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# One pot three component solvent free synthesis of N-substituted tetrazoles using $RuO_2$ /MMT catalyst



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#### ABSTRACT

A facile, one-pot three component catalytic method is developed for the synthesis of N-substituted tetrazole using RuO<sub>2</sub>/MMT nanocomposite. It is characterized with low and wide angle XRD which suggests that RuO<sub>2</sub> nanoparticles are evenly dispersed on the surface of MMT while FESEM images indicate a spherical morphology having size in the range of 40-50 nm. The catalytic efficiency is evaluated for three component one-pot synthesis of the tetrazole using various amine, sodium azide and triethylortho-formate under solvent free condition. This strategy has resulted in good to excellent yields (84 – 97%) of N-substituted tetrazoles within moderate reaction time. Moreover, the catalyst possesses excellent reusability up to five cycles with only 5% decrease in the yield of tetrazole after 5<sup>th</sup> cycle. The beneficial catalytic activity of the bifunctional nanocomposite is attributed to the uniformly dispersed RuO<sub>2</sub> nanoparticles on the surface of MMT where RuO<sub>2</sub> site is responsible for coordination of isocyanide intermediate while strong acidic character of MMT induces condensation and cyclization steps in a synergic manner. Thus, it can be argued that RuO<sub>2</sub>/MMT nanocomposite possesses potential applications for Multi Component Reactions (MCR) in terms of efficient and sustainable manner.

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#### 1. Introduction

Tetrazoles; a family of nitrogen rich bioactive heterocyclic scaffolds possess wide range of applications from medicinal chemistry to high energy materials [1]. They are explored as lipophilic spacers and peptide chelating agents, peptide mimics [2], a catalyst in the synthesis asymmetric molecules [3], form an integral structural part of drugs like losartan and sartane and inhibitors of HIV [4]. Besides, they are widely used as ligands in Coordination Chemistry [5] and high energy density materials [6] for defense purpose. These compounds are synthesized by classical [3+2] cycloaddition of azide with nitriles [7] or via condensation of primary amine, azide and ortho-formate through oxidative cyclisation [8]. However, these methodologies have several drawbacks including use of corrosive and toxic metal azides, highly moisturesensitive reaction conditions, strong acidic conditions, high reaction temperature and *in-situ* generated hydrazoic acid which is highly toxic, explosive and volatile in nature. Several supported metal oxide catalysts such as ZnO/GO, ZnO/Co<sub>3</sub>O<sub>4</sub>, CoY/zeolite, CuFe<sub>2</sub>O<sub>3</sub>, BaWO<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>@Chitin, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-Arginine and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/Cu(II)-salen are efficiently been used as a cata-

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https://doi.org/10.1016/j.molstruc.2020.128985 0022-2860/© 2020 Elsevier B.V. All rights reserved. lyst towards the synthesis of tetrazoles [9–17] where beneficial catalytic activity is manifested by strong acidic nature of oxides.

Recent efforts are directed towards effective utilization of Multi-Component Reactions (MCRs) in organic synthesis that are performed in a single-pot because they don't require rigorous work-up and purification steps [18]. This approach involves onepot methodology with three or more reactants in a single vessel without isolating the products of intermediate steps in an atom economical manner [19,20]. Moderate reaction time, simplicity of performance, better yield, costs, safety and environmental acceptability are some of the facets of MCR syntheses [21]. Thus, MCRs are quite often employed for the synthesis of pharmaceuticals and natural products, agrochemicals and polymers [22]. Majority of MCRs are carried out with isocyanides-based intermediates or reactants due to their excellent reactivity and capacity to generate structurally diverse molecules using easily accessible starting materials like aldehydes or ketones, carboxylic acids, and amines [23]. Advantages of isocyanide based multi-component reactions are tandem bond formation, functional group tolerance and the higher degree of chemo-, regio- and stereo-selectivity.

The dispersion of nanoparticles on different supports is envisaged as strategy for the development of bifunctional nanocomposites which prevents the agglomeration of NPs, enhances the catalytic efficiency and these catalyst can be used in a sustainable manner [21,24–26]. Adopting this approach, previously we reported the generation of p-n heterojunction between RuO<sub>2</sub> layer and Ru NPs which is primarily responsible for the excellent catalytic activity of Ru/MMT catalyst towards the synthesis of Csubstituted tetrazoles under ambient conditions [27]. Moreover, the enhanced oxide layer on the active site of the catalyst is necessary for the sustained catalytic activity with excellent yields in lesser reaction time and beneficial TOF/TON values. Thus, it is quite logical to extrapolate this strategy by designing RuO<sub>2</sub>/MMT nanocomposite and explore its feasibility for the one-pot synthesis of N-substituted tetrazole via MCR approach. The objective of this approach stems from the fact that acidic nature of RuO<sub>2</sub> as well as Lewis and Bronsted acidity of MMT would trigger the condensation of amine with triethyl-ortho-formate while Ru-site would promote oxidative cyclization step in a concerted manner. Thus, such a bifunctional nanocomposite may exhibit a synergic effect towards one-pot three component synthesis of tetrazole in an efficient manner. Such a methodology is been utilized towards the synthesis of variety of tetrazoles that has resulted in the excellent yields within shorter reaction time and under ambient conditions [29]. Another facet of the present work involves the synthesis of these bioactive scaffolds under solvent free condition that avoids usage of toxic solvents, tedious work-up and purification steps in a greener manner [30]. In the present work, different compositions of RuO<sub>2</sub>/MMT catalyst are explored for the one-pot three component solvent free MCR type synthesis of N-substituted tetrazoles with amine, triethyl-ortho- formate and azide.

#### 2. Experimental

#### 2.1. Chemicals

All chemicals were of analytical grade and used as received. RuCl<sub>3</sub>.3H<sub>2</sub>O (Aldrich), Montmorillonite K-10 (Fluka), triethyl-orthoformate (TEOF), NaOH (Loba Chemie, UK), sodium azide and substituted amines (Aldrich), DMF (S.D. Fine) and pre-coated TLC plates (silica gel 60 F254, Merck).

#### 2.2. Pre-treatment of MMT

The pre-pretreatment of MMT clay was carried out as per the procedure reported in the literature [27].

#### 2.3. Preparation of RuO<sub>2</sub> NPs

2.05 g RuCl<sub>3</sub>.3H<sub>2</sub>O was dispersed in 100 mL water and stirred at room temperature for 4 h. It was then subsequently hydrolyzed by adding 0.54 g of NaOH pellets and the solution was stirred further for 2 h. Afterwards, the powder was filtered and washed thoroughly with deionized water to remove the excess salt. It was then calcined at 700°C in furnace for 3 h and subsequently ground so as to obtain RuO<sub>2</sub> nanoparticles.

#### 2.4. Preparation of RuO<sub>2</sub>/MMT nanocomposite

0.9 g pre-treated Na-MMT was dispersed in 50 mL water and stirred for 1 h. To this suspension, 0.205 g  $RuCl_3.3H_2O$  in 10 ml water was added and the mixture was stirred at room temperature for another 4 h. It was then subsequently hydrolyzed by adding 0.054 g of NaOH pellets, stirred further for 1 h, the powder thus obtained was filtered and washed thoroughly with deionized water to remove the excess salt. The powder was then calcined at 700°C in furnace for 3 h and subsequently grounded so as to obtain 10%  $RuO_2/MMT$  composite. Similar procedure was adopted for the synthesis of 5%, 15% nanocomposites of  $RuO_2/MMT$  by varying respective amounts of ruthenium salt and Na-MMT.

# 2.5. General procedure for the synthesis of N-substituted tetrazoles using $RuO_2/MMT$

To a mixture of primary amine (1.5 mmol), triethyl-orthoformate (1.5 mmol) and sodium azide (1 mmol) in a round bottom flask, 10 mg 10% of  $RuO_2/MMT$  catalyst was added to this mixture and it was heated at 120°C in oil bath for a desired period of time. After completion of the reaction, the catalyst was separated by centrifugation at 2000 rpm and the solid mass was extracted with 10 ml H<sub>2</sub>O:ethyl acetate (1:1). The organic layer was separated, dried over sodium sulfate, and evaporated in vacuum evaporator so as to obtain tcrude mass. It was then purified by recrystallization in a mixture of EtOAc:MeOH (3:1) to yield pure product. It was characterized by physical constant, <sup>1</sup>H and <sup>13</sup>C spectral analysis.

#### 2.6. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu Lab XRD-6100 X-ray diffractometer using Cu-K $\alpha$  radiation. FT-IR spectra were recorded on a Shimadzu (model 650 plus) Infrared spectrophotometer with KBr pellets in the range of 400-4000 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra of tetrazoles in DMSO-d<sup>6</sup> were recorded on Bruker AV 500 spectrometer. Chemical shifts are reported in ppm and the instrument wasinternally referenced to tetra methyl silane (TMS) and dimethyl sulfoxide signals. Reported data is as follows: chemical shift, multiplicity (s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dd; doublet of doublet, brs; broad singlet), coupling constants in Hz, and integration. Melting points were recorded on a Metler Toledo melting point apparatus and were uncorrected.

#### 3. Result and discussion

#### 3.1. Characterization

The power XRD pattern of RuO<sub>2</sub>/MMT composite is depicted in Fig. 1. MMT exhibits a sharp peak around 8.9° corresponding to (001) phase with a basal interlayer distance of 8.9A<sup>0</sup>. This spacing is retained even after loading of RuO<sub>2</sub> nanoparticles suggesting that they are present on the surface of MMT [28]. The formation RuO<sub>2</sub> NPs on the MMT surface is reflected from the peaks that are centered at 27.9°, 34.9° and 54.3° corresponding to (110), (101) and (211) respectively due to the rutile phase (JCPDS Card No 9007541). Also, their presence is further confirmed by low angle XRD analysis (Fig. 1 (ii)) where the peak position of (001) plane remained unaltered with progessive enhancement in the intensity pattern, implying that RuO<sub>2</sub> NP's are not intercalated within the galleries of clay [29]. The FESEM image of RuO<sub>2</sub>/MMT composite display spherical morphology with particle size in the range of 40-50 nm as well as presence of RuO<sub>2</sub> particles on the surface of MMT (Fig. 2). Furthermore, the elemental composition of the composite from EDX indicates the presence of Ru along with Al and Si from aluminosilicate structure of MMT.

#### 3.2. Catalyst screening

#### 3.2.1. Optimization

To optimize the reaction conditions, RuO<sub>2</sub>/MMT catalyst is evaluated towards one pot three component synthesis of N-substituted tetrazole with 4-chloroaniline, triethyl-ortho-formate and sodium azide under solvent free condition (**Table 1**). Inspection of this table reveals that the reaction does not proceed in presence of MMT (**Table 1; entry 1**) while 38% conversion is observed with RuO<sub>2</sub> NP's (**Table 1; entry2**) which is further enhanced to 93% and 94%



Fig. 1. XRD patterns of RuO<sub>2</sub>/MMT nanocomposites: (i) Wide angle (a) Na-MMT(b) RuO<sub>2</sub>NP's (c) 5% (d) 10% (e) 15% and (ii) Low angle (a) MMT, (b) 5%, (c) 10% and (d) 15% loading RuO<sub>2</sub> on MMT.



Fig. 2. (a) Catalyst screening FESEM image (b) EDAX with elemental composition of RuO<sub>2</sub>/MMT.

Optimization reaction conditions for the synthesis of N-substituted tetrazole <sup>a</sup> using RuO <sub>2</sub> /MMT.											
Cl	$NH_2 \qquad OEt \\ H-C-OEt \\ - OEt \\ 2a \qquad 3$	+	NaN <sub>3</sub>	Catalyst Solvent Free Temp. Time	Cl 3a						
Entry	Catalyst	An	nount (mg)	Reaction	time (h)	% Yield <sup>b</sup>					
1	MMT	10		12		No reaction					
2	RuO <sub>2</sub> NP's	10		5		38					
3	5% RuO <sub>2</sub> @MMT	10		5		58					
4	10% RuO2@MMT	10		5		93					
5	15% RuO2@/MMT	10		5		94					
6	10% RuO2@/MMT	3		5		41					
7	10% RuO <sub>2</sub> @/MMT	5		5		75					
8	10%RuO2@/MMT	15		5		93					
9	10% RuO2@/MMT	20		5		93					
10 <sup>c</sup>	10% RuO <sub>2</sub> @/MMT	10		5		No reaction					

<sup>a</sup> 4-Chloroaniline (1mmol), NaN<sub>3</sub> (1.5 mmol), TEOF (1.5 mmol), Temp.120°C,

<sup>b</sup> Isolated yield

Table 1

<sup>c</sup> Reaction at room temp.

with 10% and 15% RuO<sub>2</sub>/MMT composites respectively (Table 1; entries 4 and 5) under identical experimental conditions. Furthermore, similar effect is observed when the amount of catalyst is varied from 3-20 mg for this conversion. For example, when 3 mg of 10% RuO<sub>2</sub>/MMT is used (Table 1; entry 6), only 41% yield of 3a is obtained which further increases to 93% with concomitant increase in the amount of catalyst (Table 1; 7-9). Thus, 10 mg of 10% RuO<sub>2</sub>/MMT is found to be optimal condition for achieving better yield for 3a (Table 1; entry 4) within 5 h.

#### 3.2.2. Library synthesis

Under these optimized conditions, we explored the feasibility, scope and functional group compatibility towards thermally driven solvent-free synthesis of N-substituted 1H-tetrazoles with aromatic and heterocyclic amines using RuO<sub>2</sub>/MMT catalyst (Table 2). It is observed that this methodology has resulted in good yields (84 -97%) within reasonably good reaction time ranging from 3 – 8 h. It is observed that formation of tetrazoles with heterocyclic amines occur at the faster rate than aromatic counterparts where higher





<sup>a</sup> Reaction conditions: Amine (1mmol), NaN<sub>3</sub> (1.5 mmol), TEOF (1.5 mmol), Temp.120°C

<sup>b</sup> Isolated yield

reaction time is required for better conversion to tertrazole. This may be attributed to the beneficial adsorption of heterocyclic nitrogen through lone pair on the acidic surface of  $RuO_2/MMT$  that ebentually results in the better conversion at considerably lesser reaction time. The nature and position of substituents on the aromatic amine also seems to influence the formation of corresponding tetrazoles. For example, better yields are achieved with electron donating functionalities (**Table 2; entries 1-4**) in lesser reaction time while, deactivating effects of electron withdrawing substituent result in the longer reaction time for the synthesis of N-

substituted tetrazoles, (**Table 2; entries 5&6**). These compounds are characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectral analysis (**Supporting information Fig. S1**). Thus, it may be argued that stronger acidic nature of RuO<sub>2</sub>/MMT nanocomposite is primarily responsible for the solvent free synthesis of N-substituted tetrazoles in an easier and economical manner.

#### 3.2.3. Reusability studies

The efficiency of the catalyst is usually evaluated by its successive usage in subsequent cycles under identical experimental



Fig. 3. Reusability studies of RuO<sub>2</sub>/MMT catalyst.



Fig. 4. FT-IR spectra of (a) fresh and (b) recovered 10% RuO<sub>2</sub>/MMT catalyst.

conditions. For this purpose, conversion of **2a** to corresponding tetrazoles (**3a**) is evaluated for the recycling experiment with 10% RuO<sub>2</sub>/MMT catalyst. It is observed that, the catalytic activity of the composite remains almost constant during five successive cycles (**Fig. 3**) with marginal decrease of about **4**% in yield of **3a**. Such a behavior may be explained on the basis of acidity of the catalyst where both RuO<sub>2</sub> and MMT behaves as bifunctional sites for this catalyst. Moreover, the Bronstead acidity of MMT significantly contribute towards the sustained catalytic activity of RuO<sub>2</sub>/MMT nanocomposite [28]. Marginal decrease in the yield (4%) may be attributed to blocking of active sites by adsorbed species on the surface of the catalyst. Thus, RuO<sub>2</sub>/MMT may be regarded as robust catalyst towards one-pot three component solvent free synthesis of N-substituted tetrazoles in a sustainable manner.

#### 3.2.4. Post characterization of the catalyst

Reusability studies clearly suggest that the surface properties of bifunctional RuO<sub>2</sub>/MMT catalyst are not affected even after exposure to successive harsh chemical environment. To authenticate this fact, FT-IR spectra of fresh and recovered 10% RuO<sub>2</sub>/MMT catalysts are recorded and the data is presented in Fig. 4. Freshly prepared catalysts exhibit a strong and broad peak around 500-500 cm<sup>-1</sup> due to Ru-O stretch [30] which remains unaltered for recovered catalyst after five-catalytic cycles. Similar observations are noted for XRD studies where the crystalline phase remains unaltered even after five consecutive cycles (Fig. 5). It is interesting to note that the peak position and the intensities for (110), (101) and (211) planes of fresh and recovered catalyst are almost identical with slightly sharpened nature for used catalyst probably due to the formation of crystalline phase [31,32]. On the other hand, there seems to be the thermal effect on the morphology of recovered catalyst. For example, FESEM image of used catalyst suggests the agglomeration of RuO<sub>2</sub> NPs on the surface of MMT resulting in



Fig. 5. XRD patterns of (a) fresh and (b) recovered 10% RuO<sub>2</sub>/MMT catalyst.

generating higher sized spherical particles on the surface of catalyst. (Fig. 6). These observations clearly suggest the robustness of nanocomposite even after successive exposure to the harsh chemical environment and also reflects the stronger association of  $RuO_2$  nanoparticles on the surface of MMT. Such a clustering of oxide site can be ascribed to successive heating at the elevated temperature as well as stronger electronic interactions between  $RuO_2$  sites present on the MMT surface of catalyst.

To highlight the efficiency and sustainability of RuO<sub>2</sub>/MMT towards one-pot three component methodology for MCR, a comparative account is tabulated (Table 3) for different catalysts that are employed for the solvent free synthesis of tetrazoles [33–39]. Interestingly, there are only few reports on such a methodology which itself vouch for the significance of this strategy for MCR. One of the features emerged from such an assessment is that acidity of catalyst is a crucial for the cyclisation of the key intermediate formed during the ring closure phenomenon. For example, zeolite mediated synthesis of tetrazole is achieved with excellent yield [33] while Ag-decorated borosilicate composite [34] exhibit exceptional recycling capability with almost negligible lowering in the yield of tetrazole. Better catalytic activity is reported for Cu@bentonite [35] while the leaching of acid is observed for HClO<sub>4</sub> coated SiO<sub>2</sub> during successive cycles [37]. Similarly, comparatively lower yields are reported for ZnS [36], chitosan derived magnetic ionic liquid [38] and Cu-intercalated magnetic hydrotalcite catalysts [39] towards solvent free synthesis of tetrazoles. However in our case, the yields of N-substituted tetrazole are found to be marginally lowered (4%) during five-cycles. This feature may be ascribed to the Lewis acidity RuO<sub>2</sub> while the Bronsted acidity of MMT significantly contributes for the beneficial catalytic activity towards the formation of cyclic product. Moreover, RuO<sub>2</sub>/MMT catalyst explored in the present work exhibits sustained catalytic activity in terms of yield and reusability due to the synergistic effect of both RuO<sub>2</sub> and MMT support. Thus, it may be conluded that RuO<sub>2</sub>/MMT catalyst is robust, resistant to heat and its catalytic activity is retained even after continuous exposure to harsh synthetic conditions.

#### 3.2.5. Plausible mechanism

Three component one-pot cyclization process necessarily involves three steps [40,41]: (i) condensation of amine with TEOF under acidic condition (ii) nucleophilic attack of the azide on iso-cyanide like intermediate and (iii) cyclization of the intermediate.



Fig. 6. FESM images of (a) fresh and (b) reused 10% RuO<sub>2</sub>/MMT.

Table 3	
Reusability studies of different catalysts for the synthesis of N-substituted tetrazole.	

Entry	Catalyst	Time (h)	Temp. (°C)	Reusability (no. of cycles; respective %yield)	Ref.
1	Natrolite zeolite	4	120	I-IV; 93-87	33
2	Ag@borosilcate	3	120	I-V; 94-91	34
3	CuNPs@bentonite	3	120	I-V; 93-85	35
4	ZnS	3-7	130	I-V; 78-72	36
5	HClO <sub>4</sub> -SiO <sub>2</sub>	3	120	I-V; 94-91	37
6	Nano-CSMIL	2	70	I-V; 90-84	38
7	Fe <sub>3</sub> O <sub>4</sub> /HT-NH <sub>2</sub> -Cu	1-3	90	I-V; 87-80	39
8	RuO <sub>2</sub> /MMT	6	120	I-V; 93-89	Present work



Fig. 7. Proposed mechanism for the synthesis of N-substituted tetrazoles.

Initially, one of the ethoxy functionality of ortho formate is liberated due to the strong acidic nature of the catalyst thereby forming a carbocation, followed by nucleophilic attack of the amine (Fig. 7) on this carocation. The formation of iminium cation is initiated by the expulsion of another ethoxy group with concomitant addition of azide that generates a pseudo-cyclic imidoylazide intermediate by RuO<sub>2</sub> site of the catalyst. Eventually the cyclisation of this intermediate leads to the formation of tetrazole in a concerted manner. Amongst these catalytic steps, the rate determining step is found to be condensation of ortho formate with amine which is manifested by the stronger acidic nature of MMT. Furthermore, RuO<sub>2</sub>site is responsible for coordination of imidoyl azide intermediates as well as cyclization process. Thus, bifunctional nature of nanocomposite arises from the acidic nature of both  $\rm RuO_2$  nanoparticles and MMT in a coherent manner. The adsorptive capacity of MMT is another influencing factor that accounts for better conversion in lesser reaction time.

#### 4. Conclusion

The present work demonstrates that a facile, one-pot three component solvent free synthesis of tetrazole may be achieved with a simple, versatile and greener approach. The strong acidic nature of  $RuO_2$  site and MMT surface indeed contributes towards the formation N-substituted tetrazole. The  $RuO_2$  surface beneficially promotes the adsorptive coordination of isonitrile while

MMT surface induces the condensation of amines with formate moiety. Another facet of present methodology involves the synthesis of tetrazole under solvent free condition that itself vouch for the simple, cost-effective and environmentally benign process. Thus, it may be concluded that RuO<sub>2</sub>/MMT nanocomposite is robust, thermally stable and sustainable catalyst towards cyclization reactions under ambient conditions.

#### Supporting information

<sup>1</sup>H and <sup>13</sup>C NMR spectra tetrazoles.

#### **Credit Author Statement**

RCC conceptualised the idea, preparation of manuscript and interpretation of results.

HRP conducted the experiments, collected the data and helped in formulating the manuscript.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.128985.

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