Fine tuning of the physico-chemical properties of a MIL-53(Al) type - mesoporous

Alumina composite using a facile sacrificial-template synthesis approach

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Abstract: Though Metal Organic Frameworks (MOF's) and MOF-derived solids have been employed in various applications, especially catalysis, there is still a constant search for better performing MOF-based hybrid catalysts. In this work, we employed sacrificial template method in synthesizing MIL-53(Al) type - porous Alumina (MA) composites that exhibit different physico-chemical and catalytic properties compared to parent solids (MIL-53 and mesoporous Al_2O_3). Structural investigations demonstrated that composites possess combined structure of both the parent solids. Novel composites possess hierarchical (meso- & micro-) pores, with average pore width in the range of ~14 to 16 nm. NH_3 adsorption calorimetry and isopropanol test enabled deducting the possible nature and strength of acid-basic sites in composites. 'MA' composites show intermediate chemical properties and synergistic multifunctional catalytic behavior compared to parent solids. This work reveals, for the first time, extensively tunable physico-chemical properties of a novel class of solids: "the MIL-53(Al) type - porous alumina composites" that can have a huge potential as multifunctional catalysts.

Keywords: Sacrificial template synthesis; MIL-53(Al) - Alumina Composite; Hierarchical pores; Acid-base properties; NH_3 adsorption calorimetry

1 Introduction

Metal organic frameworks (MOFs) are porous solids whose physico-chemical properties can be extensively modified due to perpetual possibilities in varying two components constituting their structure i.e. the inorganic metal nodes and/or the organic ligands [1-5]. This tunable nature of the MOFs have been exploited in numerous applications such as gas storage, energy storage, water adsorption, catalysis, membranes etc...[4,6]. It is a fact that despite of different syntheses methods employed in preparing MOF composites possessing hierarchical pores with large pore diameters, it still remains challenging to prepare mesoporous composites, especially based on MIL-53(Al) MOF, restricting their usage in specific applications like selective sorption and many catalytic reactions [7-9]. In contrast, porous oxides like silica, alumina, zirconia etc... are known to possess more stable, ordered and easily tunable hierarchical pores but it is very difficult to finely tune their chemical or acid-base properties hence restricting their use as mere supports unlike that of perovskites, hydrotalcites, hydroxyapatites etc... that are being used as both supports and catalysts. Preparation of the MOF-porous oxide composite combining a porous solid with flexible pores and a MOF with tunable inorganic/organic entities will be an excellent solution to eliminate the drawbacks of both the class of solids that in turn can broaden their field of applications [10]. Sacrificial template (also known as reactive seeding) method introduced by Hu et.al is possibly the facile and best route to prepare a MOF-porous oxide composite [11]. Authors succeeded in preparing membrane by growing MIL-53(Al) crystals on α -alumina support using reactive seeding. Only few works have been reported so far on different alumina based sacrificial templates that act as a precursor for MIL growth [11-15]. In these works either different aluminas (α , aerogel, aluminium hydroxide, boehmite) or ligands (terephthalic & benzenetricarboxylic) were used during the syntheses. Also, all works focused on employing the sacrificial template method for the membrane and gas separation applications. To the best of our knowledge, no studies have been so far reported to obtain a detailed view on the syntheses and physico-chemical properties of MIL-53(Al) - mesoporous alumina (MA)

composites with larger hierarchical pores and the scope to use them as potential catalysts. In this study, we employed the facile sacrificial template method to tune the structural, textural and chemical properties of ‘MA’ composites which reveals the potential of these composite solids in catalytic applications. MIL-53(Al) has been selected as it has been widely studied among the MOFs not only because of its flexible structure but also due to its commending hydro-thermal stability compared to many other MOFs. MIL-53(Al) solids were reported to exhibit even higher thermal stability than MIL-53(Cr) [16,17].

2 Experimental sections

2.1 Synthesis of materials

Reagent grade chemicals such as aluminum *iso*-propoxide, poly(ethylene oxide) (PEO; $M_w = 4 \times 10^3$ g.mol⁻¹), Al(NO₃)₃.9H₂O, terephthalic acid (bdc), *N,N*-Dimethylformamide (DMF) and ethanol purchased from Alfa Aesar were employed for the syntheses of different solids. The mesoporous alumina (**A**) was prepared by sol-gel method using the aluminum *iso*-propoxide and the low molecular weight PEO as aluminium precursor and phase separation inducer respectively [18]. Pure MIL-53(Al) (**M**) was synthesized by the classical synthesis route using DMF solvent as reported elsewhere [19]. 3.75 g of Al(NO₃)₃.9H₂O (10 mmol) and 1.66 g of bdc (10 mmol) were dissolved in 30 mL DMF in a container by stirring for 15 min and the mixture was transferred to a teflon lined reactor that was heated isothermally at 150°C for 12h. During the sacrificial template syntheses of different composites, a weighed amount (0.05 or 0.1 g) of bdc was dissolved in 1.5 mL (or 3 mL for 0.1 g bdc) DMF by stirring for 15min. The above mixture was then added to 0.1 g porous Al₂O₃ solid in a teflon lined reactor heated at different temperature (150 or 200 °C) for different durations (12 or 72 h). All the as-synthesized solids were washed five times with ethanol and centrifuged prior to calcination at 200°C for 4h in air. The detailed synthesis protocols used to prepare all composites are shown in Table 1 along with their designation used in this study.

Table 1. Synthesis protocols of all composite solids

Solids	Amount of alumina (g)	Amount of bdc (g)*	Temperature (°C)	Duration (h)
MA1	0.10	0.05	150	12
MA2	0.10	0.10	150	12
MA3	0.10	0.10	150	72
MA4	0.10	0.10	200	72

*0.05 g and 0.10 g of bdc corresponds to 0.3 mmol and 0.6 mmol respectively.

2.2 Characterizations

2.2.1 Structural characterizations

X-ray diffraction (XRD) patterns were collected in the 5 – 70° 2 θ range with a 0.016° step using a PANalytical Xpert Pro diffractometer (The Netherlands) equipped with a monochromator, using Cu K α radiation (wavelength of 1.54 Å). Infra-red spectra of the solids were recorded on Safas Monaco IR700 spectrometer. The sample was prepared by mixing the powdered solid with KBr in approximately 1:9 ratios. Temperature programmed transmission IR studies were carried out with a Nicolet Nexus FTIR spectrometer at a resolution of 4 cm⁻¹ (64 scans). Self-supported sample wafers (18 mm diameter, weight of 30 mg) were prepared and introduced into a homemade IR cell allowing *in situ* studies at varying temperatures under controlled atmosphere. The cell was connected to a UHV system allowing a base pressure as low as 10⁻⁷ Torr. The samples were evacuated in vacuum for 1h at room temperature before being heated in vacuum at 10°C.min⁻¹ up to 200°C (150°C for ‘M’) and kept at this temperature for 15 min before cooling down to RT. Since the IR signals of ‘M’ was intense and attained saturation above 150°C, this solid is heated only to 150°C. ¹H MAS, ²⁷Al MAS and ¹³C CPMAS NMR

spectra were obtained at 500.03MHz, 130.29 MHz and 125.73 MHz, respectively, on an AVANCE III 500WB spectrometer with a 11.7 T magnetic field. ^1H spectra were recorded by applying an excitation pulse of $\pi/6$ (1 μs) with a 10 s interval between successive accumulations. ^{27}Al spectra were obtained for an excitation pulse of $\pi/12$ (0.4 μs) and an accumulation interval of 1 s. ^{13}C CPMAS spectra were recorded for an excitation pulse of $\pi/2$ (2.5 μs) with a scan interval of 5 s and the ^1H - ^{13}C contact time of 2ms. The number of scans for the proton, aluminium and carbon spectra was 16, 4096 and 2000, respectively. Chemical shift reference was adamantane for both ^1H and ^{13}C spectra and 1M $\text{Al}(\text{NO}_3)_3$ for ^{27}Al spectra.

2.2.2 Textural characterizations

Morphology of the solids was studied using Scanning electron microscopy (SEM) images captured after copper metallization by the Zeiss Merlin Compact (Centre Technologique des Microstructures de l'Université de Lyon) operating at 10 kV. Transmission electron microscopy (TEM) was performed on a JEOL 2100F field emission instrument operating at 200 keV. Textural characterizations were realized using nitrogen adsorption/desorption isotherms on a BelsorpMini (Bel Instruments, Japan). Prior to every analysis, samples were outgassed under vacuum (150°C for 4 h). In order to determine the specific surface areas and pore volumes of the solids, *alpha*-S and Barrett-Joyner-Halenda (BJH) models have been employed. The *alpha*-S model with nanocarbon as reference is used to determine the specific surface area and microporous volume [20,21]. BJH method is used to calculate the mesoporous volume in alumina and 'MA' composites [21]. Average pore sizes and mesoporous volumes were thus calculated from the adsorption branch of the isotherms using the BJH method between $P/P_0 = 0.42$ and 0.96.

2.2.3 Characterization of chemical properties

2.2.3.1 Thermal stability of the solids

Thermogravimetric analyses of the solids were performed in a Sensys TG-DSC (Setaram), using ~5 mg of sample placed in the quartz crucible. Air/He equimolar mixture with the total flow rate of 32 mL.min⁻¹ was used in the TGA chamber during all experiments. All samples were held at 20°C for 15 min before ramping from 20 to 700°C at a rate of 5°C.min⁻¹.

2.2.3.2 Microcalorimetric investigation of acid sites by NH₃ adsorption

In order to determine the acidic behavior of the solids, NH₃ adsorption experiments were performed at 80°C in a heat flow micro-calorimeter (Tian-Calvet type, C80 from Setaram) linked to a conventional volumetric apparatus and equipped with a Barocel capacitance manometer (Datametrix) for pressure measurements. Prior to the NH₃ adsorption, the samples (50 mg except for 'A' for which 80 mg have been used) were outgassed overnight at 200°C (1°C.min⁻¹). The differential heats of adsorption were measured as a function of coverage by repeatedly sending small doses of NH₃ over the powders until an equilibrium pressure of about 67 Pa was reached [22]. The samples were then outgassed for 30 min at the same temperature and a second adsorption was performed (still at 80 °C) until an equilibrium pressure of about 27 Pa was attained in order to calculate the amount of irreversible adsorption at this pressure. The difference between the amounts of gas adsorbed at 27 Pa during the two adsorption runs corresponded to the number of strong adsorption sites.

2.2.3.3 Isopropanol test

Isopropanol (iPrOH) test is used as a probe reaction to study the acidic and basic behaviour of the composites and to envisage the possibility of using them as catalysts. Isopropanol can be transformed to acetone by dehydrogenation on basic sites, and to propylene and *di*-isopropylether by, respectively, intra- and inter-dehydration on acid and basic sites. Tests were conducted with a high throughput reactor called Multi-R® apparatus from Teamcat Solutions that consists of mainly 3 components: the feed, the reaction section and the analytical system that are detailed elsewhere [23]. During the reaction, isopropanol vapours are fed

simultaneously into the four parallel quartz reactors using a splitter provided by the manufacturer. The reactor parameters are adjusted in such a way that every reactor is fed with an isopropanol flow having same gas composition and flowrate. Tests were done using ~25 mg of solids in a flow rate of 10 mL.min⁻¹ per reactor (10% iPrOH/He) at temperatures ranging from 100°C to 200°C. All solids were pre-treated at 200°C in 10 mL.min⁻¹ He flow for 2h before starting the isopropanol test.

3 Results and discussions

3.1 Structural investigations

X-ray diffractograms of pure MIL-53(Al) 'M' and sacrificially synthesized composite solids (MA1 to MA4) are shown in Fig. 1. X-ray diffraction peaks at $2\theta = 9.3^\circ$, 12.4° , 17.8° of 'M' confirmed the formation of MIL-53(Al) [24]. The peak at $2\theta = 12.4^\circ$ indicates the existence of some low temperature narrow pore form (MIL-53(Al)_lt) resulting from the adsorption of atmospheric moisture leading to the shrinkage of pores [25,26]. However, the relative intensity of $2\theta = 9.3^\circ$ and 12.4° peaks in 'M' differ from that of reference MIL-53(Al)_lt form (CCDC 220477) which is an indirect indication of the presence of some MIL-53(Al)_as and/or MIL-53(Al)_ht forms in this solid. In addition, XRD peaks are not too intense due to the less crystalline MIL-53(Al) (M) resulted from lower synthesis duration (12h) employed in our study compared to 72h normally used in MIL-53(Al) syntheses [13,24]. We maintained 12h to use pure MIL-53(Al) as a reference sample for the comparison with 'MA' composite solids synthesized mostly at similar conditions. Alumina exhibited amorphous nature with very low intense peaks at $2\theta = 37^\circ$, 45.7° and 65.7° that are characteristic of (311), (222) and (440) crystallographic planes respectively of γ -Al₂O₃ (JCPDS# 00-029-0063 & Fig. 1) [18]. All 'MA' composites except 'MA4' exhibited very broad peaks centred at $2\theta = 9.3^\circ$, 15° and 17.8° that make it difficult to conclude the type of MIL-53(Al) forms present in the composites as these broad peaks overlap with the peaks of reference MIL-53(Al)_as and/or MIL-53(Al)_ht forms

(Fig. 1). Such amorphous nature of sacrificially prepared MIL obtained using lower synthesis time was observed previously for sacrificial MIL-53(Al) [13,27]. Also, the broad and less intense peaks of all ‘MA1’, ‘MA2’ and ‘MA3’ composites suggest their amorphous nature due to the formation of small polycrystalline MIL-53 forms in these composites which is more evident in the textural characterization section (see Fig. 6 & Fig. 7).

Figure 1. X-ray diffractograms of M, A and ‘MA’ solids along with MIL-53(Al)_{as} (CCDC 220475), MIL-53(Al)_{ht} (CCDC 220476) and MIL-53(Al)_{lt} (CCDC 220477) as references

In the ‘MA’ composites with polycrystalline forms it is likely that either two or all the MIL-53(Al) forms (as-, ht- and lt-) can co-exist in different MIL-53 crystals. ‘MA4’ exhibited a 12.5° XRD peak confirming the presence of comparatively larger amount of lt- forms in this composite compared to others. The appearance of this lt- form peak along with clearly observable 8.8° and 15.1° XRD peaks in ‘MA4’ suggest the presence of larger MIL crystallites in this composite compared to other composites. Also, XRD peaks at $2\theta = 8.8^\circ$, 12.5° and 15.1° in ‘MA4’ suggests the co-existence of the MIL-53(Al)_{lt} and the MIL-53(Al)_{as} and/or MIL-53(Al)_{ht} form in this composite structure (Fig. 1). Moreover, the presence of 12.5° XRD peak

in ‘MA4’ implies that the larger MIL crystallites present in this composite are more likely to adsorb humidity and transform to 1t- forms compared to smaller crystallites in other composites.

XRD peaks of ‘MA2’, especially $2\theta = 9.3^\circ$ peak, exhibited slightly higher intensity compared to ‘MA1’ indicating the positive influence of the amount of ligand on the MIL crystallites growth. Similarly, ‘MA3’ synthesized using higher duration (72 h) exhibited slightly higher intensity of $2\theta = 9.3^\circ$ peak than its counterpart ‘MA2’ synthesized in 12 h depicting the fact that increase in synthesis time assists in the growth of larger MIL crystals in composites (Fig. 1). Finally, composite ‘MA4’ synthesized at higher temperature (200 °C) showed more intense and narrow peaks compared to its counterpart ‘MA3’ prepared at 150°C indicating the positive influence of temperature on crystallinity of the composite (Fig. 1). ‘MA4’ prepared using the higher values of all three syntheses parameters (0.10 g ligand, 200°C & 72 h), exhibited narrow intense peaks confirming the highly crystalline nature of this composite compared to all other composites. Hence, XRD confirmed that syntheses parameters such as ligand quantity, synthesis duration and temperature have influence on the sacrificial MIL-53 growth and hence crystallinity of the composites.

Figure 2. Infrared spectra of alumina (A), MIL-53 (M) and selected composites (MA2 & MA4) observed in (a) 4000 – 2900 cm⁻¹ and (b) 2000 – 700 cm⁻¹ regions

Fig. 2a & 2b shows the infrared spectra of selected composites (MA2 & MA4) along with parents ‘A’ and ‘M’ that were recorded at room temperature. Since all composites showed

similar IR spectra, with only variations in their peak intensities, spectra of ‘MA2’ or ‘MA4’ are the representatives of other composites (MA1 & MA3) (see Fig. S1). A broad band from 3700 cm^{-1} to 2800 cm^{-1} in all solids is attributed to the structural OH groups and also from the adsorbed water (Fig. 2a). In ‘M’, two sharp peaks are observed at around 3670 cm^{-1} and 3600 cm^{-1} respectively indicating the possible presence of bridging OH groups in $\text{AlO}_4(\text{OH})_2$ and trapped H_2O [28]. However, these OH stretching vibrations connected to $\text{AlO}_4(\text{OH})_2$ structure were not observed in ‘MA2’ and ‘MA4’ possibly because it is less intense and masked under the broad water peak. IR spectra of both ‘M’ and ‘MA’ composites exhibited vibrational bands from carboxylic acid groups in the region between 1400 and 1700 cm^{-1} [24,29,30]. The absorption bands observed at 1505 cm^{-1} and 1590 cm^{-1} can be attributed to asymmetric stretching vibrations of COO^- groups, whereas the bands at 1410 and 1440 cm^{-1} correspond to the symmetric stretching vibrations of COO^- groups. Two intense bands at $\sim 760 \text{ cm}^{-1}$ and 990 cm^{-1} confirmed the wagging CH and bending mode of structural OH groups present in all solids [28].

Figure 3. Transmission IR spectra of A, M & MA2 under vacuum at 200°C (150°C for M)

Hence, infrared of all MA solids confirmed the successful sacrificial growth of MIL on alumina. Since, the MIL-53(Al) structure is sensitive to atmospheric humidity and some of the useful information related to different OH functional groups in MIL and alumina structures were masked by the presence of a broad H_2O peak, a temperature programmed (25°C to 200°C)

transmission IR was performed using selected solids (M, A & MA2) to gain more insight on their structure.

Fig. 3 shows the transmission FTIR spectra of the selected solids under vacuum at 200°C (150°C for M) in the 3000 - 4000 cm^{-1} range. Composite 'MA2' is selected from all composites as it is the optimized solid prepared using suitable parameters employed in this study which is detailed later. 'M' exhibited a sharp peak at 3702 cm^{-1} that corresponds to the stretching mode of corner shared hydroxyl groups [$\mu_2\text{-OH}(\text{MIL})$] in the $\text{AlO}_4(\text{OH})_2$ octahedra of MIL-53(Al) structure [28]. As shown in the normal KBr spectra of 'A', a broad band is still observed at 200°C in the 3000 - 3800 cm^{-1} range depicting the interactions between the OH groups in alumina. However, three peaks at 3725 cm^{-1} , 3680 cm^{-1} and 3578 cm^{-1} become more evident at 200°C in 'A' that can be assigned to the stretching vibrations of terminal hydroxyl [$\mu_1\text{-OH}(\text{Al}_2\text{O}_3)$], doubly bridged hydroxyl [$\mu_2\text{-OH}(\text{Al}_2\text{O}_3)$] and triply bridged hydroxyl [$\mu_3\text{-OH}(\text{Al}_2\text{O}_3)$] respectively [31,32]. In composite 'MA2', three peaks were clearly observed at 3702 cm^{-1} , 3680 cm^{-1} and 3578 cm^{-1} indicating the presence of $\mu_2\text{-OH}(\text{MIL})$, $\mu_2\text{-OH}(\text{Al}_2\text{O}_3)$ and $\mu_3\text{-OH}(\text{Al}_2\text{O}_3)$ respectively. Intensity of the $\mu_1\text{-OH}(\text{Al}_2\text{O}_3)$ peak at 3725 cm^{-1} decreased drastically in composite 'MA2' suggesting that the alumina with terminal hydroxyl groups is mainly consumed for the sacrificial formation of $\text{AlO}_4(\text{OH})_2$ octahedra (in MIL structure). This also indicates that the Al^{3+} attached to $\mu_1\text{-OH}$ groups in 'A' is more reactive than other coordinated or bridged Al sites which is in agreement with previous study showing highly reactive Al(III) sites that form Lewis acid-base (Al, O) pairs [33]. It is difficult to confirm the relative contributions of $\mu_2\text{-OH}(\text{Al}_2\text{O}_3)$ and $\mu_3\text{-OH}(\text{Al}_2\text{O}_3)$ groups in the MIL formation from the overlapped IR spectra but their contributions cannot be fully neglected. The aforementioned IR results confirm the sacrificial formation of 'MA' composite structure with both MIL and Al_2O_3 functionalities.

Figure 4. Hydroxyl group vibrations observed in 4000 – 3000 cm^{-1} region during temperature programmed transmission IR spectra of (a) 'A', (b) 'M' and (c) 'MA2' solids

Further, the variations in the IR spectra of each selected solid (M, A & MA2) during the temperature ramp are shown in Fig. 4. For 'A', the intensity of the broad peak (3800 - 3000 cm^{-1}) decreased with increase in temperature from RT to 200°C (Fig. 4a). Whereas, the peaks due to 3725 cm^{-1} , 3680 cm^{-1} and 3578 cm^{-1} that corresponds to $\mu 1\text{-OH}(\text{Al}_2\text{O}_3)$, $\mu 2\text{-OH}(\text{Al}_2\text{O}_3)$ and $\mu 3\text{-OH}(\text{Al}_2\text{O}_3)$ respectively become more visible due to the removal of water molecules that masked these three hydroxyl groups at ambient conditions in alumina solid (Fig. 4a). Parent MIL-53 (M) showed a sharp peak at 3702 cm^{-1} from corner shared $\mu 2\text{-OH}(\text{MIL})$ whose intensity remained almost unchanged with temperature (Fig. 4b). The aforementioned results clearly depict that the hydroxyl groups in alumina structure are more prone to form hydrogen bonds with water in presence of humidity (ambient temperature) than compared to the $\mu 2\text{-OH}$ in MIL-53(Al) structure. Composite 'MA2' exhibits four types of hydroxyl groups that is a result of combined contribution from parent Al_2O_3 ($\mu 1\text{-OH}$, $\mu 2\text{-OH}$ and $\mu 3\text{-OH}$) and MIL-53(Al) ($\mu 2\text{-OH}$). Though, terminal $\mu 1\text{-OH}(\text{Al}_2\text{O}_3)$ are mostly consumed for MIL growth during 'MA2' synthesis, the shoulder at 3725 cm^{-1} in the 'MA2' spectra confirmed that there still exist some

terminal OH groups even in the composite structure (Fig. 4c). Intensities of the terminal $\mu 1$ -OH(Al_2O_3) and $\mu 2$ -OH(MIL) groups in ‘MA2’ remained almost steady during the temperature ramp (Fig. 4c). However, the relative intensity of $\mu 2$ -OH(Al_2O_3) peak was higher than $\mu 2$ -OH(MIL) peak from the beginning of temperature ramp until 100°C but their relative intensity reversed when the temperature was further increased to 200°C. In parallel, the intensity of the respective $\mu 3$ -OH(Al_2O_3) increased with increase in temperature. This is probably because water molecules form hydrogen bonds with $\mu 3$ -OH(Al_2O_3) hydroxyls (resulting in broad OH band) that in turn mask the $\mu 3$ -OH(Al_2O_3) peak at ambient temperature. While temperature increases, H_2O molecules linked to $\mu 3$ -OH(Al_2O_3) hydroxyls are released creating free $\mu 3$ -OH(Al_2O_3) groups that become more and more evident in the IR spectra. The decrease in the intensity of $\mu 2$ -OH(Al_2O_3) with increase in the temperature is possibly because some of these hydroxyl protons in the of $\mu 2$ -OH(Al_2O_3), that were formed by adsorbing H_2O at ambient temperature, got expelled as H_2O (by reacting with neighbouring terminal hydroxyl groups) and create some coordinatively unsaturated Al^{3+} sites. Some of the formed active Al^{3+} sites might soon co-ordinate with neighbouring $\mu 2$ -OH(Al_2O_3) groups forming more $\mu 3$ -OH(Al_2O_3) entities resulting in the variations observed in the relative intensities of $\mu 2$ -OH and $\mu 3$ -OH peaks. ‘M’ and ‘MA2’ exhibited a band at around 1018 cm^{-1} with a shoulder at 1024 cm^{-1} due to $\delta\text{C-H}$ of the structural terephthalic ligand indicate the existence of MIL-53(Al)_lt and MIL-53(Al)_ht-forms respectively (Figure S2)[28].

^{27}Al MAS NMR spectra of the ‘M’, ‘A’ and a selected composite (MA2) are shown in Fig. 5a. In ‘M’, the resonances observed between 0 and -50 ppm confirmed the formation of MIL-53(Al) structure [34]. ^{27}Al signals at $\delta = 65\text{ ppm}$ and $\delta = 8\text{ ppm}$ indicate the presence of ~25% of tetra- (Al^{IV}) and ~75% of hexa- (Al^{VI}) coordinated alumina species respectively in ‘A’ [35]. Also, these two Al signals and the ratio of their relative intensities once again demonstrated the γ -phase of alumina in ‘A’[35]. ‘MA2’ showed ^{27}Al resonances of both ‘M’ and ‘A’ solids

confirming the successful formation of a composite material with combined structure of parent MIL-53(Al) and alumina.

Figure 5. (a) ^{27}Al MAS, (b) ^1H MAS and (c) ^{13}C CP-MAS NMR spectra of alumina, MIL-53 and MA2 composite

^1H MAS NMR spectrum of ‘A’ exhibited a broad signal (10 ppm to -1.5 ppm) centred at $\delta = 4.7$ ppm suggesting the presence of protons from adsorbed water and other hydroxyl groups in the alumina structure that is in line with the broad OH peak observed in IR spectra (Fig. 5b & Fig. 2). ^1H spectrum of ‘M’ showed resonances at ca. 2.7 ppm due to $\mu_2\text{-OH(MIL)}$ protons in the $\text{AlO}_4(\text{OH})_2$, ca. 5.3 ppm due to water protons and ca. 7.5 ppm of CH protons in aromatic linker that is good in agreement with the previously reported ^1H NMR of MIL-53(Al)_It forms [24,36]. Composite ‘MA2’ exhibited proton resonances at 2.7 ppm, 4.7 ppm, 5.3 ppm (shoulder) and 7.5 ppm that are the combined resonances observed in both ‘A’ and ‘M’. In addition, a signal appeared at $\delta = -0.2$ ppm in ‘MA2’ that can be attributed to some $\mu_1\text{-OH(Al}_2\text{O}_3)$ groups in the composite [35,37]. This $\mu_1\text{-OH(Al}_2\text{O}_3)$ signal was not so evident due to the broad ^1H NMR of ‘A’ that have a low intense shoulder at -0.2 ppm but the presence of

this terminal hydroxyl group in alumina was already confirmed in IR (Fig. 4c). Hence, composite 'MA2' contains all hydroxyl protons that 'M' and 'A' solids possess which is in good agreement with IR results.

Both parent MIL-53 (M) and composite 'MA2' exhibited ^{13}C signals at $\delta = 129$ ppm, $\delta = 137$ ppm and $\delta = 171$ ppm that are attributable to the aromatic proton linked C, the quaternary C and carboxylic acid C, respectively, of the terephthalic ligand (Fig. 5c). A left shoulder appeared near aromatic proton linked C peak at ca. $\delta = 132.5$ ppm for both 'M' and 'MA2' confirming the presence of small amount of trapped ligands in their structures [34]. Moreover, very low intense signals at $\delta = 175$ ppm and $\delta = 162$ ppm for 'M' can be assigned to the presence of C of terephthalic acid (COOH) and non-protonated C of terephthalate (COO⁻) associated with non-coordinated or trapped ligands [34,38].

3.2 Textural properties of the solids

SEM images of the parent solids 'A' and 'M' along with composites are shown in Fig. 6. 'M' consists of clusters of numerous irregular shaped particles whose length varies between ~100 to ~300 nm in agreement with previous studies [39]. The porous alumina has an irregular spongy appearance in SEM depicting its amorphous nature. Microscopic image of 'MA1' indicates that the surface of alumina template was covered with needle like MIL-53 particles of ~100 to 200 nm long. Whereas in 'MA2', synthesised using larger quantity of ligand than in 'MA1', the fibrillar shaped MIL-53 particles appeared slightly longer and broader than 'MA1'. When the duration of synthesis increased from 12h in 'MA1' to 72h in 'MA3', similar fibrillar morphology was observed. SEM images of all 'MA' composites demonstrate the sacrificial formation of numerous MIL-53 particles that is in good agreement with the low intense XRD peaks due to smaller polycrystalline MIL-53 crystals.

Figure 6. Scanning electron microscopic images of MIL-53 (M), mesoporous alumina (A) and MA composites

Finally, when the temperature of synthesis increased from 150°C (MA3) to 200°C (MA4), a drastic crystallite growth was observed along both directions with larger particles appeared to be ~400 nm to 1 μ m longer and ~50 to 100 nm broader (bottom right in Fig. 6). This increase in the particle size is in agreement with the increased intensity in the XRD peaks of larger ‘MA4’ crystallites compared to all other composites. Moreover, large inter-particle pores were created between the aggregates of ‘MA4’ particles, in addition to the mesopores of parent alumina template. However, the SEM images of the ‘MA4’ composite also indicate the possibility of phase separation (alumina and MIL-53) due to increased MIL growth if the higher syntheses parameters (temperature, time & duration) are employed.

Figure 7. TEM images of MIL-53 (M), mesoporous alumina (A) and composites MA1, MA2 and MA4

In order to have clearer picture on the morphology of the irregular and smaller particles of the solids, transmission electron microscopic (TEM) images were captured (Fig. 7). TEM image of ‘M’ confirmed irregular spindle like MIL-53 particles with the length of 50 nm to 250 nm. Parent alumina (A) consists of irregular thin fibrillar particles of ~50 nm to ~100 nm long (Fig. 7). Since ‘MA1’ and ‘MA3’ showed similar morphology in SEM, TEM image of ‘MA1’ was recorded as a representative. A homogeneous distribution of both the rod like MIL-53 (~50 to 150 nm long) and the fibrillar alumina particles are observed in ‘MA1’ confirming the homogeneity in the sacrificial growth of MIL particles on alumina (Fig. 7). TEM image of ‘MA2’ demonstrated both clusters of rod like MIL-53 particles and fibrillar alumina particles

but the qualitative amount of alumina fibrillar structures seems much lower compared to that observed in the TEM image of ‘MA1’ (Fig. 7). This possibly indicates the sacrificial growth of more amounts of MIL-53 particles (consuming more alumina) in ‘MA2’ composite compared to ‘MA1’. TEM image of ‘MA4’ showed presence of longer (> 300 nm) rod like MIL-53 particles and fibrillar alumina particles and their distribution is non-homogeneous confirming the phase separation of MIL-53 and alumina particles which is in good agreement with the SEM results (Fig. 7). Hence, SEM and TEM results confirmed the successful formation of ‘MA’ composites with MIL-53 and alumina particles and also demonstrated the influence of synthesis parameters on the morphology of composites.

Figure 8. (a) N_2 adsorption/desorption isotherms, (b) BJH pore size distribution curves and (c) distribution of meso- and micro- pores in parent and composite solids

Fig. 8a & 8b show nitrogen adsorption/desorption isotherms and pore size distribution curves of selected composites (MA2 & MA4) along with parent solids. The isotherms and pore size curves of all the solids can be seen in Fig. S3. ‘M’ exhibited an isotherm of type I solids, characteristic of microporous solids, with a high α -S specific surface area of $1184 \text{ m}^2 \cdot \text{g}^{-1}$.

Parent alumina 'A' showed type IV isotherm confirming its mesoporous nature with specific surface area of $297 \text{ m}^2.\text{g}^{-1}$. Mesoporous pore volume and average pore radius of 'A' are $1.72 \text{ cm}^3.\text{g}^{-1}$ and 9.3 nm respectively (Table 2). All sacrificially prepared 'MA' composites exhibited textural properties intermediate between 'M' and 'A'. While 'M' has no mesopores and alumina exhibit large mesopores, all 'MA' composites exhibit hierarchical pores containing both the micro- and the meso- pores (Fig. 8c & Table 2.). The average pore radii of all 'MA' composites lies in the range of ~ 7 to $\sim 8 \text{ nm}$ that is much higher than the parent MIL-53 having no mesopores (Table 2).

The volume of micro- and meso- pores of all solids calculated using alpha-S and BJH models respectively are detailed in Table 2. It is clear from the table that new micropores are created by the sacrificial growth of MIL-53 in all composites at the expense of mesopores in alumina structure. In order to have more insight on the distribution of the micro- and meso- pores in new 'MA' composites, the percentage relative amount of these pores were calculated (Table 2 & Fig. 8b). After the growth of MIL-53 on alumina, the relative amount of micropore volume increased in composites compared to mesoporous alumina. Increase in the ligand amount from 0.05 g in 'MA1' to 0.10 g in 'MA2' resulted in further increase in the relative amount of micropores from 14 to 32% . An increase in synthesis duration from 12h (MA2) to 72h (MA3) slightly decreased the micropores amount (32% vs 28%) in the later (Table 2). 'MA4' synthesized at 200°C and 72h possess lower relative amount of micropores (17%) than expected compared to its counterparts 'MA3' (28%) synthesized at 150°C and 72 h . This is due to the formation of inter-particular mesopores between large 'MA4' particles which is in good agreement with the microscopy (TEM & SEM) results that indicated inter-particular pore formation in this solid.

Aforementioned results confirmed that 'MA' composites, with hierarchical pores (larger than 'M') and combined textural properties of parent MIL-53(A1) and alumina, could be successfully synthesized by tuning the syntheses parameters during sacrificial template synthesis

Table 2. Specific surface area, pore volume and distribution of pores in all solids

Solids	^a <i>alpha</i> -S SA (m ² .g ⁻¹)	^b Micropore volume <i>alpha</i> -S (cm ³ .g ⁻¹)	^c Mesopore volume BJH (cm ³ .g ⁻¹)	^c Average pore radius (nm)	^d % distribution of pore volume	
					Meso	Micro
M	1184	0.45	-	-	0%	100%
A	297	-	1.72	9.3	100%	0%
MA1	622	0.13	0.79	7.0	86%	14%
MA2	787	0.23	0.48	7.6	67%	32%
MA3	877	0.24	0.62	6.9	72%	28%
MA4	808	0.20	0.98	8.4	83%	17%

^aSpecific surface areas calculated using *alpha*-S model for all solids^bMicroporous volume determined from *alpha*-S method with non-graphitic carbon standard^cMesoporous volume and average pore size from BJH model (adsorption branch)^d% ratio of the meso- or micro- pore volume to their total pore volume

3.3 Investigation on chemical properties

3.3.1 Thermal stability

Thermogravimetric analyses (TGA) were performed with the parent and composite solids to evaluate their thermal stability (Fig. 9). For all solids, only ~12 wt.% loss (16 wt.% for alumina) was observed until 350°C due to removal of only adsorbed moisture that is also an indirect indication of the absence of any non-coordinated solvent molecules present inside their structure. As expected, the alumina ‘A’ possesses higher thermal stability among all solids with only a total weight loss of ~16 wt.% due to the removal of adsorbed moisture. This high amount of moisture in ‘A’ was in good agreement with its IR spectrum that exhibited very broad water peak. A weight loss due to rapid decomposition of structural terephthalic ligand at ~450°C was observed in case of all ‘MA’ composites. Also, it is clear from the TGA curves that parent ‘M’ has more weight loss (63 wt.%) compared to all composites (~40 & 50 wt.%) indicating that more ligands were co-ordinated with Al centres when AlNO₃.9H₂O was used as precursor in ‘M’ instead of porous Al₂O₃ in ‘MA’ composites. ‘MA1’ synthesized at 150°C using lower

ligand quantity (0.05 g) exhibited only 48 wt.% loss compared to its counterpart ‘MA2’ (0.10 g) with 60 wt.% loss. This shows that more amount of MIL was grown on alumina when higher ligand/alumina ratio was used during synthesis. ‘MA2’ and ‘MA3’, prepared during 12 and 72h, respectively, by using same ligand quantity (0.10 g) and temperature (150°C), exhibited similar weight loss (60 wt.%). This suggests that the duration of synthesis (12 and 72h) has not much influence on the amount of MIL-53 sacrificially grown on alumina. Also, the composite ‘MA4’ synthesised at higher temperature (200°C) than MA3 (150°C) showed similar weight loss (60 wt.%) depicting the fact that temperature has no influence on the amount of MIL-53 formation.

Figure 9. TGA curves of alumina (A), MIL-53 (M) and MA composites

Assuming if the amount of ligand used is completely consumed to grow MIL-53 during the composite synthesis, ‘MA1’ should theoretically possess 73 mol.% Al_2O_3 and 27 mol.% MIL-53. Whereas, composites ‘MA2’, ‘MA3’ and ‘MA4’ should theoretically have 53 mol.% Al_2O_3 and 47 mol.% MIL-53. The quantitative amounts of MIL-53 and Al_2O_3 in the composites were calculated from the TGA weight loss corresponding to the ligand decomposition (after ~400°C). While the weight loss of ‘MA1’ corresponds to 69 mol.% Al_2O_3 and 31 mol.% MIL-53, the weight loss of ‘MA2’, ‘MA3’ and ‘MA4’ correspond to 55 mol.% Al_2O_3 and 45 mol.% MIL-53. Hence, a rather good agreement is obtained between the theoretical and the experimental

amounts of MIL-53 and Al_2O_3 confirming the fact that the entire amount of ligands used during the sacrificial syntheses reacted with alumina. Also, around one third of the alumina was sacrificially consumed in 'MA1' synthesis and almost half of the alumina got consumed in the syntheses of other three composites.

Hence, TGA results confirmed that ligand/ratio (or ligand quantity) is the main synthesis parameter that has influence on the amount of sacrificially grown MIL-53 in 'MA' composites. Also, in this study a ligand quantity of 0.10 g, temperature of 150°C and synthesis duration of 12 h used to prepare 'MA2' composite are the optimum conditions to sacrificially grow sufficient amount of MIL on alumina without any phase separation (SEM & TEM results). It is worth to note that increase in the quantity of ligand may still increase the amount of MIL-53 formed in the composites but it may lead to rather complete consumption of alumina and formation of pure MIL-53 phase. All 'MA' composites showed rather similar thermal stability as of parent MIL-53 (M) indicating that the stability is still maintained for the amorphous 'MA' composites synthesized by sacrificial template method.

3.3.2 Acid-base behaviour of solids

While alumina is known to possess considerable amount of both Lewis and Brønsted acid sites, most of the MOF's including MIL-53 offers only weaker Lewis acid sites in a comparatively lower amount.[40,41] 'MA' composites are supposed to have significant catalytic interests compared to parent alumina and MIL-53 solids, providing their acidity can be tuned by varying synthesis parameters. Adsorption microcalorimetry of probe molecules has gained importance as one of the most reliable method for describing in detail the quantitative and energetic features of surface sites on solid catalysts [42]. Hence, direct assessment of the acid properties, in terms of site concentrations, strength and strength distributions of some selected solids (M, A, MA2 & MA4) studied here, has been carried out by means of this technique using ammonia as probe molecule. The acidic properties of the 'MA' composites are compared with the bare alumina

and MIL-53(Al) samples in Fig. 10. In Fig. 10a the differential heats of adsorption, Q_{diff} , have been plotted vs. ammonia uptake and the corresponding volumetric isotherms (experimental curves) can be found in Fig. 10b. The initial heats of adsorption (denoted by Q_{init}), total and irreversible amounts of ammonia adsorbed under an equilibrium pressure of 27 Pa (0.2 Torr) are summarized in Table 3. Due to the differences in the surface areas of studied powders, the ammonia uptake was determined both in terms of the amount of acid sites ($\mu\text{mol.g}^{-1}$) and in the density of acid sites ($\mu\text{mol.m}^{-2}$) (Table 3). A plot of differential heat as a function of NH_3 coverage over parent solids, ‘MA2’ and ‘MA4’ composites suggests that only a fraction of the monolayer coverage was attained on all solids in the conditions employed in this NH_3 adsorption study (Fig. S4).

Figure 10. (a) Differential heats of ammonia adsorption vs. amount of ammonia uptake and (b) volumetric adsorption isotherms of NH₃ at 80 °C

For alumina (A), the evolution of differential heats of ammonia adsorption versus coverage presents a continuous decrease from the initial value of $\sim 193 \text{ kJ.mol}^{-1}$ to as low as 30 kJ.mol^{-1} (i.e. physisorption domain) with a total NH₃ uptake of approximately $500 \mu\text{mol.g}^{-1}$ (Fig. 10a). Such behavior of alumina is the characteristic of surfaces displaying a heterogeneous population of acid site strength. At 27 Pa (0.2 Torr), total amount of acid sites that correspond to the ammonia uptake is much higher on alumina ‘A’ ($372 \mu\text{mol.g}^{-1}$) and least on MIL-53(Al) ‘M’ ($147 \mu\text{mol.g}^{-1}$) (Table 3). Whereas, ‘MA2’ ($236 \mu\text{mol.g}^{-1}$) and ‘MA4’ ($197 \mu\text{mol.g}^{-1}$) composites contain intermediate amount of acid sites that lies in the range between the parents

‘A’ and ‘M’. Also, ‘MA4’ composite that contains larger MIL-53 particles and lower amount of acid sites compared to its counterpart ‘MA2’ suggests that increase in the size of the MIL-53 particles in composite structure possibly has a negative impact on creating acid sites in the composite structure. Similar trend was observed also for the density of acid sites ($\mu\text{mol.m}^{-2}$) determined by taking into account the surface area of all solids (see Table 3). The amount (and density) of acid sites in the solids follows the order: A > MA2 > MA4 > M (Table 3).

Table 3. Data obtained from microcalorimetric measurements for some ‘MA’ composites along with parent MIL and Al_2O_3

Sample	NH ₃ adsorption at 80 °C			Strength in the distribution of acid sites ($\mu\text{mol NH}_3\text{.g}^{-1}$ sample)		
	$Q_{\text{init}}^{\text{a}}$ (kJ.mol^{-1})	NH ₃ uptake ($\mu\text{mol.g}^{-1}$)*		$50 < Q_{\text{diff}} < 100 \text{ kJ.mol}^{-1}$	$100 < Q_{\text{diff}} < 150 \text{ kJ.mol}^{-1}$	$150 < Q_{\text{diff}} < 200 \text{ kJ.mol}^{-1}$
		$n_{\text{total}}^{\text{b}}$	$n_{\text{irrev}}^{\text{c}}$			
A	193	372 (1.25)	172 (0.58)	298	72	41
MA2	128	236 (0.30)	93 (0.12)	101	78	0
MA4	150	197 (0.24)	69 (0.08)	120	39	0
M	85	147 (0.12)	58 (0.05)	67	0	0

^aInitial differential heats of NH₃ adsorption; ^bAmount of NH₃ adsorbed under an equilibrium pressure of 27 Pa; ^cAmount of irreversibly chemisorbed NH₃ under an equilibrium pressure of 27 Pa.

*Values in the parentheses are the NH₃ adsorbed amounts in $\mu\text{mol.m}^{-2}$ that corresponds to density of acid sites.

Hence, ammonia adsorption results confirmed that the sacrificial synthesis method used to prepare ‘MA’ composites enabled tuning the amount of total acid sites. Furthermore, the ammonia adsorption calorimetry allowed determining the strength and distribution of acid sites in the solids which will be discussed below.

The strength of acid sites and their distribution in the solids can be determined from the differential heat (Q_{diff}) resulting from the ammonia uptake on solids. Taking into account the catalytically relevant sites, it is considered that Q_{diff} value of the solids that possess the weaker

acid sites lies in the range of 50 to 100 kJ.mol⁻¹, for the intermediate acid sites it lies in between 100 to 150 kJ.mol⁻¹ and for the stronger acid sites in the 150 to 200 kJ.mol⁻¹ domain. High heat of adsorption and a rapid increase in ammonia uptake at low equilibrium pressures observed in parent alumina (A) isotherm indicate the chemical adsorption on the stronger acid sites with broad range of strengths which is in good agreement with previous studies that reported a heat of adsorption of ~200 kJ mol⁻¹ [43]. The initial high differential heat (Q_{init}) in 'A' (193 kJ.mol⁻¹) can be ascribed to the adsorption of ammonia on strong Lewis acid sites associated with the presence of Al³⁺ ions [44]. The irreversibly adsorbed NH₃ corresponds to an average surface density of 0.32 sites per nm². If alumina 'A' in our study possess similar density of Al sites as reported in previous study (8 aluminium per nm²), about 4% of total Al (in the form of Al³⁺) are available as Lewis sites in 'A' [45]. Q_{init} is higher for 'MA4' (150 kJ.mol⁻¹) compared to 'MA2' (128 kJ.mol⁻¹) possibly because more acid sites in the alumina structure in 'MA4' are initially exposed to ammonia due to the separated phases (alumina & MIL-53) in this composite Initial differential heat of adsorption is least for MIL-53 (80 kJ.mol⁻¹) depicting its weak acidic nature compared to other solids.

Table 3 shows that ammonia adsorption on 'A' resulted in a Q_{diff} value > 150 kJ.mol⁻¹ that corresponds to stronger acid sites (41 µmol.g⁻¹). As aforementioned, the presence of these stronger acid sites on the surface of alumina is due to the presence of Lewis acid sites (coordinatively unsaturated tetrahedral Al³⁺ sites) [44]. However, 'MA2' and 'MA4' solids that also possess tetrahedral Al sites as evidenced by NMR did not exhibit heats of adsorption in the domain of stronger acid sites (> 150 kJ.mol⁻¹). This is because almost all of the unsaturated tetrahedral Al³⁺ sites in alumina were consumed to coordinate with the ligand during the sacrificial synthesis and these coordinated tetrahedral Al sites can no more exhibit strong Lewis acid behavior. The aforementioned results are in good agreement with IR results where terminal reactive OH groups (connected to Al³⁺) were only seen in alumina 'A'. As mentioned previously, these µ1-OH(Al₂O₃) groups in 'A' were formed by reversible reaction of

atmospheric humidity and Lewis acid-base (Al, O) pairs connected to terminal and reactive Al^{3+} sites.³³ Though IR showed the presence of very small amount of Al-OH groups in composite ‘MA2’, these Al sites are always linked to OH groups and cannot exist as free unsaturated Al^{3+} like in parent alumina which is the reason for the absence of stronger acid sites in the composites. It may be also possible that these small amounts of free Al^{3+} sites in ‘MA2’ composite rest in the bulk with organic ligand covering the surface hence making it difficult for the ammonia to access these sites. This can also explain the absence of stronger acid sites (coordinatively unsaturated Al^{3+}) in ‘M’ where all the Al sites are coordinated with the ligand molecules. Hence, total ammonia adsorbed on pure MIL ‘M’ ($\sim 240 \mu\text{mol g}^{-1}$) resulted in lower differential heat that lie in the range of 85 to about 15 kJ mol^{-1} depicting the presence of smaller amount of acid sites that too in the narrow domain of weaker strengths. In composites ‘MA2’ and ‘MA4’, the incorporation of MIL-53 to alumina eliminated all stronger acid sites with heats greater than 150 kJ mol^{-1} and reduced the number of weak acid sites ($Q_{\text{diff}} < 100 \text{ kJ mol}^{-1}$).

In the domain of intermediate strengths ($100 \text{ kJ.mol}^{-1} < Q_{\text{diff}} < 150 \text{ kJ.mol}^{-1}$), the amount of acid sites follow the order ‘MA2’ > ‘A’ > ‘MA4’. Hence, we propose that $\mu_2\text{-OH}(\text{Al}_2\text{O}_3)$ and $\mu_3\text{-OH}(\text{Al}_2\text{O}_3)$ hydroxyl groups that are present in ‘A’, ‘MA2’ and ‘MA4’ (but absent in ‘M’) behave as Brønsted acid sites of medium strength. However, hexa-coordinated Al sites (Al^{VI}) observed in NMR of ‘A’ and ‘MA’ composites may also act as medium Lewis acid sites as previously reported in alumina [44]. ‘MA4’ with larger MIL crystallites contains lower amount of medium acid sites than ‘MA2’ depicting the fact that synthesis parameters have influence not only on the total amount of acid sites but also on their strength.

Acid sites with weaker strengths ($50 \text{ kJ.mol}^{-1} < Q_{\text{diff}} < 100 \text{ kJ.mol}^{-1}$) are present in both parents and composite solids. The weaker acidic sites present in the parent ‘M’ can be attributed to bridged hydroxyl [$\mu_2\text{-OH}(\text{MIL})$] groups, the only possible Brønsted type acidic sites present in its structure. It is in good agreement with the report that suggested weaker strength of the acid sites in MIL-53(Al) that are not strong enough to catalyze the aromatic alkylation reactions [46].

However, presence of mild Lewis acid sites is also reported for MIL-53(Al) though the nature of sites responsible for its acidity was not revealed [47]. Though, these Lewis acid sites were not evident from our results, the coordinated Al centres or the presence of any unsaturated Al sites due to defects may also create some weak Lewis acidity as reported previously in MOFs [40,48]. Alumina 'A' does not possess μ_2 -OH(MIL) groups but contains sufficient amount of terminal hydroxyl [μ_1 -OH(Al_2O_3)] sites that act as weaker Brønsted acid sites. Hence, bridged hydroxyl group in MIL structure and terminal hydroxyl group in alumina structure probably act as weaker Brønsted acid sites in 'M' and 'A' solids respectively. The presence of sufficient amount of μ_2 -OH(MIL) and small amount of [μ_1 -OH(Al_2O_3)] groups in the 'MA' composites, as evident in IR of 'MA2', together contribute to weaker acid sites that are Brønsted type. In addition, the possible presence of some Al centres (coordinated or unsaturated) in MIL-53 structure of composites is the reason for the weak Lewis acidity as aforementioned in 'M'.

Hence, the incorporation of MIL-53 to alumina matrix is possibly an effective way for both increasing the acidity of the MIL-53 based composite compared to pure MIL-53 possessing only weaker acid sites that are not strong enough to catalyze reactions like aromatic alkylation [46]. MIL-53 incorporation to alumina also aids in controlling the nature and strength of acid sites of the alumina by suppressing the strong acid sites and preserving its weak and medium acidity which cannot be achieved by mere physical mixing of MIL-53 and alumina, as the mechanical mixture will have sites of all three strengths (weak, medium, strong). Hence, the possible strengths and nature of acid sites in alumina (A), MIL-53 (M) and the composites (MA) deduced from this study are given below in Table 4.

Table 4. Possible nature and strength of acid and basic sites in alumina, MIL-53 and selected composites deduced both from our study and previous reports

Solids	Nature & strength of acid sites			Basic sites*
	Weak	Medium	Strong	
A	$\mu 1\text{-OH(A)}$	$\mu 2\text{-OH(A)}$, $\mu 3\text{-OH(Al)}$, Al^{VI}	Al^{3+}	Al-O^-
MA composites	$\mu 1\text{-OH(A)}$, $\mu 2\text{-OH(MIL)}$, Al metal centers	$\mu 2\text{-OH(A)}$, $\mu 3\text{-OH(A)}$, Al^{VI}	few bulk Al^{3+}	Al-O^- , deprotonated $\mu 2\text{-OH(MIL)}$, non-coordinated COO^-
M	$\mu 2\text{-OH(MIL)}$, Al metal centers	-	-	deprotonated $\mu 2\text{-OH(MIL)}$, non-coordinated COO^-

$\mu 2\text{-OH(MIL)}$: bridged hydroxyl group in the MIL-53 structure that can behave as weak Brønsted acid sites.

$\mu 1\text{-OH(A)}$: terminal hydroxyl group [$\mu 1\text{-OH(Al}_2\text{O}_3)$] in the mesoporous Al_2O_3 structure that can behave as weak Brønsted acid sites.

$\mu 2\text{-OH(A)}$: doubly bridged hydroxyl group [$\mu 2\text{-OH(Al}_2\text{O}_3)$] in the mesoporous Al_2O_3 structure that can behave as medium Brønsted acid sites.

$\mu 3\text{-OH(A)}$: triply bridged hydroxyl group [$\mu 3\text{-OH(Al}_2\text{O}_3)$] in the mesoporous Al_2O_3 structure that can behave as medium Brønsted acid sites.

Al^{VI} : hexa-coordinated Al centers that can act as medium Lewis acid sites [44].

Al^{3+} : coordinatively unsaturated tetrahedral Al ions in the mesoporous Al_2O_3 structure that act as Lewis sites.

Al metal sites: coordinated or unsaturated Al sites present in MIL-53 that can act as Lewis sites as previously reported [40,48].

*Possible basic sites assumed combining the isopropanol test and IR results

As a partial conclusion to this section, the amount and the strength of acid sites on the ‘MA’ composites were successfully modulated by sacrificial growth of MIL on alumina. ‘MA’ composites revealed intermediate amount of acid sites in their structure compared to parent alumina and MIL-53. While parent ‘M’ possessed low amount of only weak acid sites and parent ‘A’ possessed acid sites of all strengths, ‘MA’ composites exhibited weak and medium acid sites with intermediate strengths. These results clearly evidence that the number, the reactivity and the distribution of surface acid sites are significantly modified when different parameters are used during sacrificial synthesis process. The combination of alumina (A) and MIL-53 (M) by sacrificial synthesis method created new ‘MA’ composites with a surface structure exhibiting tunable acidities and hence adjustable chemical properties.

In order to have more insights on the behaviour of ‘MA’ composite as an acidic-base catalyst, isopropanol test has been conducted using the selected solids (A, M, MA2 & MA4).

Selectivities of the propylene, *di*-isopropylether and acetone at an isopropanol (iPrOH) iso-conversion of ~15% are shown in Fig. 11. Around 56 to 72% selectivity of propylene (intramolecular dehydration product) was observed on all solids. Propylene is known to be the major product of iPrOH decomposition and generally formed on acid sites that are comparatively stronger than needed to produce *di*-isopropyl ether, the minor dehydration product. Hence, higher propylene selectivities indicate the predominant acidic nature in all solids. The propylene selectivity (72%) is higher for alumina 'A', the only solid with stronger Lewis acid sites (unsaturated Al^{3+}) and with more amounts of total acid sites.

Figure 11. Product selectivities at isopropanol iso-conversion of 15%

In contrast, propylene selectivity (56%) is least for 'M' with least amount of total acid sites (Table 3) that are all weak in nature depicting the fact that weaker acid sites [$\mu 2\text{-OH(MIL)}$] in 'M' are sufficient to produce propylene. Propylene selectivities (~60%) are almost same over 'MA2' and 'MA4' composites though the former has comparatively more amount of acid sites than later (Table 3). This clearly depicts that it is not only the amount but also their initial differential heat and strength of acid sites that influence the propylene selectivity. Also, the results suggest that it is not the medium acid sites but the weaker acid sites that affect propylene

selectivity on ‘MA’ composites. If medium sites took part in propylene formation, then ‘MA2’ (78 $\mu\text{mol.g}^{-1}$) with double amount of medium acid sites than ‘MA4’ (39 $\mu\text{mol.g}^{-1}$) might have shown higher propylene selectivity. In short, the propylene is formed mainly over stronger and weaker sites in ‘A’ and over weaker acid sites in ‘M’ and ‘MA’.

It has been reported the *di*-isopropyl ether is formed over surfaces with high alkoxide coverage and by formation of a stable metal alkoxide intermediate that in turn requires both acid and basic sites [49]. In the case of alumina based solids, the only possible alkoxide forming sites are Al^{3+} (unsaturated acid sites) and AlO^- (basic sites). During pre-treatment at 200°C before tests, the water coordinated to Al^{3+} sites in ‘A’ might have been removed to form some basic Al-O^- sites as previously reported [33]. Hence, the Lewis acid sites (Al^{3+}) and some basic sites (Al-O^-) probably accounts for higher *di*-isopropyl ether selectivity (26%) in ‘A’ compared to other solids. In composites, ‘MA2’ (23%) showed higher *di*-isopropyl ether selectivity than ‘MA4’ (17%) because of the presence of more amount of medium strength acid sites [$\mu 2\text{-OH}(\text{Al}_2\text{O}_3)$, $\mu 3\text{-OH}(\text{Al}_2\text{O}_3)$, Al^{VI}] in the former than in latter. A rather linear co-relation is observed between the amount of medium acid sites and *di*-isopropyl ether selectivity confirming the role of acid sites of medium strength on ether formation. Though, ‘A’ possesses slightly lower amount (72 $\mu\text{mol.g}^{-1}$) of medium strength acid sites than ‘MA2’ (78 $\mu\text{mol.g}^{-1}$), the former still showed slightly higher ether selectivity (26%) than later (23%) possibly because of the presence of stronger Lewis acid sites (unsaturated Al^{3+}) in addition to medium sites in ‘A’. Though it is not clear about the role of small amount of Al^{3+} (in the form of Al-OH) present in the bulk of ‘MA’ composites towards *di*-isopropyl ether selectivity, it cannot be fully neglected. Finally, parent ‘M’ with no such medium and/or strong acid sites might be the reason for it to show zero selectivity to *di*-isopropyl ether once again confirming the role of medium and strong acid sites in *di*-isopropyl ether selectivity. Hence, it is clear that the composites prepared using sacrificial template method enabled creation of new acid sites, possessing medium and strong strengths

[$\mu 2\text{-OH}(\text{Al}_2\text{O}_3)$, $\mu 3\text{-OH}(\text{Al}_2\text{O}_3)$, Al^{VI} & few Al^{3+}], with entirely different catalytic properties compared to parent MIL-53 (M).

Acetone is formed by dehydrogenation of isopropanol over basic sites. Though alumina ‘A’ may possess basic Al-O^- sites as mentioned above, it exhibits negligible dehydrogenation activity and acetone selectivity (1%) due to the highly predominant acidic nature of alumina (Fig. 11). Parent ‘M’ showed much higher acetone selectivity (33%) compared to all other solids depicting relatively higher basic nature of this solid (Fig. 11).

Since, IR and NMR spectra of ‘M’ showed presence of bridged hydroxyl ($\mu 2\text{-OH}(\text{MIL})$) and COO^- group, the only possible basic sites in ‘M’ are some deprotonated $\mu 2\text{-OH}(\text{MIL})$ groups (formed via elimination of acidic proton during reaction with iPrOH and non-coordinated COO^- groups. ‘MA2’ and ‘MA4’ composites exhibited moderate acetone selectivity of 16% and 19% respectively, depicting their intermediate basic behaviour compared to parent alumina and MIL-53 (Fig. 11). This is supposedly due to the contributions from non-coordinated COO^- groups (in MIL structure), Al-O^- (in alumina) and some deprotonated $\mu 2\text{-OH}$ groups (in MIL & alumina structures) to the basicity of these composite solids. Moreover, similar acetone selectivities on ‘MA2’ and ‘MA4’ indicate that change in the syntheses parameters used to prepare them in this study has not much influence in modulating their basic sites. From the above results of the dehydrogenation of isopropanol to acetone, the possible basic sites involved in the solids are summarized in Table 4. Aforementioned results confirm that composites prepared by growing of MIL-53 on an alumina (with no dehydrogenation property) impart some basic behaviour and dehydrogenation behaviour to the resulting composites. Hence, *isopropanol* test demonstrates that the sacrificially synthesized ‘MA’ composites are capable of producing all three (propylene, ether and acetone) isopropanol reaction products, while only two reaction products are formed over parent alumina (propylene & ether) and MIL-53 (propylene and acetone). Above results confirm the synergistic and enhanced multifunctional (acid-base) catalytic behaviour of the composites compared to parent alumina and MIL-53 solids. These ‘MA’ composites can be

thus explored to conduct some tandem chemical reactions that require multifunctional catalysts possessing acid-base sites of different amounts/strengths.

In short, the ammonia calorimetric experiments along with isopropanol tests help to deduct the nature and strength of the acid-base sites in both the composite and the parent solids. Results confirmed that the acid-base properties of 'MA' composites can be tuned by varying the syntheses parameters (temperature, time, and ligand quantity). Interestingly, 'MA' composites exhibited synergistic catalytic behaviour that in turn is a result of their entirely new acid-base properties compared to the parent alumina and MIL-53 solids.

4 Conclusions

This study reveals, for the first time, the detailed physico-chemical and catalytic properties of a novel class of tunable catalyst i.e. "the MIL-53(Al) type - mesoporous alumina composite" prepared using sacrificial template method. Structural investigations of composites demonstrated the formation of polycrystalline MIL-53(Al) forms in which both MIL-53(Al)_{ht} and MIL-53(Al)_{lt} phases co-exist. Temperature programmed IR along with NMR results confirmed different types of alumina and hydroxyl groups present in the composite structure. Textural studies demonstrated the formation of hierarchical (meso- & micro-) pores in 'MA' composites with the average pore width lying in between ~14 to 16 nm and confirmed their synergistic textural properties compared to parent solids (MIL-53 & alumina). Ammonia calorimetric studies suggested that novel 'MA' composites possess acidic properties that are entirely different from what is expected from a mere mechanical mixture of parent solids. Isopropanol test confirmed the synergistic and multifunctional catalytic behaviour of the new 'MA' composites compared to MIL-53 and alumina. The possible nature of the catalytically active acido-basic sites in 'MA' composites was deducted by correlating the ammonia adsorption calorimetry and isopropanol test results. Hence, sacrificial template method allowed preparing 'MA' composites with entirely different physico-chemical properties and synergistic

multifunctional catalytic behaviour compared to parent MIL-53(Al) and alumina solids. In near future, the sacrificial template synthesis approach will be used to prepare various novel composites/catalysts by combining different types of MOFs (or ligands) and porous oxides.

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Conflicts of interest

The authors have no conflicts to declare.

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Figure captions

Figure 1. X-ray diffractograms of M, A and ‘MA’ solids along with MIL-53(Al)_{as} (CCDC 220475), MIL-53(Al)_{ht} (CCDC 220476) and MIL-53(Al)_{lt} (CCDC 220477) as references

Figure 2. Infrared spectra of alumina (A), MIL-53 (M) and selected composites (MA2 & MA4) observed in (a) 4000 – 2900 cm⁻¹ and (b) 2000 – 700 cm⁻¹ regions

Figure 3. Transmission IR spectra of A, M & MA2 under vacuum at 200°C (150°C for M)

Figure 4. Hydroxyl group vibrations observed in 4000 – 3000 cm⁻¹ region during temperature programmed transmission IR spectra of (a) ‘A’, (b) ‘M’ and (c) ‘MA2’ solids

Figure 5. (a) ²⁷Al MAS, (b) ¹H MAS and (c) ¹³C MAS NMR spectra of alumina, MIL-53 and MA2 composite

Figure 6. Scanning electron microscopic images of MIL-53 (M), mesoporous alumina (A) and MA composites

Figure 7. TEM images of MIL-53 (M), mesoporous alumina (A) and composites MA1, MA2 and MA4

Figure 8. (a) N₂ adsorption/desorption isotherms, (b) BJH pore size distribution curves and (c) distribution of meso- and micro- pores in parent and composite solids

Figure 9. TGA curves of alumina (A), MIL-53 (M) and MA composites

Figure 10. (a) Differential heats of ammonia adsorption vs. amount of ammonia uptake and (b) volumetric adsorption isotherms of NH₃ at 80 °C

Figure 11. Product selectivities at isopropanol iso-conversion of 15%

Fig. S1 IR spectra of all solids in (a) 4000 – 2900 cm⁻¹ and (b) 2000 – 700 cm⁻¹ regions

Fig. S2 IR spectra of ‘M’ and ‘MA2’ recorded using temperature programmed FTIR under vacuum at 50°C

Fig. S3 (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution curves of all solids

Fig. S4 Plot of differential heats as a function of monolayer coverage of NH₃ on ‘M’, ‘A’, ‘MA2’ and ‘MA4’ solids