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Mixed cobalt/nickel metal–organic framework, an efficient catalyst for one-pot synthesis of substituted imidazoles

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Abstract In the present work, a three-dimensional bimetallic metal-organic framework, $[CoNi(\mu_3-tp)_2(\mu_2-tp)_2(\mu_3-tp)_2(\mu_$ $[pyz)_2$ (tp = terephthalic acid, pyz = pyrazine) was applied as a highly efficient and recoverable heterogeneous catalyst. The catalyzed reaction was the one-pot threecomponent condensation reaction between benzil or benzoin with various substituted aromatic aldehydes and ammonium acetate to synthesize the corresponding imidazoles in solvent-free conditions and high to quantitative yields. The catalyst can be recycled at least five times without significant loss in the catalytic activity. To the best of our knowledge, 2,4,5-trisubstituted 1H-imidazoles were not previously synthesized using MOFs as heterogeneous catalyst. The structure of previously reported cobalt/nickel MOF has been confirmed by various techniques, such as X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, and Brunauer-Emmett-Teller.

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Keywords Heterogeneous catalysis \cdot Substituted imidazole derivatives \cdot MOF \cdot Cobalt \cdot Nickel

Introduction

Metal organic frameworks (MOFs) or porous coordination polymers (PCPs) are crystalline porous materials whose structures are defined by metal ions or clusters containing metals acting as lattice nodes and rigid bipodal or multipodal organic linkers as spacers [1–3]. Exceptionally high porosity, crystallinity, compositional and structural variability, large surface area, and acceptable thermal and mechanical stability of MOFs make them ideal materials to satisfy the needs of various applications, such as gas and vapor sorption, chemical separation, catalysis, and so forth [4-9]. Heterogeneous catalysis, an important cornerstone of chemistry, is commonly carried out by traditional porous materials such as zeolites. Early catalytic applications of MOFs were mainly motivated by their analogy to zeolites [10]. MOFs are constituted of large density of active metal sites with free of exchangeable coordination positions and

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show poor solubility in common solvents as well as tunable and uniform pore sizes, which make them smart heterogeneous catalysts. However, with the ability to assemble well-defined molecular building blocks into their structures, MOFs are particularly suited for immobilizing molecular catalysts to lead to a new generation of solid catalysts with uniform catalytic sites and open canal structures for shape-, size-, chemo-, and stereoselective reactions. The heterogeneous nature of these MOF-based catalysts allows simple recovery and reuse, which is highly desirable for reducing processing and waste disposal costs in large-scale reactions [9]. The most intriguing but also most unpredictable class of MOF catalysts is undoubtedly that in which structural metal ions at the nodes serve themselves as the catalytic centers. Some MOFs contain metal ions that can directly coordinate to the substrates to catalyze a chemical transformation, and these are what we refer to MOFs with coordinatively unsaturated sites [11]. Catalytic reactions of MOFs include Lewis acid catalysis, Lewis base catalysis, enantioselective catalysis, etc. MOFs having coordinatively unsaturated metal centers can potentially interact with the substrate and act as Lewis acid catalyst [12-15]. As a consequence, Lewis acidic properties of metal centers and Bronsted basic sites in organic linkers of MOFs can easily catalyze the organic transformations. Thus, occurrence of these two combined properties in MOFs makes them good and highly efficient candidates in the field of catalysis. Several MOFs have been employed as solid catalyst or catalyst supports for a variety of organic reactions. These include oxidation [16], Friedel-Crafts [17], Biginelli [18], Sonogashira [19], Knoevenagel condensation [20], Henry [21], Friedlander [22], and cyclization reactions [23].

Heterometallic MOFs have been investigated for the modulation of framework properties, such as the enhancement of framework stability, gas sorption behavior, catalytic activity, and the tuning of breathing behavior, luminescence, and magnetic properties [24–26]. A general strategy toward heterometallic MOFs, especially bimetallic MOFs, is to use different metal ions as reactants during the conventional solvothermal reaction process. The reaction of a ligand with two different metal ions sometimes results in a bimetallic MOF as a pure phase rather than a mixture of two different homometallic MOFs [27, 28].

Multicomponent reactions (MCRs) are one-pot reactions, which involve reaction of three or more accessible components to form a single product, where most or all the atoms of starting materials are incorporated in the final product. The rapid and easy access to biologically relevant compounds by MCRs and the scaffold diversity of MCRs have been recognized by the synthetic community in industry and academia as a preferred method to design and discover biologically active compounds. In recent years, the importance of imidazoles in biological systems has attracted considerable interests because of their chemical and biochemical properties, and compounds with imidazole ring system also have many pharmacological properties and can play an important role in biochemical processes. The heterocyclic scaffolds comprising 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles are present in compounds possessing versatile pharmacological action, such as being antibacterial agents, anti-inflammatory agents, CSBP kinase inhibitor, antitumor agents, inhibitors of mammalian 15-LOX, and inhibitors of B-Raf kinase [29]. Thus, several methods for the construction of these heterocyclic scaffolds have been developed. Among these methods, the one-pot reaction of diketone is extensively used for the synthesis of 2,4,5-trisubstituted imidazoles. Various catalysts can be employed in this reaction, such as nano SnCl₄·SiO₂ [30], NBS [31], NiCl₂·6H₂O [32], silicasulfuric acid [33], silica chloride [34], H₁₄[NaP₅W₃₀O₁₁₀] [35], and so on. Nevertheless, many of these approaches suffer from one or more drawbacks, such as a long reaction time, unsatisfactory yields, strong acidic conditions, difficult work-up and purification procedures, generation of significant amount of waste materials, occurrence of side reactions, low yields, use of moisture sensitive reagents/catalysts, and excessive use of reagents and catalyst. Therefore, the development of a new mild method to overcome the disadvantages still remains a challenge for organic chemists.

There are a few reports on the application of MOFs as a heterogeneous catalyst in the one-pot synthesis of multicomponent reaction [36]. Also, channels of MOF materials acting as nanoscale reaction vessels (nano reactors) have been used in the last decades [37].

Surprisingly, interpenetrated mixed (Co/Ni) metal–organic framework acts as a highly efficient recoverable heterogeneous catalyst for the one-pot synthesis of 2,4,5trisubstituted imidazoles under mild solvent-free conditions.

To the best of our knowledge, there are a few reports on the application of bimetallic MOFs as a catalyst in MCRs. We herein report the results for the application of $[CoNi(\mu_3-tp)_2(\mu_2-pyz)_2]$ as a suitable, efficient, and green catalyst for the one-pot synthesis of substituted imidazoles without any solvents, salts, and additives, with good to excellent yields of 2,4,5-trisubstituted imidazole derivatives due to biological and medicinal interest.

Results and discussion

The synthesized MOF was characterized by several techniques including X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), and Brunauer-Emmett-Teller (BET). The results were in good agreement with the reported analyses [38]. The comparison analyses are given in SEI.

The excess analyses including thermogravimetric/differential thermal analysis (TG/DTA), energy dispersive X-ray spectroscopy (EDX), and BET/BJH were performed. The TG/DTA studies on polycrystalline sample under oxygen-free nitrogen atmosphere with a heating rate of 10 °C/min in the temperature range of 0–800 °C, were conducted to characterize the thermal stabilities of MOF structure. As shown in Fig. 1, on heating the compound, no obvious decomposition was observed until ca. 400 °C. The TGA plot shows an obvious weight loss of 80 % above 410 °C, relating to the organic parts. The two interpenetrated mixed (Co/Ni) metal–organic frameworks exhibited a high thermal stability in comparison with similar structures that start to lose weight in the region of 150 °C [39].

It seems that the observed stability of MOF structure up to 400 °C is due to the interpenetration of two highly coordinated mixed metal as nodes and lack of any cocrystals or solvent coordinated in the structure, and this leads to one-step weight loss compared to analogous structures that decompose in two or three steps because of their water ligands or presence of co-crystallized species in their framework [40].

In another point of view, interpenetrated motifs that minimize the empty space could significantly enhance the stability of frameworks, not only through filling of void space but also in the formation of repulsive forces that serve to prevent one net from collapsing in on itself [38]. The EDS analysis given in Fig. S1 of ESI indicates surface elemental analysis as Co, Ni, O, N, and C in weight% ratio of 10.5, 10.8, 17.1, 20.9, and 40.7, respectively. The percentages are in agreement with the reported formula [38].

To put in evidence the role and effect of the catalyst in rate of reaction, the model reaction was carried out in the absence of any catalyst (Table 1, entry 1). The results revealed that yield of reaction was very low, and the time has not had significant impact on efficiency of reaction. To evaluate the appropriate catalyst loading, the model reaction was carried out using different amounts of catalyst. It was found that the most effective amount of catalyst was 15 mg (Table 1, entry 8) and larger amounts of catalyst do not increase the reaction yield.

Subsequently, to investigate the efficiency and applicability of this catalyst in the synthesis of 2,4,5-trisubstituted 1*H*-imidazoles **4a-4n**, the reaction was extended to other substituted benzaldehydes **3** (Scheme 1) at 120 °C in solvent-free conditions (Table 2). It is obvious from Table 2 that when benzoin (1) is used instead of benzil (2), the reaction time is increased. All the aromatic aldehydes having either electron-withdrawing substitutes or electron-donating ones demonstrated excellent reactivity and yields for the synthesis of 2,4,5-trisubstituted imidazole derivatives.

Lower yields obtained for electron-donating and orthosubstituted aldehydes as compared with the electron-withdrawing para groups may be attributed to the competitive formation of less reactive corresponding imines. On the other hand, electron-withdrawing para derivatives have excellent yields relative to other derivatives, because para derivatives have minimum steric hindrance, and electrondeficient derivatives can stabilize the intermediate in comparison to electron-rich substituents (Table 2).



Fig. 1 TGA/DTA diagram of [CoNi(µ₃-tp)₂(µ₂-pyz)₂]

Entry	Catalyst weight/mg	Condition	Temperature/°C	Time/min ^a	Yield/% ^b
1	0	Solvent-free	80	30	0
2	1	Solvent-free	100	30	10
3	5	Solvent-free	120	30	10
4	8	Solvent-free	120	30	50
5	10	Solvent-free	120	30	70
6	12	Solvent-free	120	30	75
7	15	Solvent-free	25	60	30
8	15	Solvent-free	120	10	95
9	15	Solvent-free	130	35	87
10	15	Solvent-free	150	35	75
11	15	EtOH	Reflux	60	86
12	15	H ₂ O	Reflux	60	30
13	15	CH ₃ CN	Reflux	60	5

 Table 1
 Optimization of reaction conditions catalyzed by mixed (Co/Ni) metal-organic framework

Experimental condition: benzil (1 mmol), 3-nitrobenzaldehyde (1 mmol), ammonium acetate (2.5 mmol), solvent-free at 120 °C, and 15 mg of catalyst

^a Reaction progress monitored by TLC

^b Isolated yield

Scheme 1



A proposed mechanism for the synthesis of 2,4,5trisubstituted 1*H*-imidazoles is shown in Scheme 2. According to the mechanism, ammonia as a nitrogen source exists in the reaction environment from the decomposition of NH₄OAc. It can be proposed that the hydrogen atoms in ammonia and free-orbitals of the metal centers of MOF having the Lewis acidic properties, are responsible for the activation of carbonyl groups, and thus increase the rate of imine production through coordination bonding for nucleophilic attack of amines (Scheme 2) [41].

In more details, in the initial step, the flexible Lewis acid Co(II) and Ni(II) ions in the MOF might be preferentially coordinated by one oxygen atom from the benzaldehyde according to the soft and hard acids and bases theory. Electron flow from the Co(II) and Ni(II) atoms with unsaturated coordination environments accelerates the rate of imine production. It seems that Lewis acidic sites of the (Co/Ni)-MOF catalyst synergistically affect the reactive substrates and intermediates during the progress of reaction. Presence of unsaturated Co(II) and Ni(II) metal nodes

in the MOF structure is the driving force for the activation of carbonyl groups and causes the quick conversion of initial precursors to desirable products. We have also calculated the turnover number (TON) and turnover frequency (TOF) in the synthesis of 2,4,5-trisubstituted 1*H*-imidazoles (Table 3). According to the obtained results, TON has greater values from the TOF due to a very short reaction time.

We compared the catalytic performance of our system with the previously reported results for the synthesis of 2,4,5-trisubstituted 1H-imidazole derivatives. The results are summarized in Table 4.

In the XRD pattern of MOF shown in Fig. 2, all the diffraction peaks are indexed as the orthorhombic (Co/Ni)-MOF structure. According to JCPDS card number (36-1451), the peaks at 2θ values of 9.98°, 11.1°, 14.1°, 14.5°, 18.9°, 20.7°, 22.4°, 25.1°, 25.6°, 27°, 28°, 30°, 32°, 34°, 38°, 40°, and 45° can be indexed to 020, 021, 022, 111, 032, 040, 132, 042, 133, 200, 124, 044, 231, 026, 302, 321, and 175 crystal planes, respectively. No other impurity

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Entry	Aryl	Comp	Time/min		Yield/% ^a		M.p./°C	Lit. M.p./°C	References
			Benzil	Benzoin	Benzil	Benzoin			
1	C ₆ H ₅	4 a	10	14	95	93	270-271	270	[42]
2	$4-CH_3-C_6H_4$	4b	10	15	94	90	190–191	226-227	[43]
								158-161	[44]
3	$4-CH_3O-C_6H_4$	4 c	15	20	90	86	227-229	227-228	[43]
4	$2-OH-C_6H_4$	4d	12	16	92	85	203-205	203-205	[43]
5	$4-OH-C_6H_4$	4e	15	20	95	92	260-262	260-261	[43]
6	2-Cl-C ₆ H ₄	4f	20	25	94	91	190-192	187–188	[45]
7	$2-NO_2-C_6H_4$	4g	15	25	87	85	230-231	230-232	[46]
								230-231	[47]
8	$3-NO_2-C_6H_4$	4h	7	15	95	93	290-291	297-299	[48]
9	$4-NO_2-C_6H_4$	4i	8	10	94	91	199–201	199–201	[49]
10	2,4-Cl ₂ -C ₆ H ₃	4j	10	15	95	93	174–175	173–174	[45]
11	$4-Br-C_6H_4$	4k	12	20	94	92	261-263	261-263	[43]
12	3,4,5-(CH ₃ O) ₃ -C ₆ H ₂	41	15	20	95	91	262-263	261-262	[42]
13	4-(CH ₃) ₂ N-C ₆ H ₄	4m	15	30	89	84	260-261	260-261	[44]
14	3,4-(CH ₃ O) ₂ -C ₆ H ₃	4n	20	25	95	92	216-218	213-216	[41]
								215-219	[42]

 Table 2
 Synthesis of 2-aryl-4,5-diphenyl-1H-imidazoles using Co/Ni-MOF in solvent-free conditions (Scheme 1)

^a Yields refer to isolated pure products. The known products were characterized and compared by their physical properties with authentic samples



 Table 3 Calculated values of turnover number (TON) and turnover frequency (TOF) for 2-aryl-4,5-diphenyl-1*H*-imidazoles

Entry	Comp	TON ^a		TOF/h^{-1}	TOF/h^{-1}		
		Benzil	Benzoin	Benzil	Benzoin		
1	4 a	8.7	8.5	54.38	36.95		
2	4 b	8.62	8.25	53.87	33		
3	4 c	8.25	7.88	33	23.87		
4	4d	8.44	7.8	42.2	30		
5	4 e	8.7	8.44	34.8	25.57		
6	4f	8.62	8.34	26.12	20.34		
7	4 g	7.98	7.79	31.92	19		
8	4h	8.7	8.53	79	34.12		
9	4 i	8.62	8.34	66.3	52.12		
10	4j	8.7	8.5	54.37	34		
11	4k	8.62	8.44	43.1	25.57		
12	41	8.7	8.34	34.8	25.57		
13	4m	8.16	7.7	32.64	15.4		
14	4n	8.7	8.4	26.36	21		

peaks were detected, indicating the highly crystalline structure of MOF structure. XRD pattern indicates the high purity of the synthesized MOF and is also in accordance with the previously reported MOF [36]. The general scheme of placing the reactants in the pores of MOF crystal lattice is suggested in Fig. 3.

Moreover, to study the pore structural and the specific surface area of the title MOF, Brunauer-Emmett-Teller

Entry	Catalyst	Reaction condition		Yield/%	References
1	Nano SnCl ₄ SiO ₂	Solvent-free, 130 °C	120	95	[30]
2	NBS	Solvent-free, 120 °C	45	92	[31]
3	NiCl ₂ 6H ₂ O	EtOH, reflux	25	94	[32]
4	Silica sulfuric acid	Water, reflux	480	81	[33]
5	Silica chloride	Solvent-free, 80 °C	30	85	[34]
6	Zeolite	EtOH, reflux	60	80	[50]
7	Yb(OPf) ₃	C ₁₀ F ₁₈ /80 °C	360	80	[51]
8	(Co/Ni)-MOF	Solvent-free, 120 °C	10	95	Present work
9	Ni-MOF	Solvent-free, 120 °C	15	92	Present work
10	Co-MOF	Solvent-free, 120 °C	20	90	Present work

Table 4 Comparison of efficiency of various catalysts with (Co/Ni)-MOF in the synthesis of trisubstituted imidazoles



Fig. 2 Powder XRD patterns of simulated (bottom) and synthesized (up) [CoNi(µ₃-tp)₂(µ₂-pyz)₂]

(BET) gas sorption measurement is carried out. Nitrogen adsorption–desorption isotherm of the (Co/Ni)-MOF electrochemical tests is shown in Fig. 2S (provided in ESI), and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution plot is illustrated in Fig. 3S (provided in ESI). The N₂ adsorption and desorption experiment of the sample shows a typical type IV isotherm, and proposes the microporous structure. The BET specific surface area of the sample is measured to be 1054 m² g⁻¹. Also, the average pore size was 2.1 nm, and pore volume was 0.43 cm³ g⁻¹,

according to the Barrett-Joyner-Halenda (BJH) plot. The data are given in ESI.

To understand the location of the catalytic performance in the MOF structure, we have calculated the kinetic diameter of reactants and reaction product molecules with the aid of molecular mechanics (MM+) method [52] and compared the results with the textural properties (pore sizes, pore windows) of (Co/Ni)-MOF structure. The calculated kinetic diameters for reactants and products participated in the synthesis of imidazole derivatives are



Fig. 3 Crystal packing of the title MOF along the a axis, and a *scheme* of entering reactants in its pores and exit of imidazole as product. The coordination polyhedron around the two interpenetrated

given in Table 5. According to the obtained results, it seems that the catalytic reaction can be done on the surface and in the pores of (Co/Ni)-MOF catalyst.

Conclusion

In summary, a bimetallic MOF consisting of Co and Ni as metal nodes with the mixed O- and N-donor ligands was used as heterogeneous and highly efficient catalyst for the synthesis of 2,4,5-trisubstituted 1*H*-imidazoles under solvent-free conditions. The high catalytic activity of the (Co/Ni)-MOF is further highlighted when compared with the other catalysts in this reaction. The results show that the MOF performed its catalytic activity on both outer and inner surfaces. Remarkable advantages of our work are environmentally benign reaction conditions, improved efficiency of reaction using solvent-free system, reduced reaction time using recyclable catalyst, and enhanced reaction rates.

Experimental

In this study, all reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Melting points were measured on Electrothermal 9100 apparatus. FT-IR analyses were

mtallic sites, with labled atoms are shown in the circle. The *crystal* packing is *drawn* using cif of the title MOF [38]

carried out on a Shimadzu FTIR-8400S spectrophotometer using KBr pallet for sample preparation. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer at 400 and 100 MHz, respectively. X-ray powder diffraction (XRD) patterns were recorded using a Cu radiation ($\lambda = 1.5406$) source on a STOE Powder diffraction system. A Netzsch Thermoanalyzer STA 504 was used for the thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under air atmosphere. Field emission scanning electron microscopy (FESEM) was carried out on a Zeiss Supra ATM 55 at an acceleration of 15 kV. The surface area of the MOF structure was determined using the Brunauer-Emmett-Teller (BET) method from N₂ adsorption and desorption isotherms which were measured on a Micrometritics ASAP 2020 system. The pore size distribution was calculated from desorption branches of the nitrogen isotherms applying the Barret-Joyner-Halenda (BJH) method.

Synthesis of [CoNi(µ₃-tp)₂(µ₂-pyz)₂]

 $[\text{CoNi}(\mu_3\text{-tp})_2(\mu_2\text{-pyz})_2]$ was synthesized using a recently reported procedure which was slightly modified [38]. In a typical preparation approach, a solid mixture of $\text{Co}(\text{NO}_3)_2\cdot\text{6H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot\text{6H}_2\text{O}$, terephthalic acid, and pyrazine was dissolved in water. The resulting suspension was stirred and then transferred into Teflon-lined stainless steel autoclave, which was sealed and maintained at 200 °C for 48 h. After gradually cooling in oven to RT, the

 Table 5
 Calculated kinetic diameters of reactants and products in imidazole synthesis

Compound name	Kinetic ter/nm	diame-
Benzaldehyde	0.445	
4-Chlorobenzaldehyde	0.436	
3-Nitrobenzaldehyde	0.527	
2,4-Dichlorobenzaldehyde	0.501	
Benzil	0.564	
Benzoin	0.564	
Dimethylaminobenzaldehyde	0.437	
Cyanobenzaldehyde	0.437	
2-Chlorobenzaldehyde	0.499	
3,4,5-Trimethoxybenzaldehyde	0.769	
2-(2,4-Dichlorophenyl)-4,5-diphenyl-1 <i>H</i> - imidazole	0.971	
2-(4-Methoxyphenyl)-4,5-bis(4-methoxyphenyl)- 1 <i>H</i> -imidazole	1.01	
2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole	0.925	
2-(3,4-Dimethoxyphenyl)-4,5-diphenyl-1 <i>H</i> - imidazole	0.911	
2-(4-Nitrophenyl)-4,5-diphenyl-1H-imidazole	0.924	
2-(4-Bromophenyl)-4,5-diphenyl-1H-imidazole	0.924	
2-(4-Methylphenyl)-4,5-diphenylimidazole	0.924	
4-Methylbenzaldehyde	0.504	
4-Methoxybenzaldehyde	0.503	
2-Hydroxybenzaldehyde	0.468	
4-Hydroxybenzaldehyde	0.437	
2-Chlorobenzaldehyde	0.499	
2-Nitrobenzaldehyde	0.584	
2-(3-Nitrophenyl)-4,5-bis(4-methoxyphenyl)-1 <i>H</i> -imidazole	1.02	

solid product was obtained by decanting the mother liquor and washed with water $(4 \times 20 \text{ cm}^3)$ [36]. Solvent exchange was then carried out with DMF $(4 \times 20 \text{ cm}^3)$ at room temperature. The product was activated in vacuum at 80 °C for 12 h to remove residual DMF molecules that coordinated to the metal sites and stayed under nitrogen environment.

General procedure for the preparation of 2,4,5trisubstituted imidazole derivatives

 $[\text{CoNi}(\mu_3-\text{tp})_2(\mu_2-\text{pyz})_2]$ was used as a solid catalyst in the synthesis of 2,4,5-trisubstituted imidazoles in solvent-free conditions. In a typical approach illustrated in Scheme 1, the mixture of benzoin (1) or benzil (2) (1 mmol), benzaldehyde **3** (1 mmol), and ammonium acetate (2.5 mmol) was heated to 120 °C in the presence of 0.015 g catalyst in solvent-free conditions. After completion of the reaction which was monitored by TLC, the resulting reaction



Fig. 4 Reusability of $[CoNi(\mu_3-tp)_2(\mu_2-pyz)_2]$ as a catalyst for the synthesis of 2,4,5-triphenyl-1*H*-imidazole

mixture was dissolved in appropriate amount of EtOH and filtered to separate the catalyst. The filtered solution containing the product was placed in the refrigerator to obtain pure crystalline products in good to high yields.

Catalyst recycling procedure

One of the most important parameters in heterogeneous catalysis is the reusability of the catalyst. Hence, we examined the heterogeneity and recyclability of the MOF catalyst. The supernatant from synthesis of trisubstituted imidazoles after filtration through a regular filter did not afford any additional product. To evaluate the stability of the solid catalyst, we investigated recycling and reusing the (Co/Ni)-MOF in the mentioned synthesis reactions. Upon completion of the reaction, the catalyst could be recovered in nearly quantitative yield and used repeatedly with negligible loss of activity for the following five runs. According to the obtained results, the MOF behaves as a truly heterogeneous catalyst. The conversions versus reaction time of the fresh and recycled catalysts are given in Fig. 4. Furthermore, as an evidence to recyclability of the catalyst after five cycles, the MOF catalyst remained highly crystalline and still performing the catalytic action, indicating maintenance of its porous structure.

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