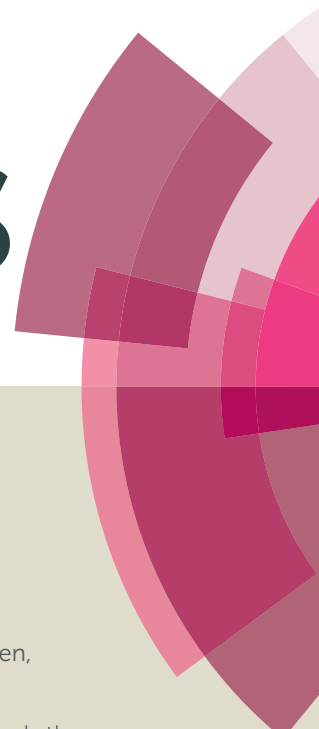


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Insight into the Catalytic Properties and Applications of Metal-Organic Frameworks in the Cyanosilylation of Aldehydes

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Here we present a systematic investigation of the cyanosilylation of aldehydes with trimethylsilyl cyanide (TMSCN) by using metal-organic frameworks (MOFs) as the catalysts. Four types of thermal stable MOFs (MIL-47 (V), MIL-53 (Al), MIL-101 (Cr), and UiO-66 (Zr)) constructed with the same organic linker, terephthalic acid, were studied, among which MIL-101 (Cr) exhibits the highest catalytic activity. Experimental results revealed that the catalytic activities are in close relation with the types of coordinatively unsaturated metal ions, pore sizes as well as solvents. Using MIL-101 (Cr) as the catalyst, both aliphatic and aromatic aldehydes were efficiently transformed to cyanohydrin trimethylsilyl ether, meanwhile significant size selectivities and electronic effects have also been observed. The solvent-free reaction conditions not only provide a high TON for MOF catalyzed cyanosilylation, but also render current protocol more attractive to industrial applications.

Introduction

Cyanohydrins play an important role in chemistry and biology. They are widely employed as versatile building blocks for fine chemicals, agrochemicals and pharmaceuticals, i.e. α -hydroxy acids, β -amino alcohols, etc.¹ Generally, the addition of cyanide to carbonyl compounds represents one of the fundamental approaches for their preparation and has frequently been at the forefront of synthetic chemistry.² In consideration of easy and safe management, the most often used cyanide source is trimethylsilyl cyanide (TMSCN), which allows the cyanohydrins to be prepared as the corresponding trimethylsilyl ether.^{2b,3}

In the past several decades, a variety of activators or promoters have been reported for this transformation.^{1a,1c,2b,3-}

⁴ In light of environmental benign pressures, organocatalysts have grown rapidly in promoting the cyanosilylation of carbonyl compounds with TMSCN.⁵ Although organocatalytic systems comply with some features of green chemistry, they are still encountered with tedious separation and recycle problems in practical applications. Therefore, a mild, efficient and environmental friendly synthetic method for cyanohydrin trimethylsilyl ethers is still highly desirable.

Metal-organic frameworks (MOFs) are a new generation of materials, which were constructed via the coordination of organic ligands with metal clusters.⁶ The unique properties of MOFs, such as porosity, high specific surface area, tunable

pore sizes and diverse functionalizations have pointed toward their potential utility to be size- and shape-selective heterogeneous catalysts.⁷ The vacant coordination sites in MOFs can activate carbonyl compounds for nucleophilic addition in a manner similar to Lewis acids. Since the first example of MOFs catalyzed reaction was reported by Fujita et al.,⁸ dozens of papers concerning MOF-based heterogeneous catalysis have been thus far published.⁹ More specifically, Kaskel and co-workers¹⁰ demonstrated that pure MIL-101 (Cr) is an efficient catalyst for the cyanosilylation of benzaldehyde. Recently, Corma and coworkers¹¹ selected several MOFs to catalyze the cyanosilylation of benzaldehyde with TMSCN, in which they demonstrated the differences in the catalytic performance of MOFs with their homogeneous counterparts and other conventional solid catalysts.

Interestingly, despite the progress on MOFs catalyzed reactions, there has been little focus on the investigation of reaction mechanisms and subsequent improvement of their catalytic performance. As part of our efforts to develop practically effective catalysts for cyanosilylations,^{5a} we turned our attention to several typical MOFs with diverse structures and topologies by presenting their potential and limitations using cyanosilylation of aldehydes as a probe reaction. Herein, we report our preliminary results by means of a systematic study on kinetic profile, Lewis acidity effect, solvent effect, and substrate scope, etc.

Experimental

General information

All chemicals were of reagent grade, obtained from commercial sources and used without further purification unless otherwise stated. The benzaldehyde was freshly

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distilled before use and the solvents were dried by standard methods prior to use.

The FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the range of 400–4000 cm^{-1} by using potassium bromide pellets. ^1H NMR spectra were measured on a Bruker 400 MHz NMR spectrometer. The catalytic results were monitored by a gas chromatography (GC) on an SHIMADZU GC2010 Plus. Nitrogen adsorption and desorption isotherms were measured on a 3Flex instrument. The powder X-ray diffraction (XRD) pattern of MIL-101 (Cr) was obtained on a SHIMADZU XRD-6000 diffractometer with Cu K α radiation. Following conditions were used: 40 kV, 40 mA, scan speed = 4 deg/min, increment = 0.02°.

Synthesis and Characterization of MOFs

MIL-47 (V),¹² MIL-53 (Al),¹³ MIL-101 (Cr)¹⁴ and UiO-66 (Zr)¹⁵ were synthesized and purified according to the methods described in literature (see ESI†).

General procedure for cyanosilylation reactions

All kinds of MOFs were treated at 150 °C for 12 h previously to get solvent free catalysts. In a typical cyanosilylation procedure, the activated MOF was introduced into a mixture of TMSCN (1.2 mmol) and aldehyde (1.0 mmol). The reaction mixture was stirred vigorously at room temperature. The conversion of aldehyde was determined by gas chromatography at a given time interval by using tridecane as the internal standard. The yields were determined by ^1H NMR analysis. The mol percent amount of catalyst was refers to the whole formula of MOFs.

Results and discussion

Catalytic properties

The cyanosilylation reaction between TMSCN and benzaldehyde was chosen as the model reaction system to assess the catalytic properties of four MOFs, including MIL-47 (V), MIL-53 (Al), MIL-101 (Cr) and UiO-66 (Zr) (Fig. 1). As showed in Table 1, the reaction without catalyst (Table 1, entry 5) resulting only 19% conversion of benzaldehyde. However, in the presence of 1.0 mol% of catalyst, we are pleased to find that all MOFs can accelerate this reaction under solvent free conditions and MIL-101 (Cr) (Table 1, entry 3) gives the highest conversion at the same time intervals.

Since these MOFs are constructed by the same organic linker but with different metal clusters, we had initially hypothesized that the reaction rate is mainly related with the nature of metal ions in the catalysts. The coordinatively unsaturated metal ions can act as Lewis acid sites and coordinate with the carbonyls. In order to obtain experimental evidences for such interactions, we applied FT-IR spectroscopic method using benzaldehyde as a probe molecule.¹⁶ After comparison of the frequency shift between pure benzaldehyde and the MOFs absorbed benzaldehyde in FT-IR spectrum, we found that all the C=O stretching vibrations of the absorbed benzaldehyde are shifted to low-frequency. As shown in Table

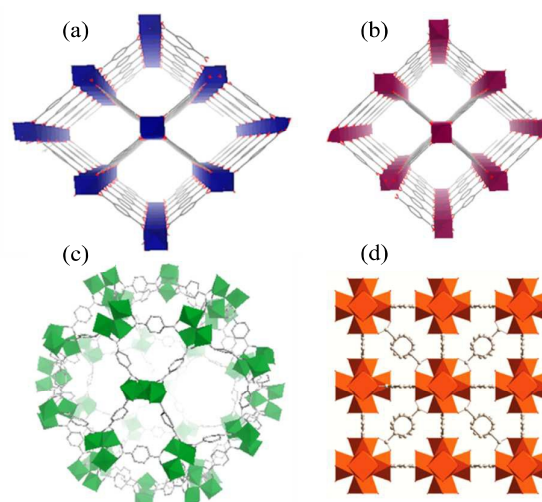


Fig. 1 The crystal structures of (a) MIL-47 (V), (b) MIL-53 (Al), (c) MIL-101 (Cr), and (d) UiO-66 (Zr). Grey, red and white balls or sticks represent carbon, oxygen and hydrogen atoms, respectively. Vanadium octahedron in (a), aluminum octahedron in (b), chromium octahedron in (c) and zirconium octahedron in (d) are in blue, rose red, green and orange, respectively. Hydrogen atoms in the framework are omitted for clarity.

2, MIL-53 (Al) (Table 2, entry 2) had a least influence on $\nu(\text{C}=\text{O})$, indicating the weak interaction between benzaldehyde and MIL-53 (Al), which consequently resulted in lowest catalytic activity. The effect of MIL-47 (V) (Table 2, entry 1) on $\nu(\text{C}=\text{O})$ is medium, and MIL-101 (Cr) (Table 2, entry 3) and UiO-66 (Zr) (Table 2, entry 4) had a strong influence on $\nu(\text{C}=\text{O})$. So, the interaction strength of benzaldehyde with the framework is in the following sequence: UiO-66 (Zr) \approx MIL-101 (Cr) > MIL-47 (V) > MIL-53 (Al).

The larger low-frequency shift of $\nu(\text{C}=\text{O})$ in MIL-101 (Cr) and UiO-66 (Zr) absorbed benzaldehyde, indicating the strong interaction between the metal centres and the carbonyl oxygen atoms. From another point of view, it should be noted

Table 1 Comparison of MOFs catalyzed cyanosilylation of benzaldehyde.^a

Entry	Catalyst	Formula	Time (h)	Conv. ^b (%)
1	MIL-47 (V)	$\text{V}^{\text{IV}}\text{O}[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$	3	46
2	MIL-53 (Al)	$\text{Al}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$	3	26
3	MIL-101 (Cr)	$\text{Cr}_3\text{XO}[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]_3$ (X=F/OH)	3	96
4	UiO-66 (Zr)	$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$	3	68
5	none	-	3	19

^a Conditions: benzaldehyde (1.0 mmol), TMSCN (1.2 mmol), catalyst (1.0 mol%), rt, 3 h.

^b The conversion of benzaldehyde was determined by GC analysis using tridecane as the internal standard.

Table 2 FT-IR spectroscopic studies on the interaction of benzaldehyde with MOFs.

Entry	MOFs	$\nu(\text{C=O})/\text{cm}^{-1}$	$\Delta\nu(\text{C=O})^a/\text{cm}^{-1}$
1	MIL-47 (V)	1693.2	10.4
2	MIL-53 (Al)	1697.3	6.3
3	MIL-101 (Cr)	1689.5	14.1
4	UiO-66 (Zr)	1688.4	15.2

^a Calculated by subtracting the carbonyl stretching vibration frequency of the observed value from that of the pure benzaldehyde (1703.6 cm^{-1}).

that, the pore size (30 to 40 \AA)^{14b} inside the framework of MIL-101 (Cr) is the largest amongst these four MOFs, which allows the easy diffusion and permeability of substrates to the exposed metal sites within the pores; while accessing to the internal surface of UiO-66 (Zr) is restricted by triangular windows with opening of 6 \AA .¹⁵ Therefore, given that MIL-101 (Cr) and UiO-66 (Zr) have similar influence on $\nu(\text{C=O})$, they showed different catalytic activities (Table 1, entry 3-4). Similarly, the low catalytic activities of MIL-47 (V) and MIL-53 (Al) might also be affected by their respective small pore sizes ($10.5 \times 11.0 \text{ \AA}$ and $8.5 \times 8.5 \text{ \AA}$).¹²⁻¹³ Furthermore, the deficiency of active Lewis acidic sites within MIL-47 (V) and MIL-53 (Al) is probably the main restriction on the catalytic performance. This study suggested that both active Lewis acid sites and pore sizes are crucial to the MOF catalyzed cyanosilylation. Taking advantage of both the biggest pore size and the strongest Lewis acidity among MOFs tested, MIL-101 (Cr) was selected to be the catalyst for further studies on cyanosilylation reaction.

With the optimal catalyst in hand, we then focused on optimizing the reaction conditions. First, different loadings of MIL-101 (Cr), 1.00 mol\% , 0.55 mol\% , 0.30 mol\% , 0.25 mol\% and 0.15 mol\% , were employed to catalyze the cyanosilylation reaction of benzaldehyde. The reactions were carried out under the following conditions: 1.0 mmol of benzaldehyde, 1.2 mmol of TMSCN, and the chosen amount of MIL-101 (Cr), and the resulting mixture was stirred vigorously at room temperature under solvent free conditions. Aliquot of the reaction mixture was taken out to be analyzed by GC to measure the conversion of benzaldehyde. The conversion of

Table 3 MIL-101 (Cr) catalyzed cyanosilylation of benzaldehyde in various solvents.^a

Entry	Solvent	Conv. ^b (%)
1	Solvent free	96
2	Heptane	87
3	Acetonitrile	9 ^c
4	Dichloromethane	11
5	Tetrahydrofuran	trace

^a Reaction conditions: benzaldehyde (1.0 mmol), TMSCN (1.2 mmol), catalyst (0.3 mol\%), solvent (3 mL), rt, 4 h .

^b The conversion was determined by GC analysis using tridecane as the internal standard.

^c Using *o*-xylene as the internal standard for GC analysis.

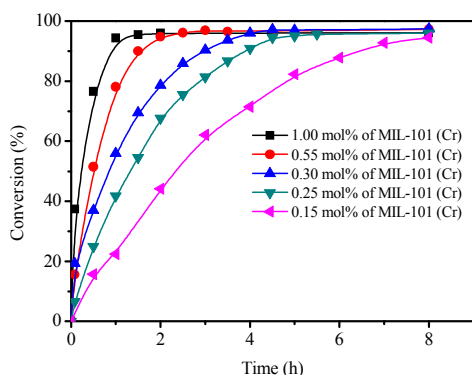
benzaldehyde vs. time was plotted in Fig. 2. The catalyst loading of MIL-101 (Cr) can be reduced to 0.3 mol\% without obvious influence on reaction outcome. In addition, 0.15 mol\% of MIL-101 (Cr) is still sufficient to activate this transformation albeit at the expense of somewhat time elongation. Finally, 0.3 mol\% of MIL-101 (Cr) was chosen for further studies (Table S1, ESI[†]).

Solvent effect

In order to investigate the role of solvents in the cyanosilylation reaction, the additions of TMSCN to benzaldehyde were carried out in different solvents. As seen in Table 3, in contrast to 96% conversion within 4 hours under solvent free condition (Table 3, entry 1), the rate of the reaction was found to decrease when heptane was added (Table 3, entry 2). Furthermore, much lower conversion was observed when the reaction was performed in CH_3CN (Table 3, entry 3) or CH_2Cl_2 (Table 3, entry 4) probably due to competitive coordination of Cr with negatively charged atoms in solvents. Finally, THF (Table 3, entry 5) can completely inhibit the reaction to occur by its strong coordination ability to unsaturated Cr sites and shut down the active Lewis acid sites. Therefore, solvent free conditions proved to be superior to those performed in conventional solvents. Hence, this reaction condition was further applied to other aldehydes.

Substrate scope

Using 0.3 mol\% of MIL-101 (Cr) as the catalyst under solvent free conditions, we next explore the generality of MIL-101 (Cr) for the cyanosilylation of various aldehydes. As indicated in Table 4, both aliphatic (Table 4, entry 1-3) and aromatic aldehydes (Table 4, entry 4-16) are well tolerated with this reaction protocol and could be converted to the corresponding *O*-trimethylsilyl cyanohydrin in good yields. Aliphatic aldehydes (Table 4, entry 1-3) and benzaldehydes bearing electron-withdrawing groups on aromatic rings (Table 4, entry 5-10) proceed smoothly to give the respective cyanosilylation

**Fig. 2** Kinetic profiles for the cyanosilylation of benzaldehyde catalyzed by different amounts of MIL-101 (Cr).

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products with high yields. Benzaldehydes bearing electron-donating groups (Table 4, entry 11–12) react much more slowly than benzaldehydes with electron-withdrawing groups. The electronic effects are more significant for *para*-substituted substrates, as the yield of 3-methoxybenzaldehyde (Table 4, entry 11) is much higher than that of *p*-anisaldehyde (Table 4, entry 12).

To further probe the size selectivity of MIL-101 (Cr), larger size of aromatic aldehydes i.e. 1-naphthal- (Table 4, entry 15) and 9-anthryl aldehydes (Table 4, entry 16) were used as substrates. It is with no surprise that significant size selectivity is observed with MIL-101 (Cr) and yields for both substrates decrease dramatically as compared with benzaldehyde in the following order: benzaldehyde > 1-naphthaldehyde > 9-anthraldehyde. The relative substrates dimension indicated that the pore windows of MIL-101 (Cr) are large enough to allow benzaldehyde ($8.21 \times 5.83 \text{ \AA}$)¹⁷ to diffuse swiftly through the channels to reach the catalytic active centres. In contrast, a significant decrease in reaction rate was observed for larger size substrates. The yield for 1-naphthaldehyde ($9.69 \times 8.29 \text{ \AA}$)¹⁷ and 9-anthraldehyde ($10.88 \times 8.60 \text{ \AA}$)¹⁷ reduced to 64% and 19% under similar conditions, respectively. As evident for

the above results, MIL-101 (Cr) demonstrated its size selectivity and applicable substrate dimensions.

It is worthy of noting that the TON of the cyanosilylation of benzaldehyde catalyzed by MIL-101 (Cr) under solvent free condition is 320 (refers to metal ions), which exhibits high catalytic performance in comparison to those protocols reported in literature (Table S2, ESI†). It suggests that this present protocol by combination of MIL-101 (Cr) as catalyst and solvent free conditions is advantageous in MOF-catalysed cyanosilylations.

Heterogeneity and reusability of catalyst

In order to check if the cyanosilylation of carbonyl compounds was promoted in a heterogeneous manner, we carried out a filtration test. After a reaction time of 1 h, the reaction mixture was divided into two equal portions. One portion was stirred continuously. And the other portion was filtered and the filtrate was stirred under the same conditions. Both of which were monitored by GC analysis. The conversion of benzaldehyde was shown in Fig. 3. It revealed that the removal of MIL-101 (Cr) completely shut down the reaction. This result verified that the reaction was catalyzed in a heterogeneous way.

Consequently, we shifted our attention to the reusability of this heterogeneous catalyst and a recycling experiment was carried out. After a reaction time of 4 h, the solid catalyst was recovered by centrifugation, then washed with ethanol and activated at 150 °C under vacuum for 12 h. The catalyst was introduced into the reaction system again. The conversion of benzaldehyde was analyzed by GC. After that, the procedure was repeated for another two times. The conversion of benzaldehyde in four consecutive runs was displayed in Fig. 4. There is only a slight decrease in the conversion of benzaldehyde in the latter three runs. Hence, MIL-101 (Cr) can be recycled and reused for several times in the cyanosilylation reaction.

Based on the experimental results and previously reported

Table 4 Cyanosilylation of Aldehydes Catalyzed by MIL-101 (Cr).^a

$\text{R}-\text{CHO} + \text{TMSCN} \xrightarrow[\text{neat, rt}]{\text{MIL-101 (Cr) (0.3 mol\%)}} \text{R}-\text{CH}(\text{NC})\text{OTMS}$			
Entry	R	Yield ^b (%)	TON ^c
1	(CH ₃) ₂ CH	100	333
2	<i>n</i> -C ₇ H ₁₅	100	333
3	<i>cyclo</i> -C ₆ H ₁₀	100	333
4	C ₆ H ₅	96	320
5	2-NO ₂ C ₆ H ₄	100	333
6	2-ClC ₆ H ₄	100	333
7	4-ClC ₆ H ₄	97	323
8	3-FC ₆ H ₄	100	333
9	4-FC ₆ H ₄	97	323
10	4-CF ₃ C ₆ H ₄	99	330
11	3-OCH ₃ C ₆ H ₄	90	300
12	4-OCH ₃ C ₆ H ₄	68	227
13	2-furanyl	93	310
14	2-thienyl	79	263
15	1-naphthyl	64	213
16 ^d	9-anthryl	19	63

^a Reaction conditions: aldehyde (1.0 mmol), TMSCN (1.2 mmol), catalyst (0.3 mol%), rt, 4 h.

^b The yields were determined by ¹H NMR spectroscopy.

^c TON = yield/(mol% of metal ions).

^d The amount of TMSCN was 3.0 mmol.

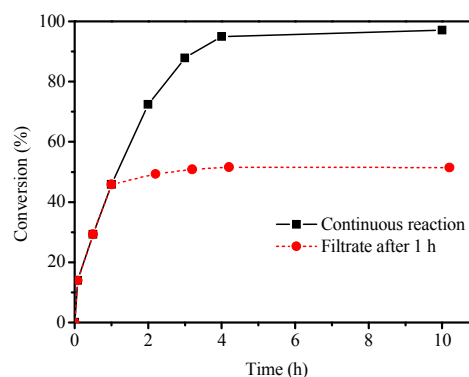


Fig. 3 The filtration test of the cyanosilylation of benzaldehyde catalyzed by MIL-101 (Cr). Reaction conditions: benzaldehyde (1.0 mmol), TMSCN (1.2 mmol), MIL-101 (Cr) (0.3 mol%), rt, and the conversion was monitored by GC analysis using tridecane as the internal standard.

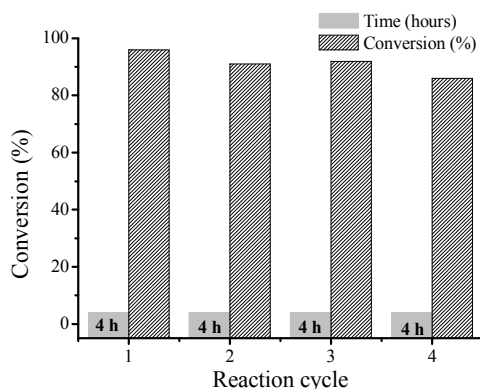
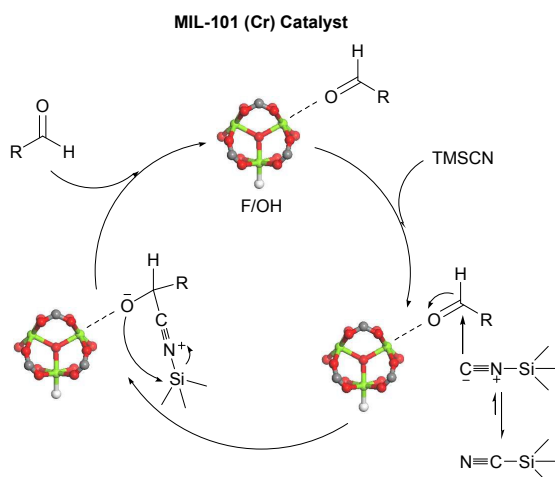


Fig. 4 Recycling test of the cyanosilylation of benzaldehyde catalyzed by MIL-101 (Cr). Reaction conditions: benzaldehyde (1.0 mmol), TMSCN (1.2 mmol), MIL-101 (Cr) (0.3 mol%), rt, 4 h.

results,¹⁷⁻¹⁸ a plausible reaction mechanism is proposed to illustrate the process of MIL-101 catalyzed cyanosilylation reaction. The labile water molecules in the channels of MIL-101 (Cr) were removed by heating to expose the unsaturated metal centres previously. The aldehydes were activated by the coordinatively unsaturated Cr centres to react with TMSCN (scheme 1). The products were replaced by aldehydes, and the catalysts were continued to activate the aldehydes in the next catalytic cycle.

Conclusions

In conclusion, we have carried out a comprehensive study on using different kinds of MOFs as catalysts for the cyanosilylation of aldehydes with TMSCN. While these MOFs tested are engineered with the same organic linker but with different metal clusters, they showed different catalytic activities. The FT-IR spectroscopic investigation showed that



Scheme 1 Proposed mechanism for the cyanosilylation reaction of carbonyl compounds catalyzed by MIL-101 (Cr).

both Lewis acidities and pore sizes in MOFs are vital to the catalytic activity. Taking both advantages, MIL-101 (Cr) was the most active catalyst. In addition, the cyanosilylation of aldehydes catalyzed by MIL-101 (Cr) was showed to be a heterogeneous way, and MIL-101 (Cr) could be recycled and reused for several times with a somewhat decrease in activity. Using MIL-101 (Cr) as catalyst, a range of aldehydes was well tolerated with this protocol, but for aromatic aldehydes with large dimensions reacted much slowly due to size selectivity. It is worthy of noting that the solvent free condition in MOFs catalyzed cyanosilylation was superior to those in conventional volatile solvents, which is more attractive to industrial applications. Future studies will be directed toward developing cheaper, more stable, or even chiral MOFs for asymmetric transformations.

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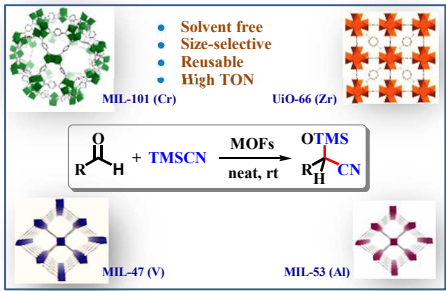
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Table of Contents

(Key Topic)



This paper presents a systematic investigation of the cyanosilylation of aldehydes with $TMSCN$ by using several MOFs as the catalysts.