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Metal organic frameworks as heterogeneous catalysts for the selective N-methylation of aromatic primary amines with dimethyl carbonate

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ABSTRACT

Metal organic frameworks (MOFs) with aluminium, copper and iron as central metal atoms with 1,4-benzenedicarboxylic acid (aluminium) and 1,3,5-benzenetricarboxylic acid (copper and iron) as ligands are selective and active catalysts in promoting the polymethylation of aromatic amines with dimethyl carbonate (DMC). N-methylation prevails over carbamoylation even though they are competing parallel processes. The present N-methylation protocol using DMC enjoys advantages such as convenient reaction conditions, benign, reusable, cost-effective catalyst, avoids the use of additional solvent and uses a safe, green methylating agent that only produces CO_2 and methanol as by-products.

1. Introduction

Alkylation is a general organic transformation that is widely used in industry for the production of a wide range of fine and bulk chemicals [1,2]. N-methylation of aromatic amines is still a challenging process from the catalytic point of view since aromatic amines are considerably more reluctant than aliphatic amines to undergo N-methylation [3]. Generally methylation reactions are carried out with alkyl halides [4] or dimethyl sulfate [5] which are known to be toxic, hazardous, mutagenic compounds [6] and hence it would be convenient to find the suitable alternative reagents. Besides toxicity, stoichiometric amounts of halides or sulfates wastes are formed when using these conventional methylating reactants. Recently, the need to develop more environmentally acceptable processes has triggered a great interest towards dimethyl carbonate (DMC) as safe, clean and green methylating agent [7,8] with lower negative environmental impact, with carbon dioxide and methanol being the reaction by-products in the methylation [4]. The alcohol can be recycled and used in the formation of more DMC.

One of the problems that limits the application of dialkyl carbonates and particularly DMC, as alkylating agents is that their use must be combined with adequate catalysts, because the reactivity of organic carbonates at moderate temperatures is significantly lower than that of alkyl halides or dimethyl sulfate. Thus, while methyl iodide and dimethyl sulfate do not require catalysts to effect the methylation of amines, in the case of DMC, no reaction occurs at moderate temperatures in the absence of a catalyst. Another problem that is associated with the use of DMC is its dual behaviour as methylating and carbamoylating reagent, which can lead to low selectivity towards the desired *N*-methyl derivatives [9–11]. Thus, for instance, pyrroles when reacted with DMC undergo simultaneous N-methylation and carbamoylation in the presence of phosphazene as base catalysts [12]. Scheme 1 illustrates the possible dual reactivity of DMC. Therefore, highly active and selective catalysts are needed to implement DMC and other organic carbonates such as glycerol carbonate as reagents in organic synthesis [13].

Many catalytic systems have been developed for N-alkylation of amines using DMC including zirconia [14], $Zn_{1-x}CoFe_2O_4$ [15], diphenylammonium triflate [16], phosphonium salts [17], onium salts [18], aluminophosphates [19] and DBU [20]. Recently, also transition metal containing zeolites and mesoporous MCM-41 has been reported as heterogeneous catalysts for N-alkylation of amines using DMC [21,22]. On the other hand, we have also studied the N-alkylation of amines with DMC using various organocatalysts under mild conditions [23]. In pioneering studies, Tundo and coworkers have extensively reported the methylation of amines using DMC and observed good selectivity in the presence of faujasites as heterogeneous catalysts [24–26]. Calcined Mg–Al hydrotalcite has been used as an efficient catalyst in the selective mono-N-methylation employing DMC as methylating agent in the vapour phase at 275 °C [27]. Spectroscopic and theoretical calculations using NaY zeolite indicated that DMC becomes

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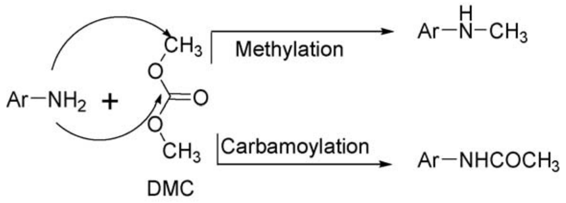


Scheme 1. Dual reactivity of DMC.

activated by the coordination of DMC to Na^+ ions present in the zeolites cavity, Na^+ acting as Lewis acid [28,29]. Al-containing MCM-41 can act as catalyst for the N-methylation of 2,4-diaminotoluene with DMC [21] as well as aniline by methanol on MCM-41 systems [30]. We anticipated that metal organic frameworks (MOFs) containing different metal ions that can act as Lewis acids could also promote N-methylation by DMC.

Metal organic frameworks (MOFs) are solid materials with infinitely extended crystal structures, which are generally constructed by cross-linking of polytopic organic ligands and metal ions or clusters via coordination bonds. Depending on the coordination geometry of the metal and the bonding preference of donating atoms as well as the geometry of the bridging ligand, polymeric structures may result in different dimensionalities with high porosity, stability and surface area and these properties make them attractive in the field of catalysis through their catalytic sites either integrated at metal nodes or located on the backbones [31–35]. The reader is referred to recent reviews on the use of MOFs as heterogeneous catalysts for organic reactions [36,37]. In the present study, we will show the catalytic activity of MOFs with different metals for the N-methylation of amines with DMC. We will present the data that indicate that the activity and the selectivity of MOFs are similar to that previously reported for zeolytes [21].

2. Experimental

2.1. General remarks

All reagents and starting materials were obtained commercially from Aldrich and used without any further purification. The percentage conversion, purity and relative yields of the final products were determined using Hewlett-Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by comparing them with authentic samples and using a GC-MS Hewlett-Packard 6890 series.

2.2. Catalyst characterization

The MOFs used in the present work are commercially available from Aldrich. $Al_2(BDC)_3$ is constituted by Al^{3+} as a nodal metal atom coordinated to 1,4-benzenedicarboxylic acid (BDC) as a ligand. This is supplied by Sigma–Aldrich with the sample code as Basolite A100 with BET surface area of $1500\,m^2\,g^{-1}$ and corresponds to MIL-53 (MIL stands for Materiaux Institute Lavoisier). The structure of Fe(BTC) is constituted by Fe^{3+} as a central metal atom coordinated to 1,3,5-benzenetricarboxylic acid (BTC) as a ligand. This is commercialized by Sigma–Aldrich with the sample code as Basolite F300 with BET surface area of $1600\,m^2\,g^{-1}$ corresponding to MIL-100. $Cu_3(BTC)_2$ is constituted with Cu^{2+} as a central metal atom with 1,3,5-benzenetricarboxylic acid (BTC) as a ligand. This is also supplied by Sigma–Aldrich with the sample code as Basolite C300 with BET surface area of $2100\,m^2\,g^{-1}$ corresponding to commercial HKUST (HKUST stands for Hong Kong University of Science and Technology) were used as received. Figs. 1 and 2 show the XRD and IR spectra of the MOFs used in the present work.

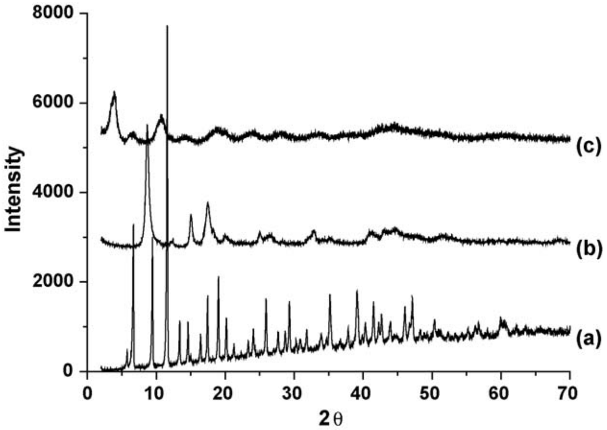


Fig. 1. Powder XRD pattern of (a) $Cu_3(BTC)_2$, (b) $Al_2(BDC)_3$ and (c) Fe(BTC).

2.3. Catalytic test

The reaction was carried out by charging 5 mL hermetic glassware that can withstand pressures up to 20 bar with 100 mg of the corresponding MOF, 5 equiv. of DMC and 50 mg of substrate. The flask that contained the reactants and catalyst was sealed and then deeply introduced into a preheated oil bath and stirred magnetically. After the required time, the reaction mixture was diluted with diethyl ether (15 mL) and filtered. A known amount of decane as external standard was added before analyzing the products by GC and GC–MS. The reusability of $Al_2(BDC)_3$ was tested for the methylation of aniline. At the end of the reaction, the mixture was filtered, washed with diethyl ether (5 mL), dried at 70 °C for 2 h and $Al_2(BDC)_3$ was reused directly without further purification for a subsequent run with fresh aniline. The same $Al_2(BDC)_3$ sample was used for four consecutive runs with some loss in activity. Powder XRD patterns of fresh and four-times used $Al_2(BDC)_3$ were recorded in a Philips X'Pert diffractometer using the CuK_α radiation (λ 1.5418 nm) at a scan rate of $0.2^\circ\,min^{-1}$. IR measurements were carried out by KBr pellet method.

3. Results and discussion

Three different types of MOFs have been tested for their catalytic activity in N-methylation of 2,4-diaminotoluene (DAT) using DMC as green methylating agent. Among the three MOFs, two contain transition metals and the third one has aluminium as the coordinating metal. In the three cases the organic ligands are benzenecarboxylic acids. The crystal structure of $Al_2(BDC)_3$ is constructed from corner sharing octahedral Al^{3+} ions linked by BDC ligands. $Al_2(BDC)_3$ has the pore dimension of 8.5 Å with good thermal stability [38]. The structure of $Cu_3(BTC)_2$ is constituted by a cluster of two metal atoms with paddle wheel shape that has a square planar coordination [39]. The BTC ligand acts as a trigonal planar ligand connecting the diatomic metal clusters [39] which defines nano cages of about 2.5 nm with windows of 0.8 nm. Similarly, the structure of Fe(BTC) is constituted by the trimers of iron octahedra sharing a common vertex μ_3-O linked by the benzene-1,3,5-tricarboxylate moieties in such a way that this leads to two types of mesoporous cages of free apertures of 25 and 29 Å, accessible through microporous windows of 5.5 and 8.6 Å [40].

3.1. Polymethylation of DAT using MOFs as solid catalysts

DAT was selected as aromatic amine, because it contains two amine groups, offering possibility to discuss regioselectivity of monomethylation and polyalkylation in addition to N-carbamoy-

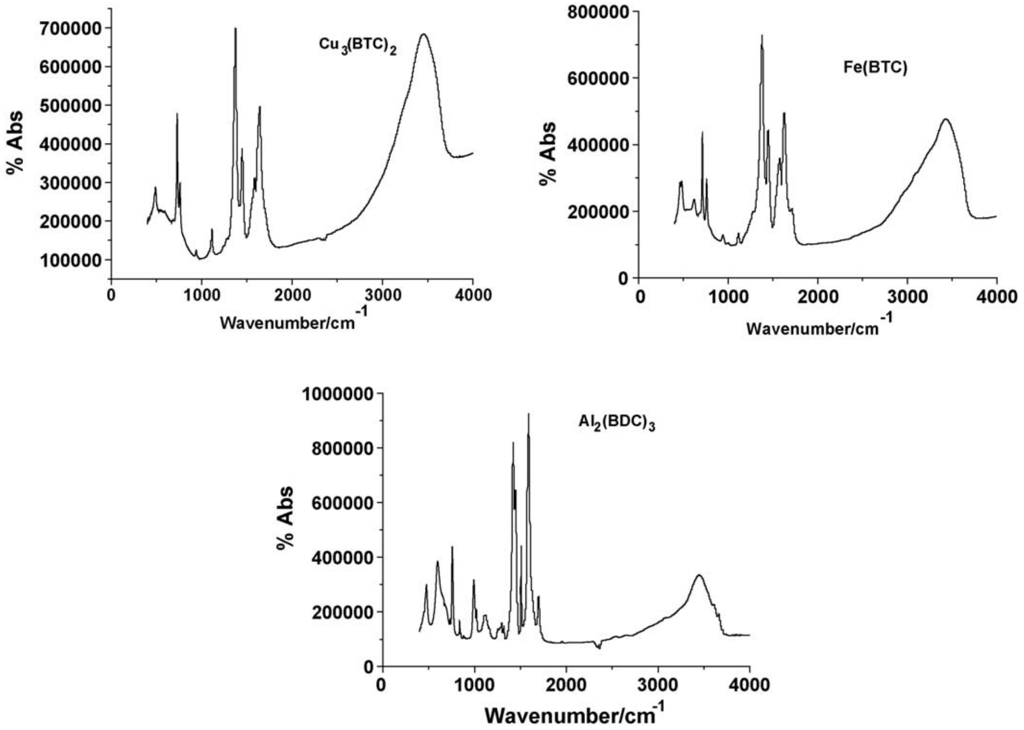


Fig. 2. IR spectra of the various MOF catalysts used in the present work.

lation. Blank controls in the absence of catalyst at 170 °C and 1:30 DAT to DMC ratio at 24 h yielded 21% DAT conversion mainly to the *para* mono methyl isomer.

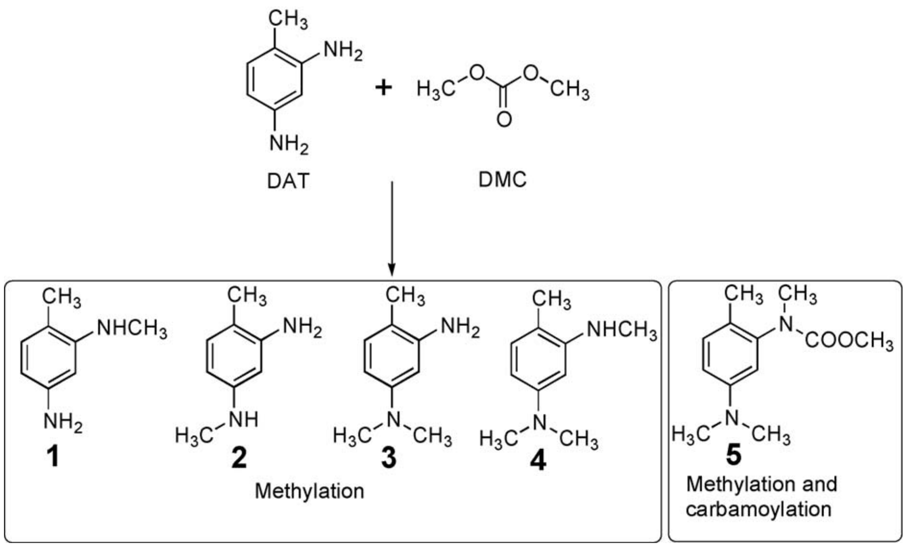
Besides the nature of MOF, other reaction parameters that have been considered are the DAT to DMC ratio (1:30, 1:20, 1:10 and 1:5; see Table 1), the reaction temperature (from 90 to 170 °C) and catalyst loading (from 50 to 100 mg). The results obtained using different DMC-to-DAT molar ratios at different temperatures are included in Table 1. The reaction mixtures contain a distribution of *N*-mono (mainly *para* with some *ortho*), *N*-di (mostly *para-*, *para-*) and minor amounts of *N*,*N*,*N*-trimethylated (mostly *para-*, *para-*, *ortho-*) derivatives of DAT, together with variable proportions of compound 5 arising from simultaneous N-methylation and N-carbamoylation. Scheme 2 shows the various products observed for the reaction between DAT and DMC. Concerning the catalytic behaviour of MOFs, it is appropriate to comment that transition

Table 1

Reaction between DAT and DMC using MOFs as catalyst under various reaction conditions.[a] The products formed are compounds 1–4 with minor amounts of compound 5 (S_{car}).

$Al_2(BDC)_3$						$Cu_3(BTC)_2$					Fe(BTC)				
T (°C)	DAT Con (%)[b]	S_{1+2}	S_3	S_4	S_{car}	DAT Con (%)[b]	S_{1+2}	S_3	S_4	S_{car}	DAT Con (%)[b]	S_{1+2}	S_3	S_4	S_{car}
DAT/DMC 1:30															
170	88	51	34	15	4	95	56	22	22	36	93	48	26	26	23
150	60	76	18	6	–	64	87	4	9	–	–	–	–	–	–
115	26	90	8	2	2	55	89	3	8	–	–	–	–	–	–
90	5	100	–	–	–	7	100	–	–	–	4	100	–	–	–
DAT/DMC 1:20															
170	85	46	40	14	2	94	52	23	25	23	90	33	40	27	4
150	80	43	42	15	2	77	48	38	14	2	82	41	48	11	–
115	42	85	12	3	1	51	90	4	6	2	34	85	15	–	–
90	3	100	–	–	–	14	100	–	–	–	5	100	–	–	–
DAT/DMC 1:10															
170	91	31	42	27	1	99	63	20	17	38	96	43	27	30	9
150	83	47	42	11	2	83	43	41	16	4	83	37	46	17	–
115	20	93	7	–	–	38	87	13	–	–	31	84	16	–	–
90	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DAT/DMC 1:5															
170	99,89[c], 88[d]	38	40	22	1	97	52	24	24	19	95	37	30	33	6
150	82	44	43	13	1	93	36	38	26	8	90	34	42	24	1
115	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
90	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

[a] DAT (50 mg), catalyst (100 mg), 8 h.
[b] Determined by GC. % Selectivity of methylation is always 100%.
[c] With 75 mg of catalyst.
[d] With 50 mg of catalyst.



Scheme 2. Products formed in a reaction between DAT and DMC.

metal exchanged zeolites exhibit similar tendency to promote a polymethylation of DAT by DMC but generally zeolites do not promote N-carbamoylation [21].

To compare the selectivity of different MOFs, we have distinguished the products arising exclusively from N-methylation (1–4) from compound 5 that is the only one containing a *N*-carbamoyl group. In Table 1, the selectivity towards carbamoylation (S_{car}) refers to the selectivity towards compound 5.

As it can be seen in Table 1, high DAT conversion to various products [polymethylation as well as carbamoylation (compound 5)] is achieved for reaction temperatures in the range of 150–170 °C for the series of the catalysts studied. The percentage conversion is very poor at temperatures 115 °C or below irrespective of DMC molar ratio. Based on related precedents in the literature about the influence of the reaction temperature in the range of 80–150 °C on the selectivity towards carbamoylation, it could be expected that lower temperatures should favour carbamoylation [26]. However this influence of the temperature was not observed and higher percentages towards carbamoylation are for $Cu_3(BTC)_2$ and Fe(BTC) only at high temperatures.

Generally, all the three MOFs accelerate the rate of the reaction of DAT at higher temperatures. To be more specific, $Al_2(BDC)_3$ gives almost exclusively methylated products and the other two MOFs with transition metal gives methylated as well as carbamoylated product 5. None of the conditions studied with three MOFs is able to give carbamoylated product with high selectivity for a reaction

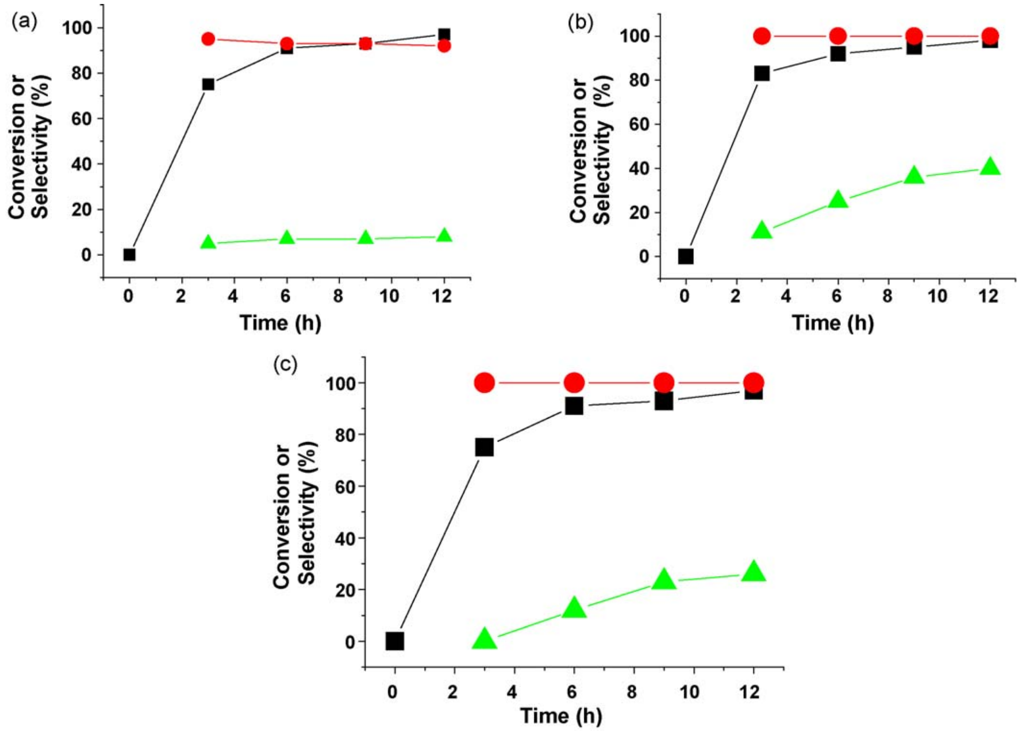


Fig. 3. Conversion of DAT or selectivity for methylation or carbamoylation for the reaction of DAT with DMC as a function of time in the presence of (a) $Al_2(BDC)_3$, (b) $Cu_3(BTC)_2$ and (c) Fe(BTC). (●) DAT conversion; (■) methylation selectivity; (▲) methylcarbamoylation selectivity. Reaction conditions: DAT (50 mg), DMC (1.1 mL), catalyst (100 mg), 8 h, 170 °C.

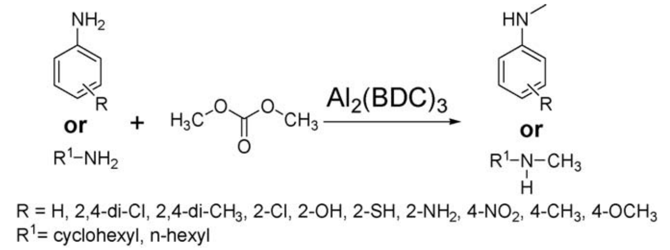
between DAT and DMC. In this context, $Cu_3(BTC)_2$ is the catalyst for which higher percentage of carbamoylated products (up to 36% selectivity) at 170 °C with excess DMC. The observed product distribution and particularly formation of compound 5 indicates that DAT reacts with DMC in the presence of MOFs giving initially mono *N*-methylated products mainly the *para* isomer as reported [21]. Then, methylation increases the nucleophilicity of the N atom and then trimethyl amine reacts with different selectivity than DAT and carbamoylation is observed but only for the trimethylated DAT derivative. Thus, according to our kinetics, N-methylation precedes always to carbamoylation which should be considered a consecutive reaction and hence selectivity of methylated products is always 100% as it can be seen from Fig. 3. This figure shows the time conversion plot and product selectivity for the reaction of DAT and DMC in the presence of the three MOF catalysts. Fe(BTC) exhibits similar activity as $Cu_3(BTC)_2$ but the carbamoylated product 5 is formed with somewhat lower yield than for $Cu_3(BTC)_2$. From the point of view of selectivity towards N-methylation, $Al_2(BDC)_3$ shows the highest selectivity. The variations in the percentage of carbamoylation should reflect the influence of the structure of MOF (cation type and cavity size) on the activity of the catalyst. In zeolites and mesoporous aluminosilicates, it has been found that large pore sizes are necessary to observe the formation of carbamoylation and it has been attributed to the larger size of the transition state leading to carbamoylation compared to methylation. In this regard, it is remarkable that also for MOFs carbamoylation is only observed for catalyst with higher porosity (BTC ligands). Also, it has been reported that the softness and hardness of the Lewis acid sites influences the ratio between methylation/carbamoylation [7]. This could explain why $Cu_3(BTC)_2$ having softer metal ion exhibits higher tendency to form carbamoylated products. For $Al_2(BDC)_3$, the effect of catalyst loading is tested at 170 °C with 5 equiv. of DMC (see Table 1) and it is noticed that DAT conversion gradually decreases from 100 to 50 mg.

3.2. $Al_2(BDC)_3$ as solid catalyst for the methylation of aromatic amines

After optimizing the reaction conditions with DAT, the present protocol was extended to other aromatic amines with various substituents as well as aliphatic amines (Scheme 3) with 5 equiv. of DMC and $Al_2(BDC)_3$ as catalyst. The results obtained are presented in Table 2. In related precedents in the literature that have used DMC as a methylating agent, an even larger excess of DMC (74-fold molar excess, with respect to amine) has been used [17,24].

The reaction of aniline with DMC in the presence of $Al_2(BDC)_3$ yields 89% conversion with 96% selectivity of methylated products. Selectivity towards dimethylation increases with the reaction time. In the case of aniline carbamoylation occurs in a minor extent. The catalytic activity of $Al_2(BDC)_3$ was also determined in the presence of an excess of aniline (500 mg) with 2 equiv. of DMC. After 24 h, 60% of aniline was methylated selectively without any carbamoylation and the mono- and dimethylaniline formed with 66% and 34% selectivity, respectively.

In a similar fashion, substituted anilines are also subjected to N-methylation. Good conversions are obtained in most of the cases except for nitro substituted aniline. The strong electron withdrawing effect of the nitro group decreases the reactivity of this aniline. Also, carbamoylated products are absent except with a small amount (4%) for *p*-toludine and anisidine (Entries 4 and 5 in Table 2). These results are in line with the previous observations on DAT that increasing nucleophilicity on the N atom favours N-carbamoylation [23]. In order to gain information on the reaction pathway an aliquot of the sample for the reaction of *p*-toludine was subjected to GC analysis after 30 min and it clearly indicates that the initial product is the mono *N*-methylated derivative and as the reaction time progress the formed mono is converted to di *N*-methyl and *N*-methyl-*N*-carbamoyl products. *Ortho* substitution with respect to the amino group makes difficult dimethylation due to steric hindrance. For this reason, 2,4-dichloroaniline and 2,4-dimethylaniline yield the corresponding mono *N*-methyl derivative with high selectivity without any carbamoylation (entries 6 and 7, Table 2).



Scheme 3. Methylation of primary aromatic and aliphatic amines with DMC in the presence of $Al_2(BDC)_3$.

Likewise, heteroatom substituted anilines are subjected to N-methylation and carbamoylation products are completely suppressed (entries 8 and 9, Table 2). Here, *O*- and *S*-methylation is only observed after N-methylation at long reaction times. This is in agreement with the relative nucleophilicity of the N, O and S atoms under the reaction conditions. Hydrogen bonding influences the course of the reaction by determining the product distribution and ultimately favouring polymethylation. Hydrogen bonding where the amino group is the hydrogen donor increases the nucleophilicity of the N atom by increasing its partial negative charge. Thus, *o*-phenylenediamine is also subjected to polymethylation without carbamoylation. Bis-(4-aminophenyl)methane is also subjected to methylation and again here polymethylation is a major product.

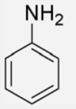
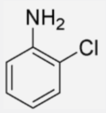
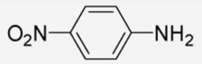
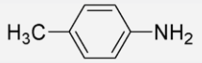
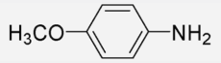
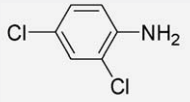
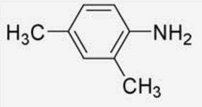
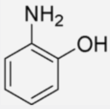
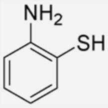
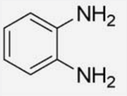
3.3. Heterogeneity of the reaction

To verify whether the observed catalysis is derived from the presence of $Al_2(BDC)_3$ or from any possible dissolved aluminium species leached from the solid to the solution, N-methylation of aniline was carried out with 20 equiv. of DMC and 100 mg of $Al_2(BDC)_3$ at 170 °C. The catalyst was filtered in hot from the reaction mixture at approximately 33% conversion of aniline. After removal of the catalyst, the solution in the absence of solid was again stirred. After 8 h, the percentage of aniline conversion was increased to 38%. This marginal increase in the conversion of aniline in the absence of catalyst may be attributed to the non-catalytic process taking place at the reaction temperature. Also the absence of dimethyl terephthalate as determined by GC analysis of the solution, as opposed to the case of aliphatic amines (see the corresponding section below), indicates the absence of free ligand. These data are compatible with the assumption that the catalysis is truly heterogeneous.

3.4. Reusability of $Al_2(BDC)_3$ as heterogeneous catalyst

Reusability of $Al_2(BDC)_3$ as heterogeneous catalyst for the reaction of aniline with DMC was also investigated under optimized conditions with 5 equiv. of DMC at 170 °C. After the reaction time, the solid was collected, washed with diethyl ether, and dried at 70 °C, and used for another consecutive run without further treatment. The catalyst exhibited a gradual decrease in the activity upon reuse, aniline conversion of the four consecutive reactions being 89, 88, 87 and 81% with minor variations in the product distributions towards lower polymethylations. Comparison of the powder XRD patterns of the fresh and four-times reused $Al_2(BDC)_3$ is provided in Fig. 4. It can be seen from Fig. 4(a) and (b)

Table 2
Selective N-methylation of various anilines with $Al_2(BDC)_3$ using DMC[a].

Entry	Substrate	Conversion[b] (%)	Selectivity[b] (%)			
			Methylation			Carbamoylation[c]
			Mono	Di	Poly	
1		89 60[d]	34 66	62 34	– –	3 –
2		80	70	29	–	1
3		53 (9)[e]	87 (100)[e]	10	–	–
4		90 (37)[e]	37 (81)[e]	59 (14)[e]	–	4 (5)
5		93	23	73	–	4
6		91	64	34	–	2
7		39	97	3	–	–
8		94[f]	5	79	14	–
9		85[f]	51	–	38	–
10		57	24	9	65	–
11	$H_2N{-}Ph{-}CH_2{-}Ph{-}NH_2$	100	–	14	86	–

[a] Reaction conditions: substrate (50 mg); DMC (5 equiv.); $Al_2(BDC)_3$ (100 mg); 170 °C; 8 h.

[b] Determined by GC. %Selectivity of methylation = $\sum$(mono + di + poly/%conversion of substrate); % Selectivity of carbomoylation = carbamoylated/% conversion of substrate.

[c] Only carbamoylated.

[d] Aniline (0.5 mL); DMC (2 equiv.); $Al_2(BDC)_3$ (100 mg); 170 °C; 24 h.

[e] Value in parenthesis corresponds to a reaction for 30 min.

[f] O- and S-methylation also occurs in long term.

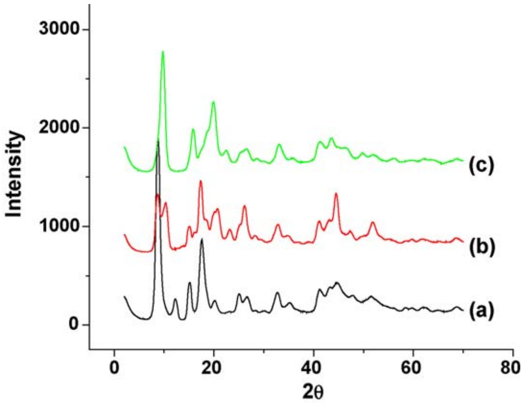


Fig. 4. Powder XRD of (a) fresh $Al_2(BDC)_3$, (b) four-times reused $Al_2(BDC)_3$ and (c) $Al_2(BDC)_3$ after the reaction with *n*-hexylamine.

that the diffraction pattern of $Al_2(BDC)_3$ changes somewhat during its use as catalyst with some variation in the intensities of some peaks. These data indicate that the crystal structure of $Al_2(BDC)_3$ is undergoing partial damage upon its reuse as heterogeneous catalyst.

3.5. $Al_2(BDC)_3$ as heterogeneous catalyst for the methylation of aliphatic amines

We are interested to see if MOFs can also act as catalysts for the DMC reaction with aliphatic amines and the corresponding product distribution. To explore this reactivity two aliphatic amines were reacted with DMC in the presence of $Al_2(BDC)_3$ as heterogeneous catalyst (Scheme 3). As expected in view of the precedents on the reactivity of aliphatic amines with DMC, in case of cyclohexyl amine as well as *n*-hexylamine methylation was accompanied with significant amount of carbamoylated products. However in the case of aliphatic amines, considerable amount of dimethyl terephthalate was determined as by-product. This indicates that $Al_2(BDC)_3$ is not totally stable under the reaction conditions and partial destruction of MOFs is gradually taking place during the course of reaction (see Fig. 4). This structural damage of $Al_2(BDC)_3$ in the reaction with aliphatic amines could reflect a strong interaction of the Al^{3+} ions of the MOF with aliphatic amines replacing terephthalate as ligand. This produces the liberation of terephthalate from the solid that becomes methylated under the reaction conditions. The reason behind the instability of MOF is most probably the considerably higher basicity of aliphatic amines compared to aromatic amines. Nevertheless, in spite of the formation of detectable amount of dimethyl terephthalate powder XRD shows that the crystal structure of $Al_2(BDC)_3$ is still maintained in a large extent after its use as catalyst in the DMC methylation of *n*-hexylamine since otherwise amorphous material or complete dissolution of the solid should have been observed.

4. Conclusions

The present results show that MOFs can be used as heterogeneous catalysts for the transformation of aromatic amines to their corresponding methylated amines using DMC. Although there are some differences in the activity and selectivity, depending on the nature of MOFs, all the three MOFs promote polymethylation with DMC. We have found that $Al_2(BDC)_3$ is more selective towards the methylation while the other two MOFs form also products arising carbamoylation. The present protocol enjoys many advantages over other catalytic system like cheap and cost-effective catalyst, use of DMC as methylating agent, avoids the use of conventional organic solvents. In addition, we have found that $Al_2(BDC)_3$ can be reused with some minor and gradual activity decrease. Therefore, this can be considered as a green protocol for selective N-methylation. In contrast, MOFs are not suitable catalyst for more basic aliphatic amines that causes the partial destruction of MOF with the liberation of dimethyl terephthalate.

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