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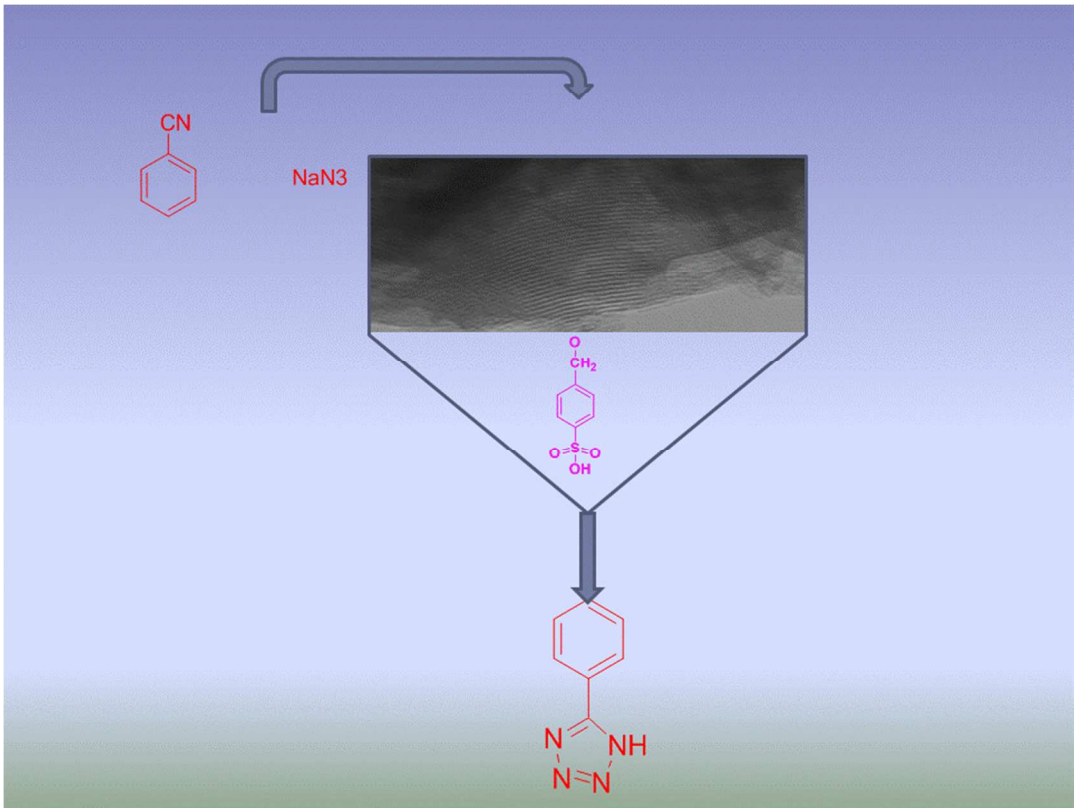
High ordered MCM-41 synthesized and functionalized with benzylic groups. The solid was used in the synthesis of aryl tetrazoles.



Application of functionalized mesoporous silica catalyst for the synthesis of tetrazoles

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Abstract: In the present study, well ordered **MCM**-41 was synthesized and functionalized with **B**enzyl group and subsequently **S**ulfonated using chlorosulfonic **A**cid (**MCMBSA**). The functionalized catalyst (**MCMBSA**) was characterized by XRD, TGA, FTIR, TEM, BET and SEM techniques. The 5-aryl-1*H*-tetrazoles was synthesised by the reaction of corresponding aryl nitriles and sodium azide catalized by **MCMBSA**. The mole ratio of nitrile to sodium azide, the amount of catalyst, reaction times, and solvent type were optimized. It was found that **MCMBSA** catalyst is more effective than that catalyst which obtained from direct sulfonation of MCM-41. The versatility of method was investigated by using various nitriles, which showed reasonable yield of tetrazoles formation. The regeneration and reusability of catalyst was examined.

Keywords: Sulfonated MCM-41, Tetrazole derivatives, Synthesis, Characterization.

1. Introduction

Tetrazoles are heterocyclic compounds with four nitrogen atoms which are explored extensively due to their wide range of biological and industrial applications [1]. Tetrazoles have been widely used as carboxylic acid isosteric pharmacophore in pharmaceutical chemistry. They have been turn out to be potential TNF alpha inhibitors, P2X7-antagonists [2], and inhibitors of anandamide cellular uptake [3]. Tetrazoles are screened for various biological activities such as antiulcer [4], anticonvulsant [5], antiviral, antibacterial, antifungal, anti-inflammatory [6], antiallergic [7], and antitubercular activities [8]. They have also significant roles in coordination chemistry as a ligand for preparation of complex heterocyclic structures [9]. In addition, tetrazoles have been applied in numerous material sciences and synthetic organic chemistry as analytical reagents [10, 11]. On the other hands, tetrazoles are also particularly interesting molecules with applications as precursor of new classes of propellants and explosives [12, 13]. Available methods for the synthesis of tetrazole ring include addition of sodium nitrite to aminoguanidines [14], addition of sodium azide to carbodiimides [15], reactions of amines with a leaving group in the tetrazole's 5-position [16], and three component reaction of primary amines with sodium azide and triethyl orthoformate [17] have been reported. On the other hands, many methods for the synthesis of 5-substituted tetrazoles proposed based on [3+2] cycloaddition of azide ion to corresponding organic nitriles. The reactions were carried out by using numerous homogenous catalysts such as $ZnBr_2$, [18] BF_3-OEt_2, [19], $Zn(OTf)_2$ [20], $Fe(OAc)_2$ [21], $AlCl_3$ [22], $Cu_2(OTf)_2$ [23], $AgNO_3$ [24], and by using some heterogeneous catalysts such as Cu_2O, [25] COY zeolites [26], Zn/Al hydrotalcite [27], Montmorrilonite [28] and modified Montmorrilonite clays [29], sulfated zirconia [30], AlPO-5 microporous molecular sieves [31], and mesoporous ZnS nanospheres [32].

Mesoporous materials such as MCM-41 and SBA-15 due to their excellent properties such as high surface area, regular pore shape, large pore volume, narrow pore size distribution, tunable pore size and good thermal stability, has been utilized for several applications such as an adsorbent of metal cations, support of various catalysts, environmental science, sensors, and etc. [33-36]. Because of the low acidity of MCM-41 in compare to mineral acids, its modification reported as a good solution [37-40]. In this paper, we report a new process for the synthesis of 5-substituted 1*H*-tetrazoles using modified MCM-41 *via* [3+2] cycloaddition from nitriles and sodium azide.

2. Experimental

2.1. Chemicals and instruments

Tetraethyl orthosilicate (TEOS, > 98%), and Cetylterimethylammonium Bromide (CTAB, >99%) purchased from Dae-Jung, S. Korea. All nitriles and solvents purchased from Merck and sodium azide were purchased from Sigma–Aldrich Chemicals. Double-distilled water was used for the preparation of all aqueous solutions. All Chemicals were used as-received. A JASCO FT/IR-680 PLUS spectrometer was used to record IR spectra using KBr pellets. NMR spectra were recorded on a Bruker 400 Ultrasheild NMR, and DMSO-d_6 was used as a solvent. Melting points reported were determined by open capillary method using a Galen Kamp melting point apparatus and are uncorrected. Progress of reactions monitored with a Hewlett Packard 1090 HPLC using a C18 analytical column (eluting with methanol:water 30:70 as mobile phase). Small-angle X-ray diffraction (XRD) patterns were recorded with a Brucker D8 Advance diffractometer using Co radiation, Kα, (40 kV and 40 mA). The surface topography of the

catalysts was evaluated using SEM analysis on a Philips XI30 microscope and TEM was performed on a Philips CN120 device. Thermogravimetric analysis (STA 503) was carried out under nitrogen atmosphere in the temperature range 25-800 ˚C with a heating rate of 10˚C/min. The nitrogen adsorption-desorption isotherm of the sample was carried out by using a Quantachrome Auto sorb IQ MP device.

2.2. Preparation of modified MCM-41 with sulfonic acid

The MCM-41 hollow tubular material was prepared based to the published procedure with slightly modification [41]. In order to synthesize MCM-41, the amount of 2.4 g cetyltrimethylammonium bromide (CTAB) surfactant was added to 120 g of deionized water and stirred for an hour until a clear solution was obtained. In the next stage, 10 mL of ammonia is added to the solution and stirring was continued for 5 minutes. Then, 10 ml of tetraethyl orthosilicate was added to the solution and the mixture kept for 24 h at room temperature under stirring. After that, the resulting white gel was transferred to a teflon lining steel reactor and heated for 48 hours in the oven at 70 ˚C. The reactor was removed from the oven and brought to room temperature, and the product was filtered and washed with water and ethanol. Finally, to remove the organic template by calcination the sample was heated in an electric furnace at 550 ˚C for 8 h. For benzyl grafting of MCM-41 material, 1 g of MCM-41 was added to benzyl alcohol solution (5 mL) in toluene (20 mL) and resulting mixture kept for 12 hours under reflux conditions. After filtration, washing and drying the sample, the white solid, was sulfonated with chlorosulfonic acid in dry chloroform (20 mL) under reflux condition for 4 hours. Then, the mixture is filtered and washed.

2.3. Synthesis of Tetrazoles

The procedure for the synthesis of the 5-phenyl-1*H*-tetrazole, **1a,** is a representative one. In a round-bottom flask, benzonitrile (0.2 g, 2 mmol), sodium azide (0.4 g, 6 mmol), modified MCM-41 (5 mg), and DMF (10 mL) were charged and reaction mixture was heated at 100 ºC. The progress of reaction was followed by HPLC. After completion of the reaction, the reaction was cooled to room temperature and insoluble material was filtered and washed several times with doubly distilled water and acetone to separate the catalyst. The solution was acidified with HCl (2 mL, 12 M). The precipitate was collected, dried, and recrystallized from water/ethanol to obtain pure 5-phenyltetrazole as a white powder, yield: 85%.

3. Results and discussion

3.1 Preparation and characterization of catalysts

Highly ordered MCM-41 was prepared according to the method of Kumar *et al*. [42] with slight modification. For benzyl anchoring, benzyl alcohol and activated MCM-41 kept under reflux condition for 12 h in toluene. The functionalized MCM-41 then sulfonated with chlorosulfonic acid as sulfonating agent to obtain (**MCMBSA**).

Please insert Scheme 1

To obtain solid acid catalysts with different acidity, values of $ClSO_3H$:MCM-41 ratio changed. In addition, for comparison of effect of aryl group on reactivity of sulfonyl group, three samples were prepared by direct addition $ClSO_3H$ to MCM-41 (**MCMSA**). (Scheme 1).

Please insert Figure 1 here

Preparation of MCM-41-SO_3H catalysts was monitored using FT-IR spectroscopy via the KBr salt dilution technique. Fig. 1 shows the FT-IR spectra of synthesized MCM-41 (a), benzylated MCM-41 (b), MCM-41 after direct sulfonation with chlorosulfonic acid (**MCMSA** catalyst) (c), benzylated MCM-41 catalyst after sulfonation (**MCMBSA**) (d), and recycled **MCMSBA** catalyst. In the case of **MCMSA** catalyst, (Fig. 1c and 1d), the sulfonic acid bonds can be observed at ~1200–1250, 1010–1100 and 650 cm^{-1}, which are attributed to the O=S=O asymmetric and symmetric stretching modes and S=O stretching vibration mode of the sulfonic groups, respectively [42].

Please insert Figure 2 here

However, in the FT-IR spectra of sulfonated nanoparticles, such bands could not be observed because they are probably overlapped by the bands of SiO_2. In addition, as can be seen from Fig. 1c, the bands at 3000–3500 cm^{-1} confirm that existence of OH groups on the mesoporous material surface after the sulfonation. Incorporation of sulfonic acid to the aromatic ring was confirmed by observation of CS stretching band at 729 cm^{-1} that presented in Fig. 2.

Please insert Figure 3 here

Fig. 3 shows the TEM and SEM images for the synthesized catalyst. It shows clearly the hexagonal pore arrangement of the synthesized MCM-41 (Fig. 3a). After entering the sulfonic groups, the hexagonal structure still retained (Fig. 3b), which indicated that the present preparation method had little effect on the uniform structure of MCM-41. In addition the Fig. 3c shows the SEM of **MCMBSA** catalyst after sulfonation. The SEM photograph shows that prepared catalysts are still in the tubular morphology.

Please Insert Figure 4 here

The X-ray difraction (XRD) pattern (Fig. 4) illustrates the typical low angle (100), (110), and (200) reflections that are related to a well-ordered MCM-41- type molecular sieve. With application of brag equation, the unit cell parameters for the MCM-41 and MCMBSA catalyst obtained 4.1 and 3.77 nm, respectively. The values indicate the unit cell parameters slightly decreased after sulfonation. With sulfonation modification, the signals shifted toward higher diffraction angles that this shift can be explained by a slight decrease in the pore size resulting from the insertion of sulfonic acid groups into the MCM-41 pores [43].

Moreover, less intense and broadened diffraction peaks were also observed for the SO_3H-MCM-41 solid acid catalyst, showing that the structural integrity in MCM-41 was slightly degraded after modification. Fig. 5 shows the representative N_2 adsorption–desorption isotherms of hollow tubular pure MCM-41 and MCMBSA catalyst. All solids exhibited type IV isotherms

with H1 hysteresis loops. Upon functionalization of the parent material with chlorosulfonic acid, changes in the N_2 sorption isotherm curves and consequently decreases in the gas uptake were observed. Therefore the BET surface area decreased from 1056 to 496 and 330 g/m^2 for the MCMBSA and MCMSA catalysts, respectively. This could be attributed to the attachment and occupation of sulfonic groups onto the surface of the inner pores.

Please insert Fig. 5 here

The calcined **MCMBSA** and **MCMSA** catalysts were run on a TGA system for knowing the existence of sulfonyl groups. The results presented in supplementary section (Fig. S1). A one-step weight loss at ~120 °C was observed for both catalysts which are due to water desorption. For the **MCMBSA** catalyst, two weight loss stages were observed at ~150-200 and ~520°C. (See Fig. S2 in SI). Based on TGA analysis a 32% total organic content assigned to **MCMBSA** catalyst. In addition, for more clarification, an inverse acid-base titration of the catalyst achieved and acid content found to be 6.5 mmol/100g of **MCMBSA** solid acid catalyst.

3.2 Catalytic Tests

To optimize the reaction conditions and to explore the catalytic activity of sulfonated MCM-41 catalysts, benzonitrile (**1a**) and sodium azide were used as test substrates to obtain 5-phenyl-1*H*-tetrazole (**1b**). It was confirmed by the results tabulated in Table 1 that no reaction was observed without the catalyst, despite prolonged reaction times, when the reaction is carried out without catalyst (Table 1, entry 1). In addition, when pristine MCM-41 was used as the catalyst, the

reaction progress was less than 10%. These results indicate that the catalyst exhibits a high catalytic activity in this transformation. In the first stage and in the reaction between benzonitrile **1a** and sodium azide (Scheme 2), the effect of the catalyst amount was investigated.

The percentage yield of the product was 75, 85 and 78 % using 2, 5 and 10 mg of catalyst, in the DMF as the solvent, respectively. (Table 1 entries 4, 9, and 10). It is evident that a low loading of catalyst still effective, although the reactivity was decreased consequently. We used high performance liquid chromatography as a powerful tool to probe the reaction progress in all runs. For example, chromatogram of reaction for conversion of compound **1a** to **1b** after 2 and 6h is presented in Figure S3 in supplementary section.

Please insert scheme 2 here

In addition, the sodium azide:benzonitrile ratio is an important factor. With application of 1:1, 3:1 and 5:1 ratios, the yields of tetrazole formation was 30, 85 and 80 % after 22, 8 and 10 hour, respectively. (Table 1, entries 6, 8, 11). The effect of different sulfonic acid loading (0.2, 0.4 and 0.6 ml chlorosulfonic acid) on MCM-41 surface was examined (Table 1, entries 3-5). The increase of acid loading from 0.2 to 0.6 ml, the reaction time was decreased from 22 to 10 h, respectively. The effect of temperature also was investigated and an increase in temperature from 80 to 110 ºC accelerates the reaction time (Table 1 entries 8, 13 and 4). The effect of aryl group anchored to silica surface may be interesting. As we mentioned in previous section with direct sulfonation of MCM-41, **MCMSA** catalysts obtained and used in conversion of benzonitrile to 5-phenyl-1*H*-tetrazole. As you can see, direct sulfonation of MCM-41 decreased the reaction rate.

The solvent has a prominent influence on the reaction times (Table 2). We also examined reaction in different solvents, but the yields of the desired products were inferior (Table 2, entries 1-6). Among the different solvents were examined, DMF gave the product in good yield at 100 ºC and 8 h. In addition, DMSO was effective at similar conditions but protic solvents such as 1-propanol and non-polar solvents such as toluene gave low product yields. It was observed that, application of 5 mg **MCMBSA** catalyst in solution of benzonitrile and sodium azide in DMF at 100 ºC is the optimized condition for conversion of aryl nitriles to the corresponding 5-substituted-1*H*-tetrazoles.

Please insert Table 1 here

To generalize the scope and versatility of this method, different aryl nitriles are used for the synthesis of these products and results tabulated in Table 3. The results indicate heteroaromatic nitriles such as 2, and 3-pyridinecarbonitriles and 2-thiophenecarbonitrile give the corresponding tetrazoles with good yields (Table 3 entries 3, 4, 7). In addition, aryl nitrile with electron donating groups gives lower yields. However, it is notable that the yields in Table 3 are reported after recrystalization. Since the solubility of tetazoles with functional groups such as COOH and COH increase in water, the overall yields slightly decreased.

Please insert Table 2 here

One of the most important advantages of heterogeneous catalysis is the recovery and reusability of the catalysts by simple filtration. In the present study, the reusability of MCMBSA catalyst

was investigated in the tetrazole formation reaction with benzonitrile under optimized condition. After completion of the reaction, the catalyst was separated by simple centrifugation, washed with 5 mL acetone, then with doubly distilled water, and dried at 80 ºC. The results of FT-IR analysis show sulfonic acid bonds can be observed in the recovered catalyst (Fig. 1d). The recovered catalyst was used in the next runs. The results of three successive runs showed that the catalyst can be reused several times without significant loss of activity (see Table 3). Partial loss of the catalyst activity is probably due to breaking of O-S bonds and copper leaching of sulfonic acid groups.

Please insert Table 3 here

In order to evaluate the efficiency of this protocol, activity of the various reagents was compared in the synthesis of 5-phenyl-1*H*- tetrazole (Table 3). In addition, the results of tetrazole synthesis with application of **MCMSA** catalyst are presented in Table S1 in supplementary section.

Please Insert Table 4 here

As shown in Table 5, phenyl tetrazole was produced in 8 h when our catalyst was used, whereas nano-ZnO and $ZnBr_2$ were used as catalyst, more reaction time was needed for reaction to complete. In addition, with application of Sb_2O_3 or $FeCl_3$ as the catalyst, the higher temperatures needed for completion of reaction.

Please Insert Table 5 here

To account for the formation of tetrazole derivatives, the following mechanism proposed (Scheme 3). In the first stage, the aryl nitrile is activated by proton of sulfonic acid group. This activated fragment after attack by azide ion subsequently cyclisize to tetrazole ring.

Please insert Scheme 3 here

4. Conclusion

In summary, we report MCM-41 grafted with sulfonic acid groups is an effective heterogeneous catalyst for the one-pot synthesis of 5-substituted 1*H*-tetrazoles in various substituted nitriles and sodium azide in DMF in good to excellent yields. The results show that application a benzonitril:sodium azide 1:3 ratio and 5 mg **MCMBSA** catalyst has the best reaction condition to formation of tetrazole derivatives. Effect of solvent was studied and the best results observed for aprotic polar solvents such as DMF. The reusability of catalyst was examined and the results of three successive runs show that the catalyst can be reused without significant loss of its activity. The easy work-up, lower catalyst loading, mild reaction conditions, clean reaction profiles, and cost efficiency render this approach as an interesting alternative to the existing methods.

Acknowledgement

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Table captions in sequence

Table 1
Initial screening of reaction parameters for the formation of 5-1H-phenyl tetrazole in DMF as the solvent

Entry	Catalyst	Solvent	Catalyst amount (mg)	Benzonitrile/ Sodium azide	T ºC	Time (h)	Yield (%)
1	-	DMF	-	1:5	100	24	-
2	MCM-41	DMF	5	1:3	100	24	10>
3	MCMBSA-0.2	DMF	2	1:3	100	20	68
4	MCMBSA-0.4	DMF	2	1:3	100	12	75
5	MCMBSA-0.6	DMF	2	1:3	100	10	80
6	MCMBSA-0.4	DMF	5	1:1	100	22	30
7	MCMBSA-0.4	DMF	10	1:1	100	20	35
8	MCMBSA-0.4	DMF	5	1:3	100	8	85
9	MCMBSA-0.4	DMF	10	1:3	100	8	78
10	MCMBSA-0.4	DMF	2	1:5	100	14	70
11	MCMBSA-0.4	DMF	5	1:5	100	10	80
12	MCMBSA-0.4	DMF	10	1:5	100	8	75
13	MCMBSA-0.4	DMF	5	1:3	80	14	70
14	MCMBSA-0.4	DMF	5	1:3	110	8	90
15	MCMSA-0.2	DMF	2	1:3	100	22	60
16	MCMSA-0.4	DMF	2	1:3	100	14	70
17	MCMSA-0.6	DMF	2	1:3	100	12	77
18	MCMSA-0.4	DMF	5	1:3	100	10	83

Table 2
The effect of different solvents on reaction times of tetrazole formation

Entry	Solvent	T ºC	Ph-CN : NaN_3	Catalyst (mg)	Time (h)
1	DMF	100	3 : 1	5	8
2	H_2O [a]	100	3 : 1	5	12

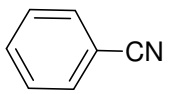
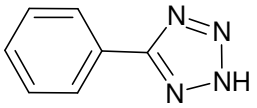
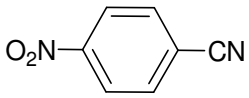
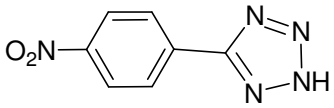
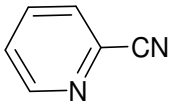
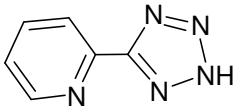
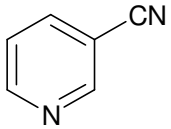
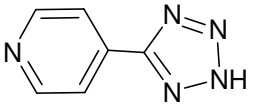
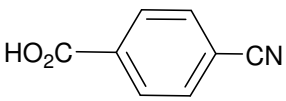
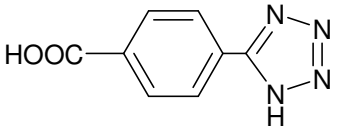
3	DMSO	100	3 : 1	5	10
4	NMP	100	3 : 1	5	12
5	n-Propanol	100	3 : 1	5	16
6	Toluen	100	3 : 1	5	-

[a] few droplets of DMF was added

Table 3
Reusability of MCMBSA catalyst in the model reaction under optimized condition

	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Time (h)	8	8	8	8
Yield (%)	85	81	77	70

Table 4
Preparation of tetrazole derivatives under optimized condition using **MCMBSA** catalyst

entry	Reactant	Product	Time (h)	Yield (%)	Mp (°C)
1			8	85	218-216
2			12	80	220-218
3			10	73	211-209
4			12	75	239-237
5			12	70	251-249

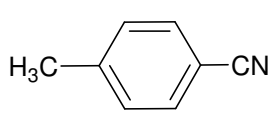
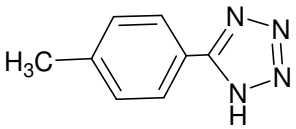
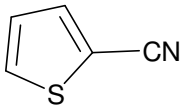
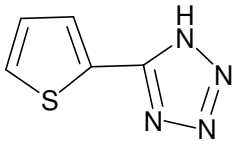
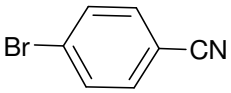
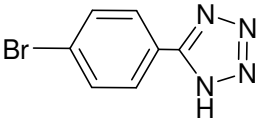
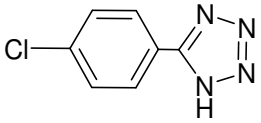
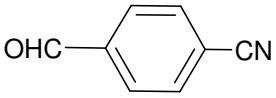
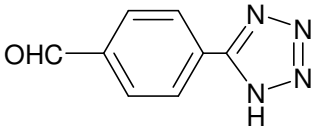
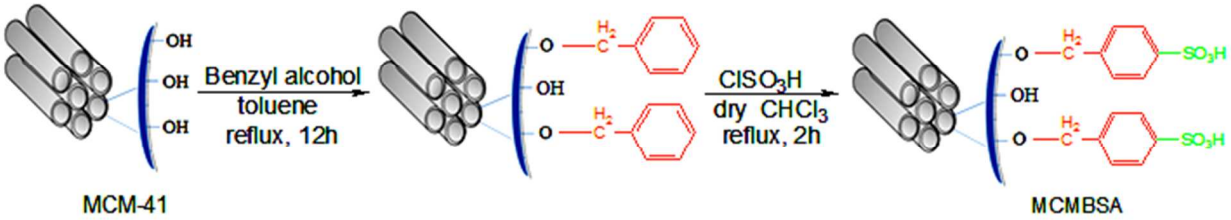
6			14	80	254-252
7			8	90	204-202
8			12	82	269-267
9			12	78	264-262
10			12	77	184-182

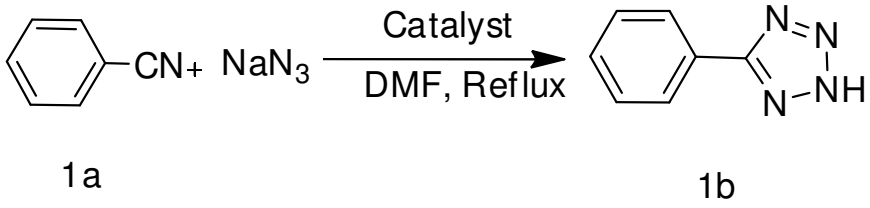
Table 5
Comparison of protocols for the synthesis of 5-phenyl-1*H*-tetrazole

Entry	Catalyst	Time (h)	Temperature (°C)	Yield (%)	Reference
1	$ZnBr_2$	24	100	76	44
2	Silica sulfuric acid	5	refluxing temperature at DMF	88	45
3	$AgNO_3$	5	120	83	46
4	Nano ZnO	14	120	72	47
5	$Fe(OAc)_2$, TMS-N_3	24	80	56	22
6	TMSN3-TBAF	18	85	86	48
7	$CdCl_2$	6	80	91	49
8	Sb_2O_3	8	120	86	50
9	$FeCl_3$-SiO_2	12	120	79	51
10	Zn/Al hydrotalcite	12	120	84	26
11	MCMBSA	8	100	85	This work

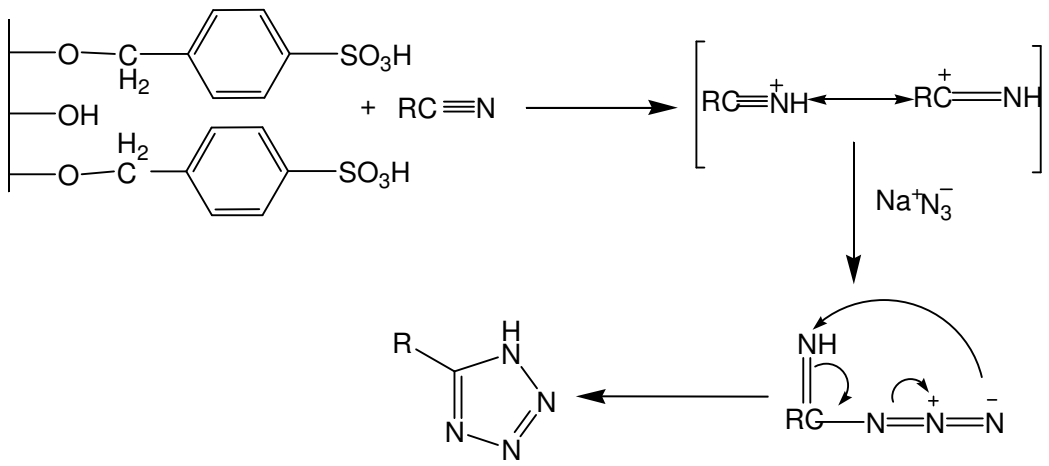
Captions of figures and schemes



Scheme 1. Schematic illustration of the catalyst preparation



Scheme 2 The synthesis of 5-substituted 1H-tetrazoles from nitriles and sodium azide catalyzed by **MCMBSA**



Scheme 3 A plausible mechanism for the conversion of aryl nitriles to tetrazole derivatives

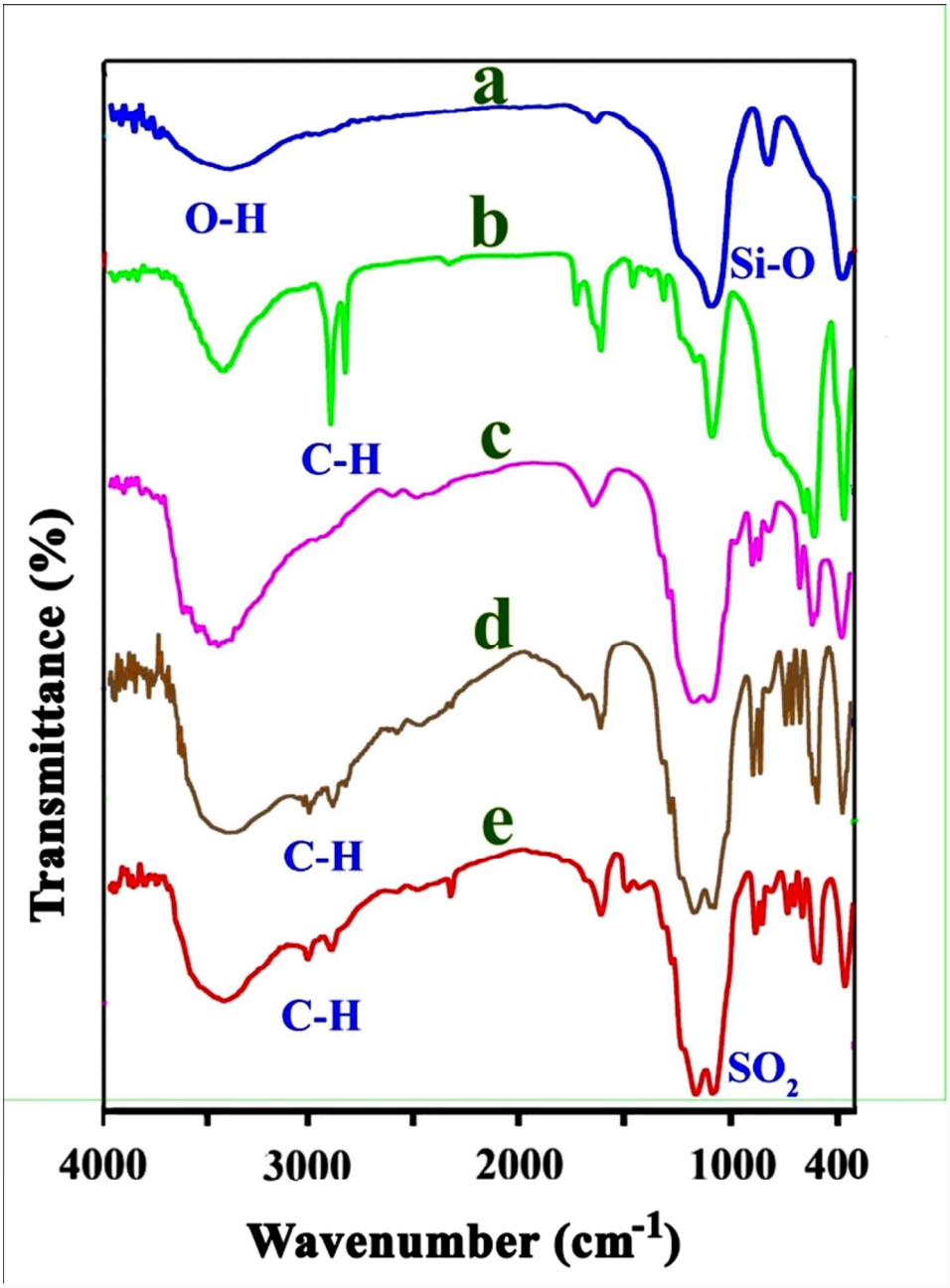


Figure 1 FT-IR spectra of MCM-41-SO_3H (a) pristine MCM-41, (b) MCM-41 after benzylation (c) MCM-41 after direct sulfonation with $ClSO_3H$ (**MCMSA** catalyst), (d) benzylated MCM-41 after sulfonation (**MCMBSA** catalyst), (e) MCMBSA catalyst after recycling.

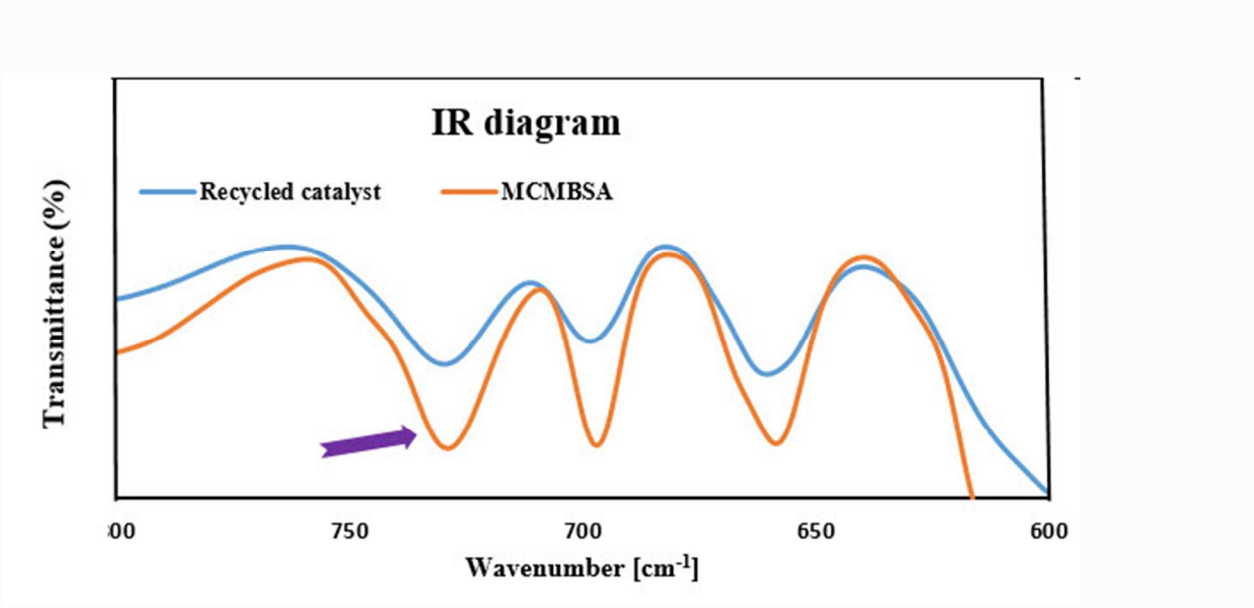
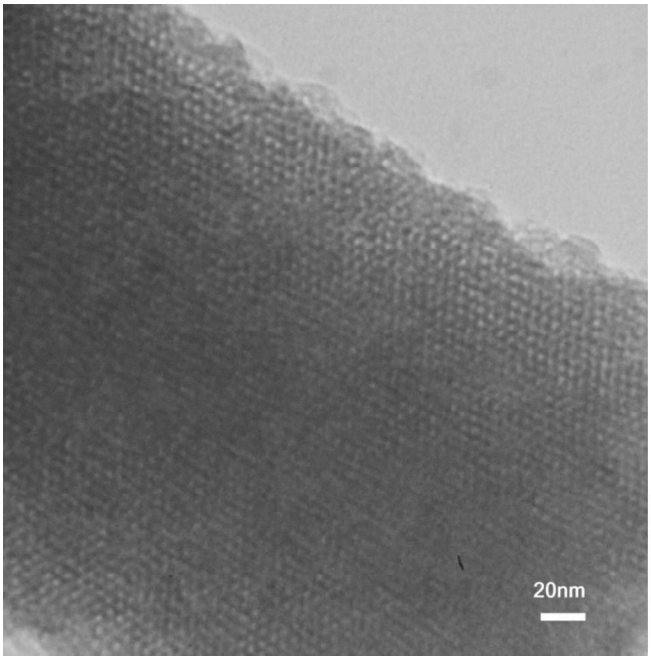
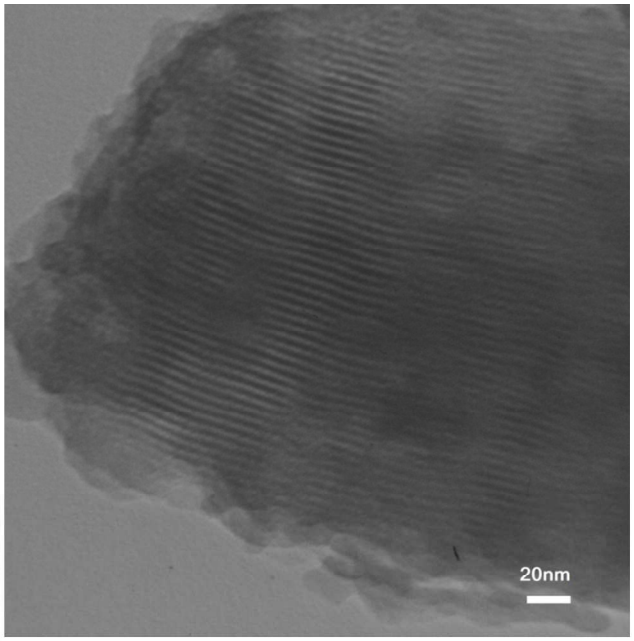


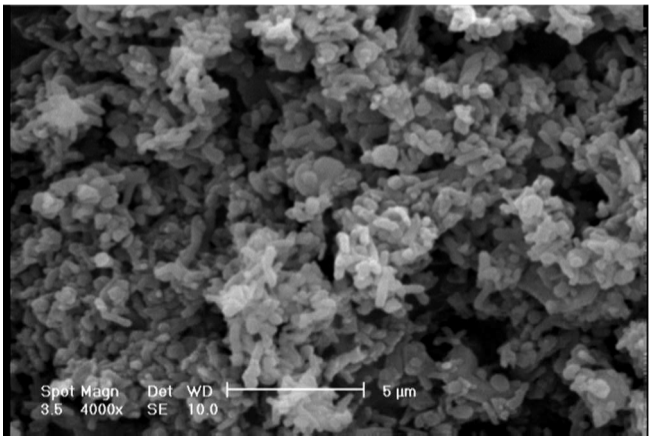
Figure 2. Expanded FTIR spectra of recycled **MCMBSA** and **MCMSA** in the 600-800 cm^{-1} region. The target indicates the stretching mode of CS bond.



a



b



c

Figure 3 (a) The TEM image of MCM-41 (b) The TEM image of MCMBSA catalyst (c) The SEM image of MCMBSA catalyst

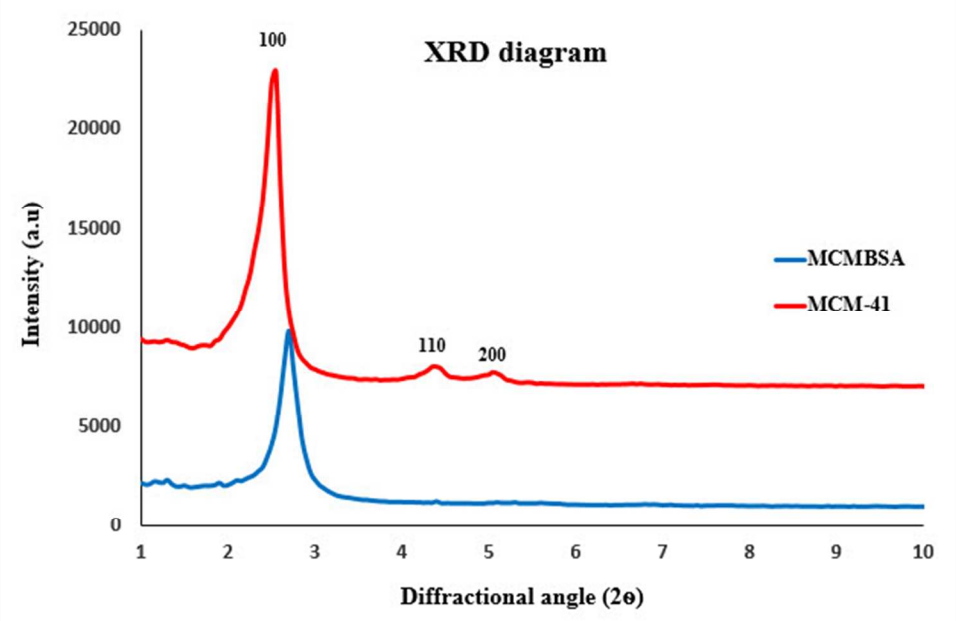


Figure 4 XRD patterns of MCM-41 and MCMBSA catalyst

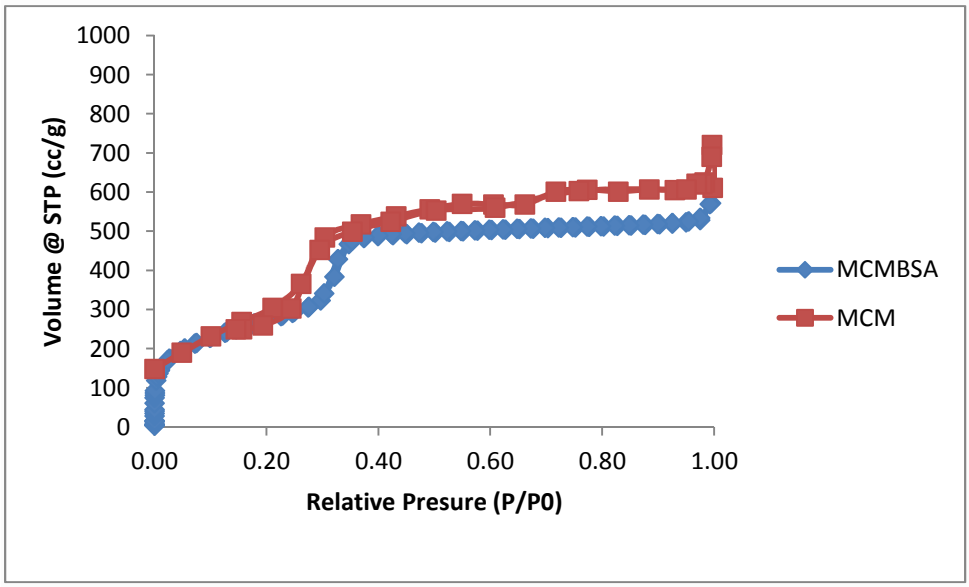


Fig 5. The N_2-sorption isotherm of MCM-41 and MCMBSA catalyst at 77 K