between  $1056$  and  $1206\text{ cm}^{-1}$  could be attributed to the asymmetric stretching of the (Si-O- and AlO-) groups.

A peak detected at  $1500\text{ cm}^{-1}$  is due to the presence of hydroxyl groups ( $\text{OH}^-$ ) at the surface. The peaks between  $2853$  and  $2928\text{ cm}^{-1}$  correspond to the symmetric and asymmetric stretching of  $\text{CH}_2$  of a template confined in Al-MCM-41.

The infrared spectrum of zeolite Y (**Figure 4**) shows that all of the infrared bands characteristic sensitive to the spectra are present. The bands in the range of  $950$ - $1250\text{ cm}^{-1}$  indicate the presence of Si-O, assigned to external asymmetrical stretching while the bands between  $500$ - $650\text{ cm}^{-1}$  are assigned to the internal tetrahedral symmetrical stretching. Absorption at approximately  $450\text{ cm}^{-1}$  was assigned to Si-O-Al stretching where Al is in the octahedral coordination.



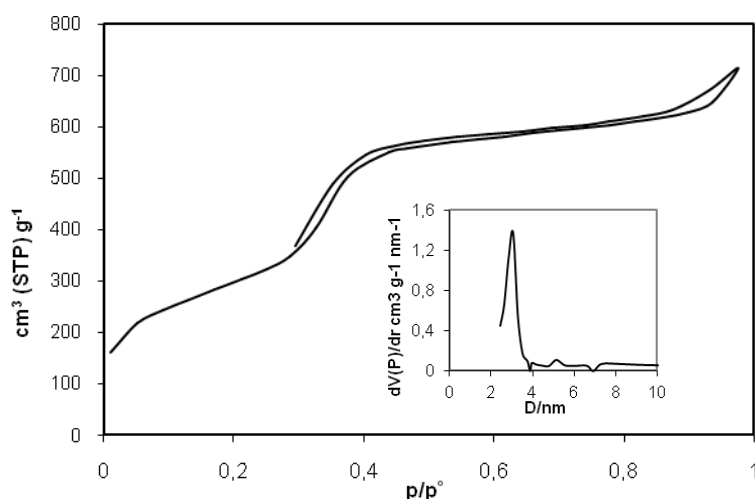
**Figure 4:** FTIR of Zeolite Y

### NITROGEN ADSORPTION ISOTHERM:

The Nitrogen adsorption-desorption isotherm and porous distribution of the calcined Al-MCM-41 is shown in **Figure 5**. This isotherm is of type IV, characteristic of the mesoporous materials according to the IUPAC classification<sup>xxxviii</sup>.

This isotherm is defined by three stages:

- A slow increase in volume adsorbed at low relative pressures ( $P/P_0 < 0,24$ ). indicates the formation of a single layer of nitrogen on the pores walls.
- A variation of the isotherm at intermediate relative pressures characterized by an inflection in the isotherm ( $0.24 < P/P_0 < 0.40$ ) corresponding to the phenomenon of capillary condensation in mesopores.
- A final stage with a low inclination towards high relative pressures ( $P/P_0 > 0.40$ ), which corresponds to the multilayer adsorption on the external surface.



**Figure 5:** Nitrogen adsorption–desorption isotherms of Al-MCM-41 mesoporous materials

The textural characteristics of the Al-MCM-41 catalyst are grouped in the **Table 1**:

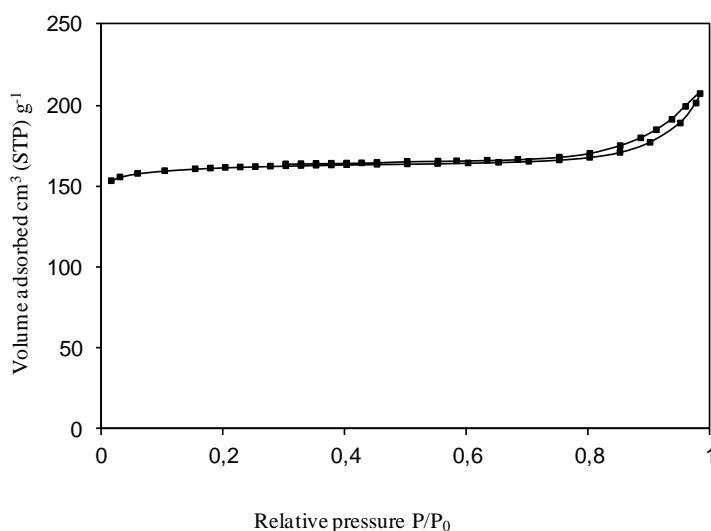
**Table 1 :** Textural characteristics of the Al-MCM-41.

	$S_{BET}(m^2/g)$	$S_{meso}(m^2/g)$	$S_{ext}(m^2/g)$	$V_{meso}(m^2/g)$	$D_p (\text{Å})$
Al-MCM-41	1014	694	519	0.80	36.6

$D_p$  : diameter of pores calculated by the BjH method.

The synthesized Al-MCMC-41 have surface area around  $700 m^2.g^{-1}$  higher than that of the zeolite Y . This results indicates that solid is an excellent mesoporous material.

The **Figure 6** shows the nitrogen sorption isotherm at 77K for the zeolite Y. According to the IUPAC classification nitrogen adsorption/desorption isotherms, the zeolite Y prepared, is type I which is characteristic of microporous materials.



**Figure 6:** Nitrogen adsorption-desorption isotherm of Zeolite Y

The zeolite Y is characterized by an almost horizontal range from very low  $P/P_0$  value to a  $P/P_0$  value near 1. The surface area, micropore volume and pore diameter are given in the **Table 2**.

**Table 2.** Textural characteristics of zeolite Y

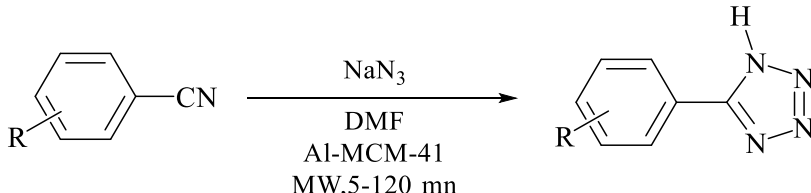
	$S_{BET}(m^2/g)$	$S_{ext}(m^2/g)$	$S_{micro}(m^2/g)$	$V_{ads}(cm^3/g)$
Zeolite Y	620.48	12.16	608.32	0.246

The synthesized zeolite Y have surface area around  $608 m^2.g^{-1}$ . The surface is similar compared to that pure commercial zeolite Y ( $604 m^2/g$ ).

## SYNTHESIS OF TETRAZOLES

We started our study with temperature optimization (**Table 3**). The reaction was performed with equimolar ratio of azide and benzonitrile (1mmol) at  $160C^\circ$  in DMF in the presence of 20 mg of catalyst. No product was detected even after 2 hours (**Table 3**, entry **1**) and only 35% yield of product was obtained at  $170C^\circ$  after 75 min (**Table 3**, entry **3**).

The yield increased between  $180C^\circ$  and  $190C^\circ$ . The best yield was obtained at  $190C^\circ$  after 17 min (**Table 3**, entry **10**). We then optimized catalyst quantity and the ratio catalyst (20mg)-benzonitrile (1mmol) showed the best efficiency.

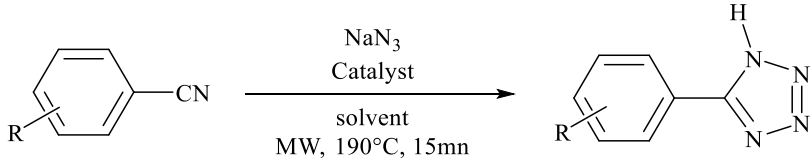
**Table 3:** Optimization of reaction parameters (temperature and time) <sup>a</sup>


Entry	Temperature (C°)	Time (min)	Yield (%)
1	160	120	-
2	170	45	-
3	170	75	35
4	170	90	40
5	180	75	42
6	185	30	60
7	190	5	-
8	190	8	-
9	190	15	68
10	190	17	85

<sup>a</sup>Reaction conditions: benzonitrile (1mmol), NaN<sub>3</sub> (1mmol), Al-MCM-41 (20mg), solvent (2mL), microwave irradiation (850W) at 190°C.

Solvent effect was explored and comparison with H<sup>+</sup> exchanged zeolite H-Y was made (**Table 4**).

The best yields were obtained with DMF (78% for Al-MCM-41, and 95% for H-Y) (**Table 4**, entries **1-2**), DMSO is less efficient (**Table 4**, entries **3-4**) and no product was observed with Al-MCM-41 in water because degradation of catalyst at high temperature (**Table 4**, entry **5**).

**Table 4:** Effect of catalysts and solvents on the formation of 5-Phenyl-1H-phenyl tetrazole <sup>a</sup>


Entry	Solvent	Catalyst	Yield (%)
1	DMF	Al-MCM-41	78
2	DMF	H-Y	95
3	DMSO	Al-MCM-41	40
4	DMSO	H-Y	55
5	H <sub>2</sub> O	Al-MCM-41	-
6	H <sub>2</sub> O	H-Y	61

<sup>a</sup> Reaction conditions: benzonitrile (1mmol), NaN<sub>3</sub> (1mmol), cat (20mg), solvent (2mL), microwave irradiation (850W) at 190°C, reaction time (15 min).

At the end of the reaction, the catalyst is recovered by simple filtration. This material can be used again for several times : the catalyst is not consumed during the reaction, it is therefore a heterogeneous catalysis.

In order to understand the role of the material, we must look at the size of their pores. Because the aromatic nitrile is too large to fit into the pores of the material, so the reaction takes place

on the surface. We can assume that the aluminum atoms located on the surface act as Lewis acids for the formation of tetrazole.

### RECYCLING:

A test of catalyst regeneration was carried out. The catalyst remains efficient for 4 cycles although a slight decrease of yield observed (95 to 90%). (Fig.7).

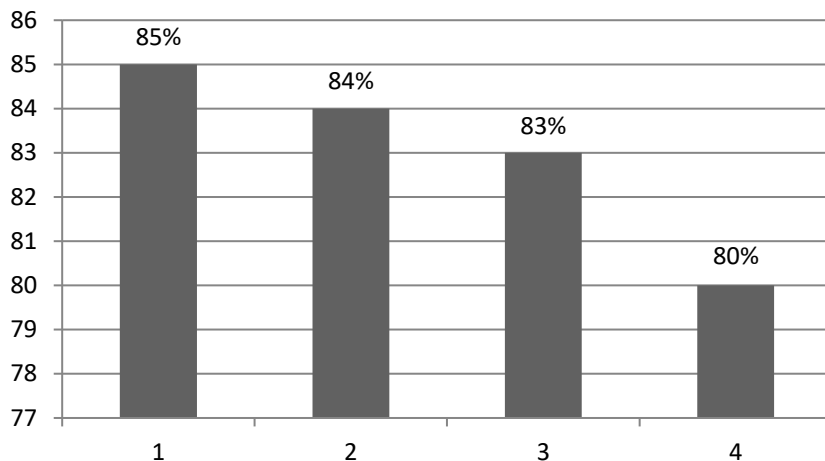


Fig.7: Reusability of catalyst

After optimization, various aromatic and heteroaromatic nitriles were tested (Table 5). Reactions were monitored by IR and time was extended until whole conversion of nitrile. Both of nitriles containing electron withdrawing and electro-donating gave desired product in good yield. It is worthy noted that reaction of terephthalonitrile with sodium azide takes place in only one position (Table 5, entry 7).

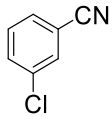
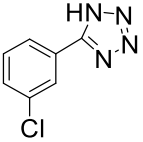
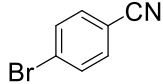
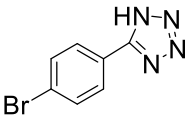
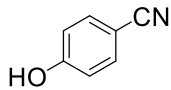
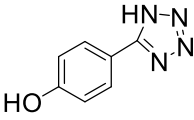
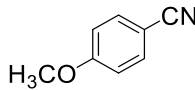
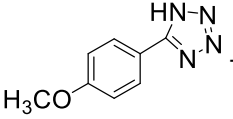
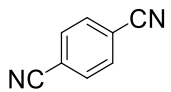
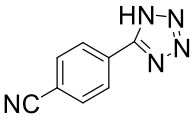
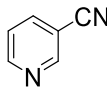
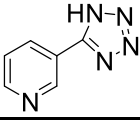
The 3-cyanopyridine did not give product with Al-MCM-41 as catalyst but 96% yield of product was obtained with H-Y zeolite. The adduct formed by endocyclic nitrogen and catalyst restrains the nitrile and promotes reaction (Table 5, entry 8).

In contrast of pyridine, chlorobenzonitrile and 4-bromobenzonitrile showed less reactivity in the presence of H-Y zeolite than Al-MCM-41 (Table 5, entries 3-4).

Table 5: Preparation of 5-Substituted 1H-tetrazoles. <sup>a</sup>

Entry	Substrate	Product	Yield (%)		Time (min)
			Al-MCM-41	H-Y	
1			78	95	15
2			90	-	30



3			84	44	35
4			88	40	35
5			-	95	22
6			-	90	25
7			86	-	35
8			-	96	28

<sup>a</sup> Reaction conditions: benzonitrile (1mmol), NaN<sub>3</sub> (1mmol), cat (20mg), DMF (2mL), microwave irradiation (850W) at 190°C.

The IR spectra of synthesized compounds showed a sharp absorption at 3421 cm<sup>-1</sup> (N-H) and group of bands at 1455 cm<sup>-1</sup> (C-H), 1285 cm<sup>-1</sup> (N-N=N-), 1208, 1120 and 1048cm<sup>-1</sup> caused by the presence of secondary amine group and tetrazole ring and absence of band at 2200 cm<sup>-1</sup> due to CN group.

## CONCLUSION

In summary, the results demonstrate efficiency of micro and mesoporous heterogeneous catalysts in 5-substituted 1H-tetrazoles from nitriles under microwave irradiation. The protocol was simple, energy-efficient and eco-friendly. The catalyst was easy to prepare, stable, easily recoverable and reusable four times. This method allowed to prevent waste generation and perform reaction as efficient as previous methods described.

## ACKNOWLEDGEMENTS

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**CONFLICT TO INTEREST:**The authors declare that there is no conflict of interest.

## ANALYTICAL DATA FOR COMPOUNDS:

Spectra of the final products were recorded on a Brüker Avance-300 spectrometer for NMR (300 MHz and 75 MHz for <sup>1</sup>H and <sup>13</sup>C respectively) in CDCl<sub>3</sub>. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Coupling constants (*J*) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet).

## SPECTRAL DATA

**5-phenyl-1H-Tetrazole** (Table 5, Entry 1):

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) ppm : 7.5-8.05 (m, 5H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): 124.6, 127.4, 129.8, 131.7, 155.8; **FT-IR (cm<sup>-1</sup>):** 3129, 3053, 2979, 2832, 2685.59, 1607.88, 1464, 1287.66, 1162.67, 1055, 788

**5-(4-methyl)-1H-tetrazole** (Table 5, Entry 2):

<sup>1</sup>H NMR (300 MHz, DMSO) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 2.39 (s, 3H); **FT-IR (cm<sup>-1</sup>):** 3044, 2976, 2850, 2767, 1651, 1455, 1215, 1124, 1051, 944, 740

**3-chlorophenyl 1H-tetrazole** (Table 5, Entry 3):

<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.03 (s, 1H), 8.00 – 7.95 (m, 1H), 7.60 (dd, *J* = 6.6, 3.4 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 154.86, 134.08, 131.42, 131.02, 126.61, 126.37, 125.64; **FTIR cm<sup>-1</sup>** 3436, 3068, 2971, 2855, 1653, 1439, 1262, 1122, 1024, 914, 889, 772

**5-(4-bromophenyl)-1H-tetrazole** (Table 5, Entry 4):

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.58, 133.90, 133.50, 132.75, 128.14; **FT-IR (cm<sup>-1</sup>):** 3084, 2964, 2849, 2672, 1654, 1434, 1254, 1117, 1024, 983, 827, 743

**4-(1-tetrazol-5-yl) phenol** (Table 5, Entry 5):

<sup>1</sup>H NMR (400 MHz, DMSO) δ 13.01 (s, 1H), 8.38 (s, 1H), 7.93 – 7.78 (m, 2H), 6.91 – 6.81 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 172.13, 161.12, 134.11, 128.11, 118.38; **FT-IR (cm<sup>-1</sup>):** 3386, 3055, 2918, 2848, 1669, 1443, 1246, 1137, 1034, 875, 746.

**5-(4-methoxyphenyl)-1H-tetrazole** (Table 5, Entry 6):

<sup>1</sup>H NMR (400 MHz, DMSO) δ 7.84 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 167.42, 161.57, 129.34, 126.50, 113.37, 55.31.

**4-(1H-tetrazole-5yl) benzonitrile** (Table 5, Entry 7) :

<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.21 (d, *J* = 8.3 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.95 (s, 1H); <sup>13</sup>C NMR (4 MHz, DMSO) δ 162.77, 134.08 – 133.88, 129.31, 127.96, 113.96.

**5-(4-pyridyl) tetrazole** (Table 5, Entry 8):

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.80 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.09 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.40, 132.98, 129.88, 127.92, 118.26, 114.35.

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