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Additional Information

Room Temperature Silylation of Alcohols Catalyzed by Metal Organic Frameworks

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Commercial Al(OH)(BDC) (BDC: 1,4-benzenedicarboxylic acid) metal organic framework (Basolite A100) is a suitable heterogeneous catalyst for the silylation of benzylic and aliphatic alcohols by hexamethyldisilazane in toluene at room temperature. Al(OH)(BDC) is stable under the reaction conditions as evidenced by powder XRD and can be reused with minimal activity decrease.

Protection/deprotection of functional groups^{1, 2} is a general strategy in organic synthesis to perform selective reactions and also a method to tune the physicochemical properties of organic compounds. One of the most convenient protecting groups for hydroxyls are silyl ethers since they can be readily formed under mild reaction conditions and silyloxy groups can be later hydrolyzed in the presence of fluorides and other reagents.³ Silylation of hydroxyl group can be achieved with a variety of silylating reagents including chlorosilanes⁴⁻⁶ and alcoxysilanes,⁷ but disilazanes had become widely used since they do not form hydrogen halide, they are relatively stable to hydrolysis and have easy work-up and can be handled in the presence of moisture. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is a commercially available silylating reagent of OH and NH groups that in contrast to halosilanes forming hydrogen halides, gives ammonia as byproduct what can be tolerated by acid labile compounds.

However, the steric encumbrance of HMDS and the poorer ability of ammonia as leaving group determines that, in comparison to halosilanes, longer reaction times, harsher conditions and the presence of catalysts are needed when using HDMS for trimethylsilylation. The list of catalysts that have been reported includes trimethylsilyl chloride,⁸ sulfonic acids,⁹ ZnCl₂,¹⁰ metal chlorides,¹¹ yttrium based Lewis acid,¹²

montmorillonite K-10,¹³ zirconium sulfophenylphosphonate,¹⁴ iodine,¹⁵ H₃PW₁₂O₄₀,¹⁶ sulfonic acid-functionalized nanoporous silica,¹⁷ ZrO(OTf)₂,¹⁸ Bi(OTf)₃,¹⁹ nanocrystalline TiO₂-HClO₄,²⁰ InBr₃,²¹ 1,3-disulfonic acid imidazolium hydrogen sulfate,²² alumina-supported heteropolyoxometalates,²³ and ZrCl₄.²⁴ More related to the present work, microporous zeolite Beta in its acid form has also been reported as heterogeneous catalyst to promote silylation by HMDS as solvent and at 80 °C.²⁵ Considering the boiling point of HDMS it would be more convenient to perform the reaction at room temperature and using equimolar amounts of HDMS.

The reaction of alcohols with disilazanes requires in general Lewis acids such as transition metal ions as homogeneous catalysts. In this regard, heterogeneous catalysts have several advantages over the use of homogeneous catalysts, including easy separation of the catalyst from the reaction mixture and the possibility to reuse the solid in subsequent runs. Metal organic frameworks (MOFs) have been increasingly used as heterogeneous catalysts for liquid phase reactions at moderate temperatures.²⁶⁻³⁰ Among the major advantages of MOFs as solid catalysts those that have been found the most important are the large metal content of these solids, their large surface area and porosity and the wide variety of structures and compositions that are available to be tested. There is much current interest in exploiting the potential of MOFs in heterogeneous catalysis of liquid phase reactions, particularly those MOFs that can be purchased from chemical suppliers.³¹ In this manuscript, we report that commercially available Al(OH)(BDC) (Basolite A 100) with MIL-53(Al) structure is a suitable solid catalyst to perform derivatization of alcohols by HMDS at room temperature in equimolar amounts in toluene as solvent.

To evaluate the catalytic activity of a series of MOFs under various conditions, benzyl alcohol was selected initially as model substrate. The results are summarized in Table 1. A preliminary control in the absence of catalyst showed that HMDS does not react with benzyl alcohol at room temperature under the reaction conditions (entry 1, Table 1). As it can be seen in Table 1, Cu₃(BTC)₂ (BTC: 1,3,5-benzenetricarboxylate)

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Electronic Supplementary Information (ESI) available: Detailed experimental procedure, catalyst characterization and insitu FT-IR data analysis are provided. See DOI: 10.1039/x0xx00000x

that is one of the favourite MOFs as heterogeneous catalysts,³⁰ gives rise to 20% conversion of benzyl alcohol in 6 h (entry 2, Table 1), although the reaction does not progress to completion even after prolonged reaction times. Commercially available Fe(BTC) (Basolite F 300) gives 42 % conversion (entry 3, Table 1) that is a higher value than that achieved with Cu₃(BTC)₂. In comparison with the performance of these catalysts, Al(OH)(BDC) affords the corresponding trimethylsilyl derivative of benzyl alcohol in complete conversion and selectivity at room temperature in 6 h (entry 4, Table 1). Figure 1 provides the time conversion plot for this reaction in the presence of Al(OH)(BDC) and Fe(BTC). Al(OH)(BDC) has the crystal structure of MIL-53 that is a flexible MOF in which the channels can have a close and open configuration. In the open form in the presence of liquids, the lattice of MIL-53 defines straight channels of about 1.67×1.32 nm².³²

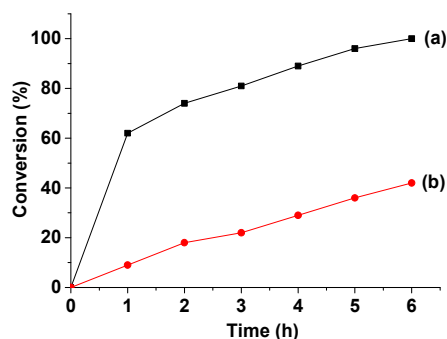


Figure 1. Time conversion plot for the silylation of benzyl alcohol with HMDS using Al(OH)(BDC) (a) and Fe(BTC) (b) as catalysts. Reaction conditions: benzyl alcohol (1 mmol), HMDS (1 mmol), catalyst (50 mg), toluene (2 mL).

Table 1. Silylation of benzyl alcohol under various reaction conditions at room temperature.^a

Entry	Catalyst	Solvent	Time (h)	Con. (%) ^b
1	-	Toluene	9	-
2	Cu ₃ (BTC) ₂	Toluene	6	20
3	Fe(BTC)	Toluene	6	42
4	Al(OH)(BDC)	Toluene	6	100
5	Al(OH)(BDC)	Toluene	6	100, ^c 96 ^d
6	Al(OH)(BDC)	Acetone	7	62
7	Al(OH)(BDC)	Acetonitrile	7	29
8	Al(OH)(BDC)	Ethanol	7	4
9	Al(OH)(BDC)	CDCl ₃	24	100
10	Al(OH)(BDC) ^e	Toluene	24	100
11	Cu ₃ (BTC) ₂ ^e	Toluene	9	18
12	Fe(BTC) ^e	Toluene	9	66
13	MIL-101(Cr) ^e	Toluene	9	88
14	Al(OH)(BDC) ^f	Toluene	24	48
15	Cu ₃ (BTC) ₂ ^f	Toluene	24	18
16	Fe(BTC) ^f	Toluene	24	61
17	MIL-53(Al)	Toluene	6	90
18	MIL-53(Al)	Toluene	24	100

19	AlCl ₃	Toluene	6	85
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^aReaction conditions: benzyl alcohol (1 mmol), HMDS (1 mmol), catalyst (50 mg), solvent (2 mL).

^bDetermined by GC.

^cFirst reuse.

^dSecond reuse.

^eWith 25 mg of catalyst.

^fReaction conditions: benzyl alcohol (1 mmol), trimethylethoxysilane (1 mmol), catalyst (50 mg), solvent (2 mL).

Besides toluene, other solvents were also screened for this reaction, but low to moderate conversions were achieved (entries 6-9, Table 1). The use of chloroform as solvent also affords complete conversion of benzyl alcohol with complete selectivity to the final product, but required 24 h reaction time. Al(OH)(BDC) was also able to perform derivatization of benzyl alcohol in complete conversion with lesser amounts, but, in this case, longer reaction times are required (entry 10, Table 1). Similar results to those achieved with Basolite A100 were also obtained with MIL-101(Cr), although in the former case lesser amounts of solid catalyst were used (entry 13, Table 1). On the other hand, we were also interested in checking the possibility of using trimethylethoxysilane for the silylation of benzyl alcohol and the observed results are given in Table 1 (entries 14-16). Using trimethylethoxysilane as reagent under identical conditions, Al(OH)(BDC), Cu₃(BTC)₂ and Fe(BTC) gave 48, 18 and 61% conversions of benzyl alcohol after 24 h. These data clearly indicate the superior activity of Al(OH)(BDC) for the silylation of benzyl alcohol with HMDS.

The catalytic activity of commercial Basolite A100 was compared with that of a MIL-53(Al) sample synthesised according to reported procedure (Table 1 entries 17 and 18). Although at long reaction times (24 h) complete silylation of benzyl alcohols was also achieved using MIL-53(Al), comparison of the temporal evolution of the reaction using Basolite A100 or MIL-53(Al) as solid catalysts showed that commercial Basolite A100 was far more efficient than the synthetic MIL-53(Al) sample (Figures S1-S3 in supplementary information for XRD and isothermal gas adsorption characterisation of MIL-53(Al) and for the comparative kinetics and Table S2 for the SEM images of the particles). This higher activity of Basolite A100 was attributed to the larger crystal size and the presence of lesser density of defects in the synthetic MIL-53, as it will be discussed below when commenting about the nature of active sites.

To put the catalytic activity of Basolite A100 into context, another experiment was carried out at room temperature under the same conditions using AlCl₃ as catalyst in equivalent amounts to that present in Al(OH)(BDC) (Table 1, entry 19). It was observed that AlCl₃ was initially similar to that of Al(OH)(BDC), but, then, it severely deactivates during the course of the reaction without reaching complete conversion (see time-conversion plot in Figure S3 in the supplementary information).

One possible advantage of heterogeneous catalysts is reusability, which was also studied for Al(OH)(BDC) under

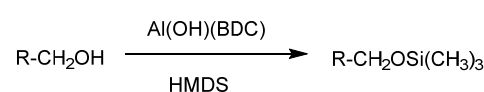
optimal reaction conditions. Basolite A100 was reused upon filtration of the solid and washing with the fresh toluene giving essentially the same temporal profile and conversion in the second use with only a very small decrease in conversion in the third use (entry 5, Table 1). These data suggest the stability of this catalyst under the present experimental conditions.

The scope of Basolite A100 as heterogeneous catalyst was screened for other benzyl alcohols containing electron donating or withdrawing substituents, aliphatic, primary, secondary, tertiary, conjugated and alicyclic alcohols at room temperature in toluene as solvent. The achieved results are presented in Table 2 and supplementary information contains the ^1H and ^{13}C NMR spectra of the products. 4-Methylbenzyl alcohol was converted to the corresponding silyl ether in complete selectivity after 5 h in the presence of Al(OH)(BDC) (entry 2, Table 2). Benzyl alcohols with phenolic hydroxy groups were also converted to their respective silyl ethers in high selectivity (entries 3-4, Table 2). 2-Methoxy-2-phenylethanol gave 97% conversion after 22 h using Al(OH)(BDC) as catalyst (entry 5, Table 2). Benzyl alcohols with electron withdrawing substituents were also converted in high yields and selectivity (entries 6-7, Table 2). Furfuryl alcohol was converted to its corresponding silyl ether in 92% after 10 h (entry 8, Table 2). Aliphatic alcohols like 1-octanol give rise to its corresponding silyl ether in complete conversion and selectivity in 8 h (entry 9, Table 2). A series of secondary alcohols including aromatic, aliphatic, acyclic were also derivatized to their respective silyl ethers with high conversion and selectivities (entries 10-13, Table 2). Allylic alcohols like geraniol and cinnamyl alcohol can also be transformed into the corresponding derivatized products in high conversion and selectivity (entries 14-15, Table 2). Condensed polycyclic compounds like 1-pyrenemethanol were also converted to the corresponding silyl ethers in high yield and selectivity after 22 h (entry 16, Table 2). Even tertiary alcohols like 2-phenyl-2-propanol do undergo silylation by HMDS in toluene under the present reaction conditions using Basolite A100 as catalyst, although the process was much slower and it was convenient to perform the reaction at 50 °C to reach complete silylation (entry 17, Table 2 and Figure S4 in the supplementary information). The slower reactivity of tertiary alcohols in agreement with the higher steric encumbrance and the fact that the reaction is being promoted on a solid surface. A competitive silylation experiment using an equimolar mixture of primary, secondary and tertiary alcohol shows that it is possible to perform consecutive silylation of primary, then, secondary and, then, tertiary alcohols with a high degree of selectivity, particularly respect to silylation of the tertiary alcohol that is comparatively much less reactive (see Figure S5 in supplementary information). In contrast, efforts to convert 2-naphthol and 2-nitrophenol to their respective silyl ethers failed under the present experimental conditions.

Chemoselective silylation of alcohols was studied for 2-aminobenzyl alcohol and 6-amino-1-hexanol as substrates and the observed results are also given in Table 2. Under the optimized reaction conditions, Al(OH)(BDC) exhibited complete silylation of 2-aminobenzyl alcohol with remarkably

high selectivity towards silylation of alcohol rather than the amino group. This was further confirmed by performing an independent control experiment using aniline as substrate under identical conditions. It was observed that no silylation was achieved for this substrate, thus, indicating that the present experimental conditions does not favour silylation of amines. Similarly, Al(OH)(BDC) gave 79% conversion of 6-amino-1-hexanol with complete selectivity towards the corresponding alcohol respect to the amino group. Further, it was observed that the crystallinity of Al(OH)(BDC) is altered during the course of this reaction. This may be due to the higher basicity of this substrate, this observation being in good agreement with earlier precedent.³³

Table 2. Silylation of various alcohols catalyzed by Al(OH)(BDC) at room temperature.^a



Run	alcohol	Time (h)	Con. (%) ^b	Sel. (%) ^b
1	benzyl alcohol	6	100	100
2	4-methylbenzyl alcohol	5	100	100
3	2-hydroxybenzyl alcohol	7	100	95(5) ^c
4	4-hydroxy-3-methoxybenzyl alcohol	22	95	96(4)
5	2-methoxy-2-phenylethanol	22	97	100
6	4-bromobenzyl alcohol	9	100	100
7	2-nitrobenzyl alcohol	24	92	100
8	furfuryl alcohol	10	92	100
9	1-octanol	8	100	100
10	cyclohexanol	10	82	100
11	1-phenylethanol	9	94	100
12	1-indanol	7	96	100
13	2-octanol	8	100	100
14	cinnamyl alcohol	7	100	91
15	geraniol	12	96	100
16	1-pyrenemethanol	22	95	100
17 ^d	2-phenyl-2-propanol	6	95	100
18	2-aminobenzyl alcohol	6	100	100
19	6-amino-1-hexanol	9	79	100
20	aniline	9	>3	-
21	2-nitrophenol	24	-	-
22	2-naphthol	24	-	-

^aReaction conditions: alcohol (1 mmol), HMDS (1 mmol), Al(OH)(BDC) (50 mg), toluene (2 mL).

^bDetermined by GC.

^cValue in parenthesis corresponds to the silylation with respect to phenolic group.

^dThe reaction was carried out at 50 °C.

Stability of Al(OH)(BDC) as catalyst was confirmed not only for their continuous reuse, but also by recording powder XRD of the used catalyst (Figure 2). As it can be seen in this Figure

2, although the material was still crystalline after its use, some shift in the position of diffraction peaks was noticed. As commented briefly earlier when describing MIL-53 as a flexible MOF, this variation in the position of the peaks appearing at lower angle is well known in the state of the art and has been referred as the “breathing effect” meaning that the structure of MIL-53 can undergo some sliding of the planes due to its framework flexibility, to increase the pore dimensions facilitating the incorporation of solvents or other guest molecules.³⁴

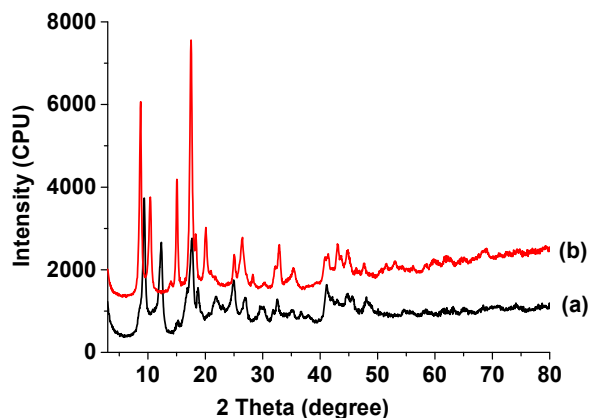


Figure 2. Powder XRD pattern of fresh (a) and two times reused (b) Al(OH)(BDC) catalyst.

Concerning the nature of active sites, it is generally assumed that the catalytic activity of MOFs as Lewis acids derives from the presence of coordinatively unsaturated sites around transition metal ions in the structure. It should be noted in this regard that the ideal structure of MIL-53(Al) constituted by chains of octahedra sharing the corners in where Al³⁺ ions are at the centre of the octahedra does not contain any unsaturated or exchangeable position around the metal ions. Therefore, it is proposed that in the present case the active sites are the population of Al³⁺ ions located at the external surface or at defects in the structure of the material. There are precedents in the literature in which also the catalytic activity of MOFs has been observed and attributed to the presence of defective sites.^{35, 36} In support of the previous proposal, a synthetic MIL-53(Al) sample having larger particle size (see Table S2 in the supplementary information) and lower defect density than Basolite A100 exhibits lower catalytic activity.

To provide further insights into the reaction mechanism, adsorption of benzyl alcohol and HMDS on thermally activated Al(OH)(BDC) and Fe(BTC) was followed by FT-IR spectroscopy. It was observed that room temperature adsorption of benzyl alcohol on Fe(BTC) results in a fast oxidation to benzaldehyde (Fig. S6). HMDS can be adsorbed on Fe(BTC) and it appears to be stable on this MOF. On Al(OH)(BDC), both benzyl alcohol and HMDS adsorb and remain stable, even upon heating at 50 °C (Fig. S7). Markedly HMDS adsorption leads to a shift in the

vNH vibration band from 1074 to 1060 cm⁻¹, providing evidence of the interaction of this group with the Lewis acid sites of Al(OH)(BDC) (see Fig. 3). When consecutive adsorption of HMDS and benzyl alcohol was performed at room temperature the IR bands at 1060 cm⁻¹ (vN-H) and 935 cm⁻¹ (vSi-N) of HMDS disappear while new bands at 1207 cm⁻¹ (vC-O) and at 1043 cm⁻¹ (v Si-O) appear. The appearance of the characteristic Si-O bond vibration clearly evidence product formation. Figure 3 provides a selection of the IR spectra of reagent adsorption on Al(OH)(BDC) to illustrate the main features of this spectroscopic study, i.e., interaction of HMDS with Lewis acid sites and the formation of the Si-O bond.

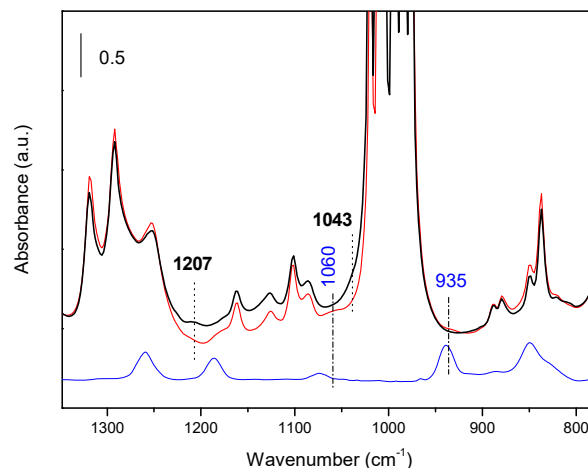


Figure 3. IR spectra at 25°C of pure HMDS (blue); adsorption of HMDS (2mbar) on Al(OH)(BDC) (red), and after 3 h of HMDS (2mbar) adsorption benzyl-alcohol (2mbar) was co-adsorbed on Al(OH)(BDC) (black).

Additionally to prove the presence of structural defects and the presence of unsaturated Al³⁺ coordination sites responsible for the catalytic activity, CO adsorption was performed on commercial Al(OH)(BDC) and Fe(BTC) and the process followed by IR spectroscopy. Upon CO adsorption, IR spectra of the Al(OH)(BDC) shows three bands at 2161, 2145 and 2137 cm⁻¹ (Figure S8 in supplementary information). The band at 2161 cm⁻¹ can be related to the presence of unsaturated Al³⁺ sites, while the band at 2145 cm⁻¹ is due to CO interacting with hydroxyl groups and the 2137 cm⁻¹ IR band is due to physisorbed CO. Analogously, in the case of Fe(BTC) (Figure S8 in supplementary information), the two IR bands at 2183 and 2175 cm⁻¹ can be ascribed to CO interacting with Fe³⁺ ions, and the IR bands at 2153 and 2135 cm⁻¹ to hydroxyl groups and physisorbed CO, respectively.

In conclusion, in the present manuscript it has been shown that commercially available Basolite A100 with MIL-53(Al) structure is a suitable solid catalyst for the room temperature silylation of benzylic, aliphatic alcohols and others. The catalyst is reusable and stable under reaction conditions and performs more efficiently than other alternative MOFs materials. Thus, the present study constitutes yet another example for the general application of MOFs as catalysts for organic transformations in liquid phase under mild reaction conditions.

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