

# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



[www.rsc.org/njc](http://www.rsc.org/njc)

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

**PAPER**

# Hierarchically porous AIPO-5-based microspheres as heterogeneous catalysts for synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition†

Dan Kong,<sup>a</sup> Yanyan Liu,<sup>a</sup> Juan Zhang,<sup>a</sup> Hongbian Li,<sup>b</sup> Xiangyu Wang,<sup>\*a</sup> Guangyu Liu,<sup>a,c</sup> Baojun Li<sup>\*a</sup> and Zheng Xu<sup>d</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

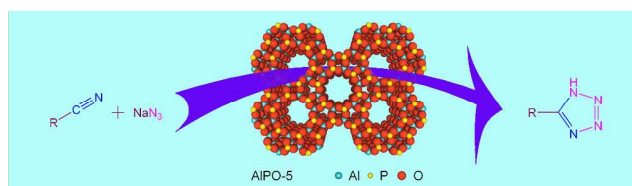
DOI: 10.1039/b000000x

The research on heterogeneously catalytic synthesis of tetrazoles has been attracting great attention. In this paper, a tungsten atoms-containing AIPO-5 microporous molecular sieve (termed as WAIPO-5) was designed and synthesized by incorporation of tungsten atoms into AIPO-5 skeleton with triethylamine as structure template from pseudoboehmite, H<sub>3</sub>PO<sub>4</sub> and tungstophosphoric acid. The incorporation of tungsten atoms into AIPO-5 skeleton has been demonstrated by systematic characterizations. WAIPO-5 can be used as efficient heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazoles by [3+2] cycloaddition from nitriles and sodium azide. As a novel heterogeneous catalyst, WAIPO-5 exhibits high catalytic activity, superior cycling stability and excellent substrate applicability. The significant advantages of WAIPO-5, such as simple procedure, mild reaction conditions and as an alternative to those corrosive, hazardous and polluting homogeneous catalysts, warrant its potential application in industrial processes.

## 1 Introduction

The research on catalytic synthesis of tetrazoles has been attracting great attention, due to their wide application, such as lipophilic spacers metabolically stable surrogates for carboxylic groups and *cis*-amide bond in pharmaceuticals, as antifogging materials in photographic, in information recording systems, propellants and special explosives, in biomedical and agriculture, and as important synthons in synthetic organic chemistry, as ligands in coordination chemistry.<sup>1-5</sup> In the early stage of conventional synthesis of tetrazoles via homogeneous catalytic [3+2] cycloaddition reactions, some drawbacks including requirements for metal-organic azide complexes, highly moisture-sensitive reaction conditions, and use of hydrozic acid, amine salts and strong Lewis acid as catalysts, which are volatile, explosive, extremely toxic and water-sensitive.<sup>6-8</sup> Afterwards, some homogeneous catalytic process have been reported with AlCl<sub>3</sub>, Zn salts, TBAF, BF<sub>3</sub>·OEt<sub>2</sub>, Yb(OTf)<sub>3</sub>, In(OTf)<sub>3</sub> and Fe(OAc)<sub>2</sub> as catalysts.<sup>9-17</sup> The drawback of homogeneous catalytic processes such as difficulty in separation and recovery of catalyst limited their application. The novel heterogeneous catalysts are desirable as alternative for the homogeneous counterparts. Recently, some heterogeneous catalysts have been reported for the synthesis of tetrazoles via [3+2] cycloaddition using ZnO nanocrystals, Zn/Al hydrotalcite, Zn hydroxyapatite, Cu<sub>2</sub>O, Cu/Zn alloy, Sb<sub>2</sub>O<sub>3</sub>, FeCl<sub>3</sub>/SiO<sub>2</sub>, CuFe<sub>2</sub>O<sub>4</sub>, BaWO<sub>4</sub>, ZnS, natural natrolite and CoY zeolite.<sup>18-31</sup> However, a large amount

of sodium azide, high temperature and long reaction time still are necessary in the above-mentioned catalytic systems.



**Scheme 1** Synthesis of 5-substituted 1H-tetrazoles from nitriles and sodium azide catalyzed by AIPO-5-based heterogeneous catalysts.

Aluminophosphate molecular sieves (AIPO) with AFI topology have been widely applied into industrial catalysis.<sup>32-34</sup> The AIPO molecular sieves with different structures and pore sizes provide suitable frameworks to construct high performance heterogeneous catalysts for many organic reactions. Metal atom substituted AIPO (MeAIPO) molecular sieves reported first in 1986 were considered as typical example for construction of heterogeneous catalysts in AIPO molecular sieves frameworks.<sup>35</sup> The MeAIPO molecular sieves are constituted by [AlO<sub>4</sub><sup>-</sup>] and [PO<sub>4</sub><sup>+</sup>] tetrahedral. The Me isomorphous substitution of [AlO<sub>4</sub><sup>-</sup>] or [PO<sub>4</sub><sup>+</sup>] for another, the different catalytic sites with acidic properties and redox behaviors in molecular sieves can be fabricated to form heterogeneous catalysts.<sup>36-38</sup> AIPO-5 and MeAIPO-5 are important members of aluminophosphate sieves, which can be employed as catalysts or frameworks and exhibit superior catalytic performances in several organic reactions. Tungstate salts are effective catalysts for the synthesis of

tetrazoles by [3+2] cycloaddition for nitriles and sodium azide.<sup>27</sup> It could be expected that the incorporation of tungsten atoms into the framework of AIPO-5 will form some effective catalytic sites and provide high performance heterogeneous catalysts for the synthesis of tetrazoles.

In this paper, a tungsten atoms-containing AIPO-5 molecular sieve (termed as WAIPO-5) microspheres were synthesized by incorporation of tungsten atoms into AIPO-5 skeleton. The WAIPO-5 microsphere also has been employed as catalyst for the synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition from nitriles and sodium azide (Scheme 1). As expected, high catalytic activity, superior cycling stability and excellent substrate applicability were obtained with WAIPO-5 microspheres as novel heterogeneous catalyst.

## 2 Experimental section

### 2.1 Catalyst synthesis

WAIPO-5 microspheres were synthesized under hydrothermal conditions from orthophosphoric acid ( $\text{H}_3\text{PO}_4$ , 85%, Merck), pseudo-boehmite, triethylamine (TEA, Merck) and tungstophosphoric acid (HPW). The molar composition of synthesis reaction gel was equal to  $0.05 \text{ WO}_3 : \text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 1.5 \text{ TEA} : 50 \text{ H}_2\text{O}$ . WAIPO-5 microspheres were prepared as follows: pseudo-boehmite (5.20 g) was added to distilled water (20.00 g) and stirred for 1 h. Then orthophosphoric acid (8.07 g) was added to the mixture drop by drop under stirring. Then the mixture was stirring for 2 h. Subsequently, an aqueous solution of HPW (7.10 g) was added to the gel drop by drop. After stirring for another hour, a uniform gel was obtained. Finally, TEA (5.37 g) was added into the mix gel drop by drop and stirred for more 2 h. The final gel was transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 36 h. Then the solid product was separated, washed with water, and dried at 120 °C for 12 h. After calcinated at 550 °C for 6 h, WAIPO-5 microspheres were obtained as white powder. AIPO-5 microspheres were synthesized with a similar process as above in the absence of HPW.

### 2.2 Catalyst characterization

The solid samples were characterized by powder X-ray diffraction (XRD) made in a Dutch P analytical Company to confirm the AFI structure, and using Cu K $\alpha$  radiation. The scan range of  $2\theta$  was between 5 and 80 ° in a scan speed of 1.2 ° min<sup>-1</sup>. The W, Al and P elements were measured by chemical analysis through Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Thermo Scientific iCAP6000, Thermo Fisher, USA), by dissolving catalyst (0.1 g) in NaOH (15%, 20 mL). The mixture was sealed in a Teflon-lined stainless steel autoclave (50 ml) and heated at 180 °C for 10 h. Keeping the final solution weak acid using HCl (12wt%). Standard curve method was adopted to determine the content of W, Al and P elements. N<sub>2</sub>-sorption isotherms were obtained on NOVA 1000e surface area and pore size analyzer (Quantachrome, USA) at 77 K. The specific surface area was estimated using multi-point Brunauer-Emmett-Teller (BET) method and the porewidth was determined using the desorption branches of N<sub>2</sub>-sorption isotherms. Fourier transform infrared (FT-IR) spectra of WAIPO-5 were recorded in the range of 400–4000 cm<sup>-1</sup> with a Thermo Nicolet 380 FT-IR

spectrometer of solid mixed with KBr. Diffuse reflectance ultraviolet and visible (DRUV-VIS) spectra were recorded in the range of 200–500 nm with a Cary 5000 against BaSO<sub>4</sub> as reference. The morphology and size of catalyst particle were observed by scanning electron microscope (SEM, JEOL, JSM-6700F operating at 20 kV).

### 2.3 Catalysis procedures

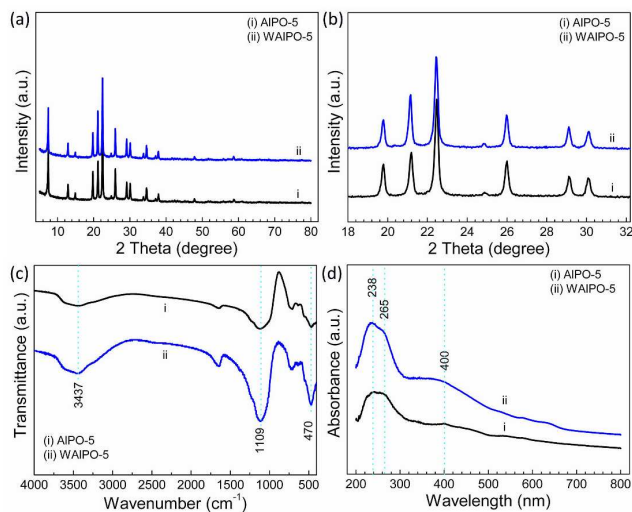
All nitriles were purchased from Aladdin. Catalyst (0.1 g) was added to a mixture of benzonitrile (0.257 g, 2.5 mmol) and sodium azide (0.350 g, 5.3 mmol) in *N,N*-dimethyl formamide (DMF, 5 mL) and the resulting composition was stirred constantly for 24 h at 120 °C. After completion of reaction, the catalyst was separated by centrifugation, washed with water (2×4 mL), and the centrifugate was treated with HCl (6 M, 20 mL) by stirring vigorously. The aqueous solution finally obtained was extracted with ethyl acetate (2×20 mL); the combined organic phase was washed with water (2×20 mL) and concentrated to precipitate the crude solid crystalline 5-phenyltetrazole. To obtain pure 5-phenyltetrazole, column chromatography was performed using silica gel (100–200 mesh), <sup>1</sup>H NMR (300 MHz, (D<sub>3</sub>C)<sub>2</sub>SO):  $\delta = 8.03$  (m, 2H), 7.59 (m, 3H). MS calculated for C<sub>7</sub>H<sub>7</sub>N<sub>4</sub> (MH<sup>+</sup>) 147.0, found 147.0.

## 3 Results and discussion

AIPO-5 molecular sieves have been synthesized by hydrothermal method from orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) as P source and pseudo-boehmite as Al source, and with triethylamine (TEA) as template. Pseudo-boehmite were added to distilled water and stirred.  $\text{H}_3\text{PO}_4$  was added to the mixture drop by drop under stirring. In the case of WAIPO-5, tungstophosphoric acid (HPW) was used as tungsten source. Subsequently, an aqueous solution of HPW was added to the gel drop by drop. After stirring, a uniform gel was obtained. Finally, TEA was added into the gel mixture drop by drop and stirred. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and treated for a designed time under hydrothermal conditions. AIPO-5 and WAIPO-5 microspheres were obtained after separated, dried and calcinated.

Powder X-ray diffraction (XRD) patterns were employed to characterize the AFI phase structure of AIPO-5 and WAIPO-5 microspheres (Fig. 1a, b). The characteristic peaks evidence directly the AFI structure of both samples.<sup>39</sup> The XRD pattern of WAIPO-5 is very similar to that of AIPO-5 in the range of large angle without extra peaks (Fig. 1a). After being doped with tungsten atoms, the AFI structure of WAIPO-5 can be maintained. The peaks of WAIPO-5 at  $2\theta = 21.2, 22.5, 26.0,$  and  $29.1^\circ$  shifts to lower diffraction angle compared to those of AIPO-5, which should be evidence for that tungsten atoms has entered into the AIPO-5 skeleton (Fig. 1b). The incorporation of tungsten atoms into AIPO-5 skeleton does not distort the ordered its AFI structure. The unit cell parameters were calculated for both samples (Table S1, seen in ESI<sup>†</sup>). The variation in XRD patterns could be evidence for that the metal atoms were isomorphously incorporated into the skeleton. Due to the different atom diameters of W from that of P and Al, the increasing cell volume should be expected with the successful incorporation of tungsten atoms into skeleton. An obvious

increasing cell volume can be observed for WAIPO-5 compared to that of AIPO-5, which provides another evidence for the incorporation of tungsten atoms into the AIPO-5 skeleton (Table S1).

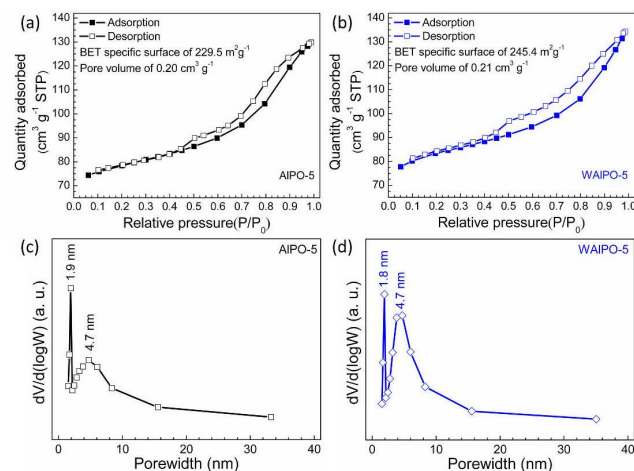


**Fig. 1** (a) XRD patterns, (b) the magnified version in low angle, (c) FT-IR, and (d) DR UV-Vis spectra of AIPO-5 and WAIPO-5.

The Fourier transformed infrared (FT-IR) spectra of AIPO-5 and WAIPO-5 are consistent to that of typical microporous AIPO-5 molecular sieves (Fig. 1c).<sup>40</sup> The main absorbance peaks of microporous WAIPO-5 shifts slightly to the lower wavenumber compared to that of AIPO-5 (Table S1). When tungsten atoms are isomorphously incorporate into the AIPO-5 skeleton, the longer bond length of W-O than that of P-O and Al-O drives the vibration of WAIPO-5 to shift slightly to the lower wavenumber, which can be taken as evidence of the presence of tetrahedral framework tungsten atoms. Diffuse reflectance ultraviolet and visible (DR UV-Vis) spectrum is very sensitive probe for the presence of extra-framework transition metal oxides in various mesostructures. The DR UV-Vis spectrum of WAIPO-5 provides three types of absorption bands at 238, 265 and 400 nm (Fig. 1d). The first band centred at 238 nm should be attributed to the charge transfer from O to Al and to the presence of template occluded in the channels of the skeleton.<sup>41</sup> The extra band at 265 nm of WAIPO-5 compared to AIPO-5 should be attributed to isolated [WO<sub>4</sub>] tetrahedral species.<sup>40</sup> The clear shifting toward higher wavelength for WAIPO-5 indicates the presence of oligomeric species. The broad band at around 400 nm maybe reflects that the tungsten oxide species are highly dispersed without WO<sub>3</sub> formed in WAIPO-5. The DR UV-Vis spectra provide further evidences for the incorporation of tungsten atoms into AIPO-5 skeleton.<sup>42,43</sup> The Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) also demonstrates the incorporation of tungsten atoms into AIPO-5 skeleton (Table S3).

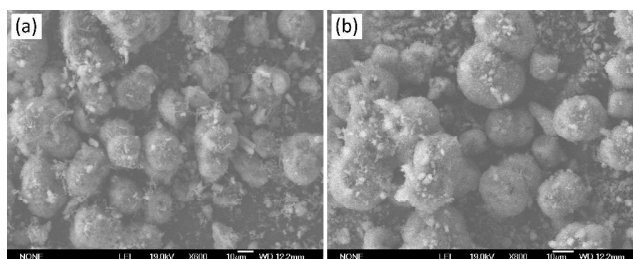
The surface areas and porosity of AIPO-5 and WAIPO-5 were measured by N<sub>2</sub>-sorption isotherms at 77 K (Fig. 2). AIPO-5 and WAIPO-5 possess high Brunauer-Emmett-Teller (BET) surface areas of 229.5 and 245.4 m<sup>2</sup> g<sup>-1</sup>, respectively (Fig. 2a, b). The most probable pore widths of AIPO-5 and WAIPO-5 are 1.9 and 1.8 nm, respectively, which are in the range of micropores (Fig. 2c, d). The improved ratio of 4.7 nm pore width in WAIPO-5 demonstrates a hierarchical porous structure. The pore volumes

also are similar to each other (Table S4). These structure features including BET surface area, pore width distribution and pore volumes show that the main structure property was maintained by WAIPO-5.



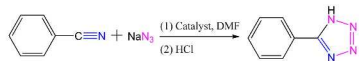
**Fig. 2** (a, b) N<sub>2</sub>-sorption isotherms at 77 K, and (c, d) pore width distributions of AIPO-5 and WAIPO-5.

The morphology of AIPO-5 and W-AIPO-5 were characterized by SEM images (Fig. 3). AIPO-5 possesses sphere-like shape with a diameter of around 30 μm (Fig. 3a). This structure feature has been maintained in W-AIPO-5 (Fig. 3b). The sphere-like shape and micrometer scale warrant that AIPO-5 and W-AIPO-5 microspheres may be used as heterogeneous catalysts.



**Fig. 3** The SEM images of (a) AIPO-5, and (b) W-AIPO-5 catalysts.

The synthesis of 5-substituted 1H-tetrazoles from nitriles and sodium azide by [3+2] cycloaddition was employed as probe reaction to evaluate the catalysts. The catalytic performances of AIPO-5-based molecular sieves as heterogeneous catalysts for synthesis of 5-phenyl tetrazoles was investigated, for comparison, the same reaction catalyzed by other homogeneous catalysts were also studied (Table 1). The blank reaction gave no yield of 5-phenyl tetrazole, which showed PO<sub>4</sub><sup>3-</sup> is not an active component for this catalytic reaction. Moderate yield can be obtained with Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as catalyst, which showed that Al<sup>3+</sup> is an efficient catalytic active component (Table 1, entry 2). However, the homogeneous intrinsic nature of Al<sup>3+</sup> ions is not desirable for catalysis application. As the starting point of heterogeneous catalysts, the amorphous AIPO<sub>4</sub> also provides a moderate yield of 5-phenyl tetrazole, which confirms the feasibility of Al species as the active components of heterogeneous catalysts (Table 1, entry 3). The γ-Al<sub>2</sub>O<sub>3</sub> gave only a low catalytic activity (Table 1, entry 3).

**Table 1.** The synthesis of 5-phenyltetrazole with various catalysts.<sup>a</sup>

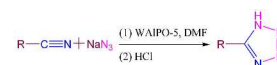
entry	catalyst	yield <sup>b</sup> (%)	TOF <sup>c</sup> (10 <sup>-1</sup> h <sup>-1</sup> )
1	no	0	~
2	Al(NO <sub>3</sub> ) <sub>3</sub>	76	2.9
3	γ-Al <sub>2</sub> O <sub>3</sub>	34	0.35
4	Na <sub>3</sub> PO <sub>4</sub>	4	0.15
5	Na <sub>2</sub> WO <sub>4</sub>	60	2.08
6	H <sub>2</sub> WO <sub>4</sub>	67	1.74
7	AlPO <sub>4</sub>	67	0.88
8	AIPO-5	87	1.15
9	WAIPO-5	92, 91 <sup>d</sup>	~
10	SiAIPO-5	19	~
11	TiCrAIPO-5	82	~
12	TiFeAIPO-5	89	~

<sup>a</sup> Reaction conditions: benzonitrile (2.5 mmol), NaN<sub>3</sub> (5.3 mmol), and catalyst (0.1 g) in DMF (5 mL) at 120 °C for 24 h. <sup>b</sup> Yields of isolated products. <sup>c</sup> Turnover frequency. <sup>d</sup> Recycling of WAIPO-5.

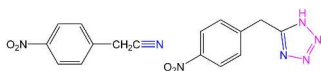
Due to the microporous structure and higher surface area, AIPO-5 molecular sieve was employed as heterogeneous catalyst. As expected, a good yield of 5-phenyl tetrazole was obtained (Table 1, entry 8). For further improvement in catalytic activity of AIPO-5 molecular sieves, some other atoms were introduced into the AIPO-5 skeleton to form the incorporation structures. The SiAIPO-5 gave lower yield than AIPO-5, which may be due to the negative effect of silicon atoms on catalytic activity. Because of the catalytic activity of tungsten species, the tungsten atoms also were introduced into AIPO-5 catalyst system (Table 1, entry 5, 6). WAIPO-5 formed by the incorporation of tungsten atoms exhibited the highest catalytic activity with a yield of 5-phenyl tetrazole up to 92% (Table 1, entry 9). The two atoms incorporation into AIPO-5 skeleton with Ti-Cr and Ti-Fe also gave good yields (Table 1, entry 11, 12). The good to excellent yields of 5-phenyltetrazole obtained with metal atoms-doped AIPO-5 molecular sieves as catalysts provided sufficient evidence of the feasibility of constructing efficient heterogeneous catalysts for synthesis of tetrazoles from nitriles and sodium azide by [3+2] cycloaddition. It is noteworthy that the recycling of WAIPO-5 still gave an excellent yield of 5-phenyltetrazole (91%) (Table 1, entry 9). The main structure features has been maintained in XRD pattern and FTIR spectrum perfectly (Fig. S1). WAIPO-5 is an efficient heterogeneous catalyst with excellent catalytic performances.

In order to obtain the optimum reaction conditions and more systematic understanding in the catalytic reaction, the effects of solvents, temperature, period and molar ratio of reagents on the catalytic performances of WAIPO-5 were optimized (Table S5).

Under these optimum conditions, some nitriles with various substitute groups on benzene cycle were used as substrates to investigate the effects of substitute groups on reaction activity of nitrile substrates (Table 2). The 4-methylbenzonitril gave good yield of the corresponding tetrazole as well as 2-methylbenzonitril, which showed that methyl groups as electron donor had no significant influence on the reactivity of nitrile (Table 2, entry 1, 2). The 3-methylbenzonitril also gave a higher yield of the corresponding tetrazole, due to the significant effect of the substitute positions on the reactivity of nitrile substrates (Table 2, entry 3). The 4-methoxybenzonitrile as substrate gave an excellent yield of the corresponding tetrazole up to 91% (Table 2, entry 4). The electron withdraw groups substituted nitriles such as 4-chlorobenzonitrile, 4-bromobenzonitrile and 4-nitrobenzonitrile also provided good to excellent yields of the corresponding tetrazoles (Table 2, entry 5-7), which demonstrated that the electron withdraw groups are able to maintain the good reactivity of nitriles. The highest yield of tetrazole was obtained with 4-cyanopyridine as substrate due to the strong electron withdraw effect of pyridine groups, which evidenced the positive effect of the electron withdraw groups on reactivity (Table 2, entry 8).<sup>9,44-46</sup> It is noteworthy that the aliphatic nitrile, 4-nitro benzyl cyanide also gave a good yield of the corresponding tetrazole (Table 2, entry 9). These results demonstrated the superior properties of WAIPO-5 as novel heterogeneous catalysts for the synthesis of tetrazoles by [3+2] cycloaddition from nitriles and sodium azide.

**Table 2.** The synthesis of 5-substituted 1H-tetrazoles with WAIPO-5.<sup>a</sup>

entry	substrate	product	yield <sup>b</sup> (%)
1			74
2			75
3			87
4			91
5			94
6			86
7			88
8			95



<sup>a</sup> Reaction conditions: benzonitrile (2.5 mmol), NaN<sub>3</sub> (5.3 mmol), and WAIPO-5 (0.1 g) in DMF (5 mL) at 120 °C for 24 h. <sup>b</sup> Yields of isolated products.

## 4 Conclusions

In conclusion, a tungsten atoms-containing AIPO-5 microporous molecular sieve, WAIPO-5 microspheres were synthesized with TEA as the structure template from pseudoboehmite, H<sub>3</sub>PO<sub>4</sub> and HPW. The incorporation of tungsten atoms into AIPO-5 skeleton has been demonstrated by the systematic characterizations. Furthermore, WAIPO-5 microspheres can be used as efficient heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazoles by [3+2] cycloaddition from nitriles and sodium azide. As a novel heterogeneous catalyst, WAIPO-5 microspheres exhibit high catalytic activity, superior cycling stability and excellent substrate applicability. The significant advantages of WAIPO-5 microspheres, such as simple procedure, mild reaction conditions and as an alternative to those corrosive, hazardous and polluting homogeneous catalysts, warrant its potential application in industrial processes. The further improvement in catalytic performances of WAIPO-5 microspheres and continuous-flow reaction process will be pursued in this laboratory.

## Acknowledgements

Financial supports from the Talent Training Unite Fund of NSFC-Henan (no. U1204203), the China Postdoctoral Science Foundation (no. 2013T60705) and the Innovation Fund for Elitists of Henan Province, China (no. 0221001200) are acknowledged.

## Notes and references

<sup>a</sup> Institute of Industrial Catalysis, College of Chemistry and Molecular Engineering, Zhengzhou University, 100 Science Road, Zhengzhou 450001, P R China. E-mail: lbjfc@zzu.edu.cn and xiangyuwang@zzu.edu.cn

<sup>b</sup> National Center for Nanoscience and Technology, 11 Beiyitiao Street, Zhongguancun, Beijing 100190, P R China

<sup>c</sup> School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, P R China

<sup>d</sup> State Key Laboratory of Coordination Chemistry and Nanjing National Laboratory of Microstructure, Department of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P R China

† Electronic Supplementary Information (ESI) available: Some characterization results and optimization of catalysis reaction parameters.

- R. J. Herr, *Bioorg. Med. Chem.*, 2002, **10**, 3379–3393.
- R. C. Tuites, T. E. Whiteley and L. M. Minsk, *US Patent*, 1971, **1**, 614.
- G. I. Koldobskii and V. A. Ostrovskii, *Usp. Khim., Usp. Khim.*, 1994, **63**, 847–865.
- M. Brown, *US Patent*, 1967, **3**, 915; *Chem. Abstr.*, 1968, 87299.
- M. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout and C. A. Bome, *Proc. Int. Pyrotech. Semin.*, 2000, **27**, 3–14.
- D. P. Curran, S. Hadida and S. Y. Kim, *Tetrahedron*, 1999, **55**, 8997–

- 9006.
- A. Kumar, R. Narayanan and H. J. Shechter, *J. Org. Chem.*, 1996, **61**, 4462–4465.
- K. Koguro, T. Oga, S. Mitsui and R. Orita, *Synthesis*, 1998, 910–914.
- D. P. Matthews, J. E. Green and A. J. Shuker, *J. Comb. Chem.*, 2000, **2**, 19–23.
- Z. P. Demko and K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945–7950.
- Z. P. Demko and K. B. Sharpless, *Org. Lett.*, 2002, **4**, 2525–2527.
- S. Hajra, D. Sinha and M. Bhowmick, *J. Org. Chem.*, 2007, **72**, 1852–1855.
- D. Amantini, R. Beleggia, F. Fringuelli, F. Pizzo and L. Vaccoro, *J. Org. Chem.*, 2004, **69**, 2896–2898.
- S. Hanessian, D. Simard, B. Deschênes-Simard, C. Chenel and E. Haak, *Org. Lett.*, 2008, **10**, 1381–1384.
- W. K. Su, Z. Hong, W. G. Shan and X. X. Zhang, *Eur. J. Org. Chem.*, 2006, 2723–2726.
- D. Kundu, A. Majee and A. Hajra, *Tetrahedron Lett.*, 2009, **50**, 2668–2670.
- J. Bonnamour and C. Bolm, *Chem. Eur. J.*, 2009, **15**, 4543–4545.
- M. L. Kantam, K. B. S. Kumar and C. Sridhar, *Adv. Synth. Cata.*, 2005, **347**, 1212–1214.
- M. L. Kantam, K. B. S. Kumar and K. P. Raja, *J. Mol. Catal. A: Chem.*, 2006, **247**, 186–188.
- M. L. Kantam, V. Balasubrahmanyam and K. B. S. Kumar, *Synth. Commun.*, 2006, **36**, 1809–1814.
- G. Aridoss and K. K. Laali, *Eur. J. Org. Chem.*, 2011, 6343–6355.
- T. Jin, F. Kitahara, S. Kamijo and Y. Yamamoto, *Tetrahedron Lett.*, 2008, **49**, 2824–2827.
- T. Jin, F. Kitahara, S. Kamijo and Y. Yamamoto, *Chem. Asian J.*, 2008, **3**, 1575–1580.
- D. G. Venkateshwarlu, K. C. Rajanna and P. K. Saiprakash, P. K. *Synth. Commun.*, 2009, **39**, 426–432.
- M. Nasrollahzadeh, Y. Bayat, D. Habibi and S. Moshae, *Tetrahedron Lett.*, 2009, **50**, 4435–4438.
- B. Sreedhar, A. S. Kumar and D. Yada, *Tetrahedron Lett.*, 2011, **52**, 3565–3569.
- J. H. He, B. J. Li, F. S. Chen, Z. Xu and G. Yin, *J. Mol. Catal. A: Chem.*, 2009, **304**, 135–138.
- L. M. Lang, B. J. Li, W. Liu, L. Jiang, Z. Xu and G. Yin, *Chem. Commun.*, 2010, **46**, 448–450.
- M. Nasrollahzadeh, D. Habibi, Z. Shahkarami and Y. Bayat, *Tetrahedron*, 2009, **65**, 10715–10719.
- A. Teimouri and A. N. Chermahini, *Polyhedron*, 2011, **30**, 2606–2610.
- V. Rama, K. Kanagaraj and K. Pitchumani, *J. Org. Chem.*, 2011, **76**, 9090–9095.
- R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 11926–11927.
- Z. S. Hou, B. X. Han, L. Gao, Z. M. Liu and G. Y. Yang, *Green Chem.*, 2002, **4**, 426–430.
- S. O. Lee, R. Raja, K. D. M. Harris, J. M. Thomas, B. F. G. Johnson and G. Sankar, *Angew. Chem. Int. Ed.*, 2003, **42**, 1520–1523.
- E. M. Flanigen, B. M. Lok, R. L. Patton and S. T. Wilson, *Pure Appl. Chem.*, 1986, **58**, 1351–1358.
- J. M. Thomas, R. Raja and D. W. Lewis, *Angew. Chem. Int. Ed.*, 2005, **44**, 6456–6482.
- R. Raja, J. M. Thomas, M. C. Xu, K. D. M. Harris, M. Greenhill-Hooper and K. Quill, *Chem. Commun.*, 2006, **4**, 448–450.
- M. Hartmann and L. Kevan, *Chem. Rev.*, 1999, **93**, 635–663.
- R. R. Xu, W. Q. Pang, J. H. Yu, Q. S. Huo and J. S. Chen, *Chemistry-Zeolites and Related Porous Materials*, 2004, **4**, 254–255.
- E. M. Flanigen and R. W. Grose, *Adv. Chem. Ser.*, 1971, **101**, 76–101.
- B. T. Holland, P. K. Isbester, C. F. Blanford, E. J. Munson and A. Stein, *J. Am. Chem. Soc.*, 1997, **119**, 29, 6796–6803.
- E. Briot, J. Y. Piquemal, M. Vennat, J. M. Bre'geault, G. Chottard and J. M. Manoli, *J. Mate. Chem.*, 2000, **10**, 953–958.
- X. L. Yang, W. L. Dai, R. H. Gao, H. Chen, H. X. Li, Y. Cao and K. N. Fan, *J. Mol. Catal. A: Chem.*, 2005, **241**, 205–214.
- F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc.*, 2002, **124**, 12210–12216.
- F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc.*, 2003, **125**, 9983–9987.
- M. Ai, L. M. Lang, B. J. Li, Z. Xu, *Chem. Lett.*, 2012, **41**, 814–816.

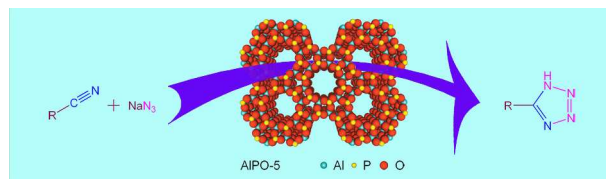


Cite this: DOI: 10.1039/c0xx00000x

[www.rsc.org/xxxxxx](http://www.rsc.org/xxxxxx)

PAPER

## Table of Content Graphic



W-containing AlPO-5 microspheres were effective catalyst for synthesis of 5-substituted 1H-tetrazoles by [3+2] cycloaddition.