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Synthesis of Aluminium Triflate Grafted MCM-41 as Water Tolerant-Acid Catalyst for Ketalization of Glycerol with Acetone

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Abstract

The aluminium triflate covalently grafted over MCM-41 (Al(TF)-MS catalyst) was synthesized by a novel route aiming to have enhanced surface acidity as compared to aluminosilicates and water tolerant mesoporous solid acid catalyst for reactions producing water as co-product. The synthesis strategy involves equimolar reaction of triflic acid and aluminium *iso*-propoxide followed by treatment with MCM-41. The direct treatment of triflic acid with Al grafted MCM-41 (Al-MCM-41) was also attempted to synthesize silica supported aluminium triflate. The MCM-41 supported aluminium triflate and triflic acid were synthesized as standard samples for comparison. The catalytic potential of the samples was studied for ketalization of glycerol with acetone into solketal. The TGA and ^{27}Al MAS NMR studies revealed the formation of aluminium triflate species on the silica surface in Al(TF)-MS sample. The covalent grafting of aluminium triflate species in Al(TF)-MS sample was confirmed from catalysis and reusability tests showing stability of the aluminium triflate species against hydrolysis by water produced during the reaction. The solvent free and selective conversion of glycerol to solketal at room temperature and simple reusability of

spent catalyst without any regeneration are some attractive features of Al(TF)-MS, which makes it a suitable catalyst for solketal synthesis.

Keywords: Aluminium triflate; MCM-41; acid catalysis; glycerol; solketal.

1. Introduction

The metal triflates received much importance as Lewis acid catalyst after their use as catalyst in amidine synthesis.[1] There has been significant exploration of metal triflates (especially triflates of lanthanides and transition metals) as excellent Lewis acid catalysts in numerous organic reactions showing their potential for replacement of conventional moisture sensitive Lewis acid catalysts such $AlCl_3$, BF_3, $SnCl_4$, $TiCl_4$ etc.[2] The supported metal triflates were synthesized for important acid catalyzed reactions[3] to make them reusable and also to enhance their activity by dispersing their small amount over the support surface.

The aluminium grafted MCM-41 (i.e., Al-MCM-41) materials, prepared by post grafting method, have been extensively studied as solid acid catalyst[4] showing higher acidity content compared to aluminosilicates (Al-MCM-41) prepared by direct hydrothermal synthesis. The Al-MCM-41 materials possess predominantly Brønsted acidity along with Lewis acidity depending upon Al content in framework (which produces Brønsted acidity) and in extra framework (which generates Lewis acidity).[5(a)] The amount of acidity increases with increasing the framework Al content.[5(b)] However, the acidity in these aluminosilicates is usually very less.[5(a-c)] To further enhance the acidity of Al-MCM-41 materials and also to have predominantly Lewis acidity looking the wide scope of Lewis acid catalysts, in the present work, the aluminium triflate species supported over MCM-41 was aimed to synthesize. The aluminium triflate ($Al(OTf)_3$) has received much attention as Lewis acid catalyst among various metal triflates.[6-12] However, aluminium triflate in the supported form has not been studied, which also motivated us to study the catalytic potential of aluminium triflate supported over MCM-41 as solid acid catalyst.

Glycerol has become a very good starting raw material for several value added chemicals because of increasing availability of glycerol from biodiesel production and hydrolysis of fats and vegetable oils, which reduced glycerol cost tremendously. One of the very important conversions of glycerol is ketalization with acetone to form solketal (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane), which is useful as oxygenated fuel additive.[13, 14] The solketal has also been found useful intermediate for synthesis of various valuable products.[15] The major issue with solketal synthesis reaction is formation of water as co-product, which deactivates the acidic sites and also causes the back reaction (hydrolysis). This has also been a serious problem in various acid catalyzed reactions involving water as reactant or co-product such as olefin hydration, dehydration of alcohols, esterification reactions, etc. The solvents such as benzene, toluene, chloroform, dichloromethane, etc. have been used to remove the formed water by distilling off to increase the yield of the solketal[16], which is not practicable owing to the hazardous effect of these solvents.

The solid acid catalysts such as zeolite Beta (Si/Al = 16),[17] sulfonic acid-functionalized mesoporous silicas,[18] mesoporous substituted silicates (Hf-TUD-1, Zr-TUD-1 and Sn-MCM-41),[19] silica supported heteropoly acids,[20] acid functionalized carbon–silica composite,[21] Ni–Zr supported on mesoporous activated carbon,[22] zirconia and modified zirconia,[23] etc. have been studied for the solvent free synthesis of solketal from glycerol and acetone. The ketalization of glycerol with acetone needs a highly stable (towards water) and recyclable catalytic system for the viability of this process. It is also highly desirable, especially in the reactions producing water as co-product, to have stable acid catalyst against poisoning by water (weakening of acid sites) and irreversible/ non-leachable loading of catalytic species (e.g., here metal triflate) over the support surface to avoid the loss of activity in subsequent reaction cycles.

There is couple of reports on the water tolerant acid catalyst[17] or methodology[18] avoiding the adverse effect of water on catalyst and product yield in the solketal synthesis. The zeolite Beta with Si/Al=16 was found to be best acid catalyst as compared to zeolites with low Si/Al ratio (14 & 28) for the reaction of glycerol with acetone and formaldehyde at 70°C.[17] The water-tolerance of the zeolite Beta (Si/Al=16) was explained in terms of its high siliceous composition providing hydrophobic environment inside the pores to expel off the water from the pores, thus preserving the integrity and strength of the acid sites and minimizing the reverse reaction. The zeolites being microporous have serious issue of poor reactant diffusion efficiency, especially for bulky molecules. So looking at broad range applicability of solid acid catalyst in acetalization reactions, it would be desirable to have a mesoporous solid acid material with high activity and water tolerance. A simple synthesis methodology involving use of versatile (for small to bulky substrates), robust (stable; reusable) and inexpensive metal based catalytic system, working under ambient and solvent free conditions would be highly beneficial for the sustainability of the process.

In the present work, aiming the synthesis of a stable solid acid catalyst for reactions producing water as co-product and with significantly high acidity, the synthesis of aluminium triflate supported over mesoporous silica (MCM-41) was attempted. We developed a two-step single-pot synthesis protocol, which gave highly stable aluminium triflate species grafted (covalently bonded) over MCM-41 catalyst having significantly high acidity with predominantly Lewis acid sites. The aluminium triflate grafted over MCM-41 showed excellent activity and stability (water tolerance) in ketalization reaction of glycerol with acetone. The study shows that this material can be suitable as water tolerant acid catalyst in many reactions producing water as co-product.

2. Experimental

2.1. Materials

The tetraethyl orthosilicate (TEOS; >99%) and aluminium triflate (99%) were purchased from Aldrich. The toluene (99%) and sodium hydroxide (NaOH; >97%), were purchased from Merck, India. The cetyl trimethylammonium bromide (CTAB; 98%), aluminium *iso*-propoxide (AIP; 97%), triflouromethanesulfonic acid (triflic acid; TfOH; TFA; 97%), dichloromethane (99%), glycerol (98%) and acetone (99.9%) were procured from SD Fine chemicals, India. All the chemicals were used without any further purification.

2.2. Synthesis of Samples

2.2.1. *Synthesis of MCM-41 and Al-MCM-41*

The mesoporous silica (MCM-41; MS) was synthesized by basic hydrolysis of TEOS using cetyltrimethylammonium bromide (CTAB) as a template and the Al grafted mesoporous silica (Al-MCM-41; Al-MS) was synthesized by the post synthesis grafting method.[5(d)] The CTAB (7.44 g) was dissolved in double distilled water (170 mL) followed by addition of NaOH (1.22 g) and the mixture was stirred to get clear solution. To the resulting solution, TEOS (17.68 g) was added drop wise in 20 min. under vigorous stirring to obtain final gel composition (0.25 TEOS : 0.09 NaOH: 27.8 H_2O: 0.06 CTAB). Thus formed gel was allowed to react for 36 h under stirring at room temperature. The solid mass was then filtered, washed with distilled water and dried at 80°C for 8 h in oven, followed by calcination at 550°C for 6 h in static air to get MCM-41 (called MS). For the synthesis of Al grafted MCM-41 sample (Al-MS) with Si/ Al molar ratio of 20; MCM-41 (2 g) was added to the solution containing 0.338 g aluminium *iso*-propoxide dissolved in 150 mL toluene and allowed to stir at room temperature for 24 h. The solid product was then filtered, dried at 90°C for 10 h and calcined at 550°C for 3h to get Al-MS sample.

2.2.2. Synthesis of MCM-41 supported samples

The covalently grafted aluminium triflate over MCM-41 was synthesized by a two-step single pot synthesis method. The triflic acid (TFA; 1.65 mmol) solution in toluene (25 mL) was slowly added to 25 mL solution of toluene containing aluminium *iso*-propoxide (1.65 mmol) and the resulting solution was stirred at room temperature for 2 h. In this solution, MCM-41 (2 g) was added slowly under stirring and the mixture was kept under stirring at room temperature for 24 h. The solid product was then filtered, washed (with toluene) and dried at 100°C in static air for 12 h. The sample was named as Al(TF)-MS.

The direct treatment of Al-MCM-41 with TFA was attempted to examine the possibility of the synthesis of supported aluminium triflate species by functionalizing the grafted Al with triflate group (TfO- group). For this, 25 mL solution of toluene containing TFA (1.65 mmol) was added to the 25 mL solution of toluene containing Al-MCM-41 (2 g). The mixture was kept under stirring at room temperature for 24 h, solid product was then filtered, washed (with toluene) and dried at 100°C in static air. This sample was named as TFA/Al-MS.

The MCM-41 supported aluminium triflate (AlTF-MS) sample was prepared as a standard sample, which will have supported aluminium triflate species on the silica surface. The characteristics of AlTF-MS was compared with Al(TF)-MS and TFA/Al-MS samples to monitor the formation of aluminium triflate species in these samples. The supported metal triflate catalysts are generally synthesized by treating the support material with metal triflate solution in an organic solvent.[3(a)] We adopted the same method with slight modification; the MCM-41 (2 g) was added in 25 mL solution of aluminium triflate (1.65 mmol) in toluene, and the solution was kept under stirring at room temperature for 24 h under nitrogen. The solid product was then filtered, washed (with toluene) and dried at 100°C in static air.

The MCM-41 supported triflic acid (TFA/MS) was also prepared as a standard sample, which will have TFA adsorbed over silica surface through silanols.[24] By comparing the characteristic data of TFA/MS with Al(TF)-MS and TFA/Al-MS, the presence of TFA adsorbed on silica surface (which is possible during synthesis) was check in Al(TF)-MS and TFA/Al-MS samples. For the synthesis of TFA/MS, 25 mL solution of TFA (1.65 mmol) in toluene was added to the 25 mL solution of toluene containing MCM-41 (2 g). The mixture was kept under stirring at room temperature for 24 h. The solid product was then filtered, washed (with toluene) and dried at 100°C in static air.

2.3. Characterization of samples

The Al content in the synthesized Al containing samples was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin Elmer Instrument, Optima 200 DV). The sample (100 mg) was dissolved in 40% HF solution (15- 20 drops) followed by addition of 5 wt.% boric acid solution making up to 100 mL in volumetric flask, which was analyzed by ICP. The BET (Brunauer-Emmett-Teller) surface area (S_{BET}) of the samples was determined from N_2 adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA 1000e surface area analyzer. Temperature programmed desorption of NH_3 (NH_3 TPD) for the samples were carried out for acidity measurement using Micromeritics, USA, taking 50 mg of sample. The sample was heated at 100°C for 1 h under helium flow (30 mL h^{-1}) as carrier gas. The NH_3 was adsorbed on the samples at 50°C by exposing to a flow of helium mixed NH_3 gas (10%, 20 mL h^{-1}) for 1 h. The desorption of NH_3 was performed by heating the sample up to the final temperature of 800°C (12°C min^{-1}) and was measured by gas chromatography with thermal conductivity detector (TCD). The solid state ^{27}Al NMR spectra of Al-MS samples were recorded at room temperature using a Bruker, Avance II (500 MHz) spectrometer and were spun at 8 kHz. Thermal analysis (TGA-DTG) of the samples was carried out using Mettler Toledo TGA/DST1 SF752 from 25°C to 800°C at temperature ramp of 10°C/min under 80mL/min air flow. FTIR of the samples were recorded on FT-IR spectrophotometer (IRPrestige-21, Shimadzu) having a Diffuse

Reflectance Scanning disc technique by mixing the sample with dried KBr (in 1/20 wt. ratio) in the range of 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1}. The type of surface acidity (Brønsted/ Lewis) in the samples was characterized by FTIR study of the pyridine adsorbed samples. For this, the sample (0.2 g) was activated at 120ºC for 2 h. The activated sample was cooled in desiccator under vacuum and was exposed to pyridine (25 mL) vapor for 12 h. The pyridine adsorbed sample was degassed under vacuum for 15 min. to remove physically adsorbed pyridine from sample.

2.4. Catalytic activity of synthesized samples for ketalization of glycerol with acetone into solketal

The ketalization of glycerol with acetone into solketal was carried out using different synthesized samples to evaluate their catalytic activity. This reaction was used as a model reaction of acid catalyzed reaction producing water as co-product to test the stability of the supported catalytic species in the samples. In a typical reaction, the catalyst sample was added into the mixture of glycerol and acetone in a glass reaction tube of reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, UK). The mixture was allowed to stir at room temperature for required reaction time, after which reaction mixture was diluted with dimethyl sulfoxide (DMSO; 3 mL) and filtered to separate the catalyst from reaction mass. The details of reaction conditions are given in the footnote of the table. The reaction mixture was analyzed by gas chromatography (Agilent 7890 A) having a HP-5 (60 meter, 250 μm diameter) capillary column with a programmed oven temperature from 50 to 280 °C, at 1 mL min^{-1} flow rate of N_2 as carrier gas and FID detector. The conversion of glycerol was calculated on the basis of its weight percent as follows,

Conversion (%) of glycerol = 100 × [Initial wt% of glycerol – Final wt% of glycerol]/ Initial wt% of glycerol.

The product (solketal) was identified by GC-MS analysis using gas chromatograph mass spectrometer (Agilent 5975C GC/MSD with 7890A GC system) having HP-5 capillary column of 60 m length and 250 μm diameter with a programmed oven temperature from 50 to 280°C, at 1 mL min^{-1} flow rate of He as carrier gas and ion source at 230°C and MS with inert MSD 5975C triple-axis detector.

3. Results and Discussion

3.1. Characterization of samples

The physico-chemical characteristics of the synthesized samples are summarized in **Table 1**. The details of characteristics of MCM-41 (MS) and Al-MCM-41 (Al-MS) samples have already been reported in our earlier report.[5(d)] The Si/Al ratio of 20 was targeted to maintain in all the samples. The grafting of Al on MCM-41 by post synthesis grafting using aluminium *iso*-propoxide resulted to Al-MCM-41 (i.e., Al-MS) with Si/Al ratio of 20.5. The Si/Al ratio in TFA/Al-MS sample was not much changed (Si/Al = 20.3), which indicates no leaching of Al during treatment of Al-MS with triflic acid solution. However, the Al content was found to be slightly less in Al(TF)-MS sample showing Si/Al ratio of 24.4, and greatly lowered in AlTF/MS sample (Si/Al = 69.4). The result indicates poor loading efficiency of Al in AlTF/MS sample prepared by wet impregnation method using aluminium triflate, which is a conventional method to prepare silica supported metal triflate catalysts.[3(a)]

This was anticipated that the synthesis of Al(TF)-MS sample (two-step single-pot synthesis method) might be involving equimolar reaction of aluminium *iso*-propoxide ($Al(iOPr)_3$) with TFA (TfOH) in the solution forming probably aluminium mono-triflate with two *iso*-propoxide groups i.e., $Al(TfO)(iOPr)_2$, followed by its reaction with silica surface (with silanols; -OH groups) ultimately producing a covalently grafted aluminium triflate species on the silica surface. Therefore, the Al(TF)-MS sample was characterized to examine the grafting of $Al(TfO)(iOPr)_2$ over the silica surface as aluminium triflate species by comparing its characterization results with the characteristics of AlTF/MS. The characteristics of Al(TF)-MS were also compared with TFA/MS to insure that no TFA was adsorbed over silica surface.

The TFA/Al-MS was characterized to investigate whether the direct treatment of Al-MS with TFA could convert grafted Al-sites (of Al-MS) into aluminium triflate species. To confirm this, the characteristics of TFA/Al-MS sample were compared with the characterization data of AlTF/MS. In TFA/Al-MS sample, there is also possibility of TFA adsorption over Al-sites or silanol sites, which was monitored by comparing the characteristics of TFA/Al-MS sample with the characterization data of AlTF/MS.

Table 1. Physico-chemical properties of the prepared samples.

Sample	**Si/Al ratio [Al content in mmol/g)]**	**S_{BET} (m^2/g)**	**Amount of surface organic species* (mmol/g)**		**B/L ratio[b]**	**Acid sites concentration and strength[c]**		
			By C,H,S	**By TGA[a]**		**Temp. (°C)**	**Acid sites (mmol NH_3/g)**	**Total acidity (mmol NH_3/g)**
MS	-	1230	-	-	-	99	0.01	0.01
Al-MS	20.5 [0.81]	1156	-	-	1.2	94	0.88	0.88
TFA/Al-MS	20.3 [0.79]	708	0.76	0.75	1.3	82 163 295 689	0.75 0.08 3.18 0.02	4.03
Al(TF)-MS	24.4 [0.70]	817	0.31	0.30	0.7	84 301 471	1.34 1.64 0.04	3.02
AlTF/MS	69.4 [0.25]	460	0.34	0.32	1.2	81 166 287 513 712	0.60 0.09 4.37 0.11 0.05	5.22
TFA/MS	-	580	0.40	0.41	1.2	132 364 447 553	1.01 1.22 0.11 0.36	2.70

S_{BET} : BET surface area;

**The surface organic species (SOS) may be a triflate group (TfO-) or surface adsorbed triflic acid (TFA).*

[a] *The surface organic species (SOS) in the samples was calculated from weight losses (attributed to decomposition of* CF_3SO_3- *species) in TGA of TFA/Al-MS, AlTF/MS and Al(TF)-MS samples in the temperature range of 230-370°C, and in TGA of TFA/MS in the temperature range of 350-470°C.*

[b] *Ratio of IR band areas of pyridine adsorbed on Brønsted and Lewis acid sites.*

[c] *By* NH_3 *TPD analysis.*

The synthesized samples were characterized by FTIR, TGA, ^{27}Al MAS NMR and NH_3 TPD. The FTIR analysis of the samples was carried out to confirm the presence of CF_3SO_3- functionality, which is present in both surface adsorbed TFA as well as aluminium triflate species present in the supported samples. The TGA study can reveal the presence as well as the amount of the surface organic species (SOS; CF_3SO_3- moiety) either as adsorbed TFA or aluminium triflate in the samples. In addition, the decomposition of surface adsorbed TFA and aluminium triflate species will occur at different temperatures, so TGA profile can also be used to distinguish the surface adsorbed TFA (on silanol sites or Al-sites) or aluminium triflate species. The ^{27}Al MAS NMR study was carried out to investigate the structural forms of Al (co-ordinations) and to distinguish the Al species as functionalized with triflate (TfO-) or un-functionalized forms. The surface acidity (amount, strength and types) in the samples was characterized by NH_3 TPD analysis and FTIR analysis of pyridine adsorbed samples.

The FTIR spectra (**Figure 1**) of samples (except MS and Al-MS) show some additional bands in the range of 1286–1176 and at ~636 cm^{-1}, which can be assigned to S=O stretching vibrations and deformation modes of SO_2 moieties, respectively, of adsorbed TFA or triflate species.[25,26] A band at 1027 cm^{-1} is attributed to C-F stretching vibration of CF_3- group. The FTIR study clearly indicates the presence of TFA or triflate species in the supported samples.

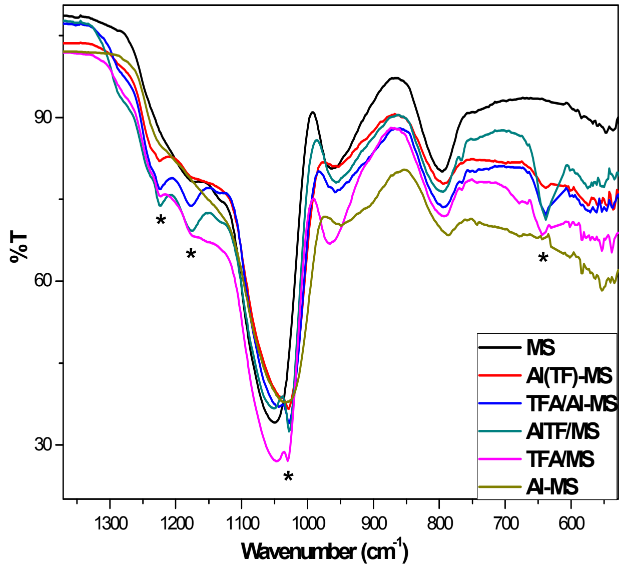


Figure 1. FTIR spectrum of synthesized samples (*characteristic bands for CF_3SO_3- moiety).

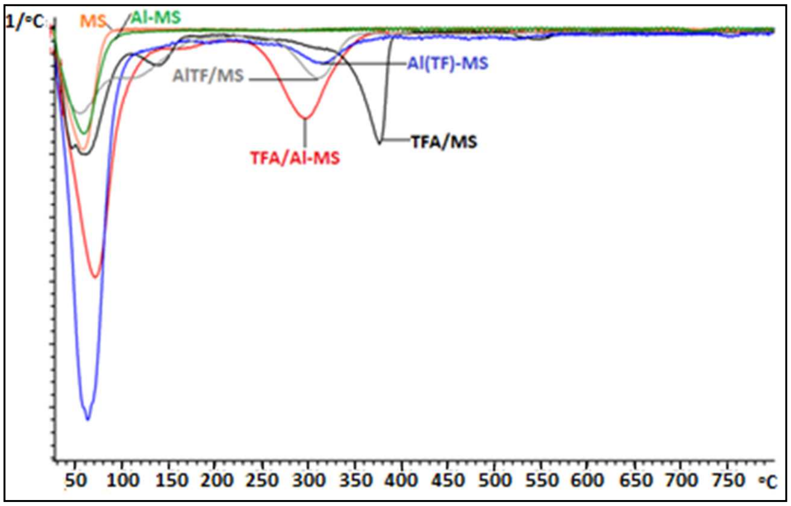
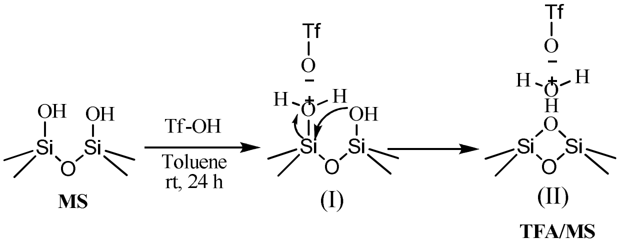
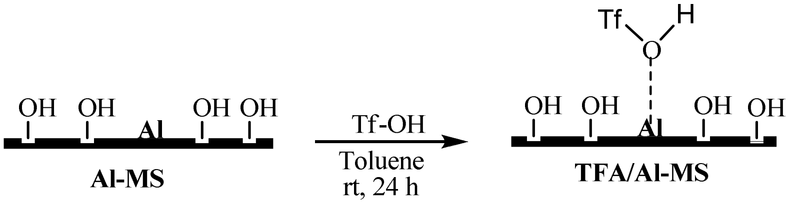


Figure 2. DTG profiles of synthesized samples.

In DTG profiles of all the samples (**Figure 2**), the weight loss below 100°C can be attributed to the loss of residual volatile organic impurities and moisture present in the samples. The additional major weight loss in different samples, except MS and Al-MS, at higher temperatures (above 200°C) is owing to decomposition of surface organic species (SOS; adsorbed TFA or triflate species) present in the samples. The DTG profile of silica supported TFA (i.e., TFA/MS) sample shows a weight loss centred at ~140°C probably attributed to loss of water associated with surface adsorbed TFA and at ~375°C for decomposition of adsorbed TFA. Angelis et al.[27] have reported the formation of TFA.H_2O on SiO_2 surface by reaction of TFA with silanol groups during the synthesis of silica supported TFA catalysts. The reaction of TFA with silanol involves the transfer of proton from TFA to silanol forming protonated silanol, which can hold triflate ions on the silica surface (**Scheme 1; structure I**)[24]. There may also be a reaction of vicinal silanol with protonated silanol forming Si-O-Si linkage and hydronium ion (protonated water; Brønsted acid site) on the surface, which remains associated with triflate (**Scheme 1; structure II**). On heating, this surface adsorbed hydronium triflate can eliminate water molecule giving weight loss at ~140°C. The TGA profile of TFA/MS (i.e., weight loss at ~140°C and ~375°C) can be used to ensure the presence of TFA adsorbed on silanol sites in Al(TF)-MS, TFA/Al-MS and AlTF/MS samples. In DTG profile of AlTF/MS sample (**Figure 2**), there is a significant weight loss at 312°C, which can be attributed to decomposition of triflate group (TfO-) of supported aluminium triflate species. So, the weight loss at around 312°C in Al(TF)-MS and TFA/Al-MS samples will confirm the presence of supported aluminium triflate species.



Scheme 1. Synthesis route for preparation of TFA/MS sample and probable structure of surface adsorbed TFA species.



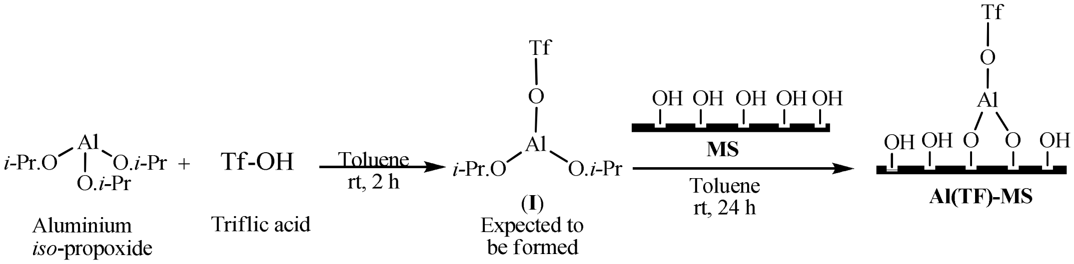
Scheme 2. Synthesis route for preparation of TFA/Al-MS sample and probable structure of surface adsorbed TFA species.

The DTG profile of TFA/Al-MS sample (**Figure 2**) shows the weight loss for organic moiety at ~295°C. This weight loss cannot be attributed to either TFA adsorbed on silica surface (which gets decomposed at ~375°C) or supported aluminium triflate species (decomposition temperature: ~312°C). From this result, it was anticipated that the TFA might be associated with (or adsorbed on) Al-sites grafted on silica surface. The adsorption of TFA over Al-sites may be due to coordination bonding between Al and TFA through oxygen as shown in **Scheme 2**. The coordinative bond between Al and TFA in TFA/Al-MS would be comparatively weaker than TFA bonded with silanols (**Scheme 1; structure I & II**), which may be the reason for lower decomposition temperature of TFA associated with Al in

TFA/Al-MS (at ~295°C) than TFA adsorbed on silica surface (in MSA/MS; at ~375°C). Similarly, the Al–triflate bond must be stronger in aluminium triflate species (in AlTF/MS) as compared to co-ordinatively bonded TFA over Al-sites (in TFA/Al-MS), and therefore, TFA associated with Al in TFA/Al-MS would decompose at lower temperature than aluminium triflate species (decomposition temperature: ~312°C). Furthermore, the water loss at ~140°C was also not observed in DTG profile of TFA/Al-MS indicating that TFA was not adsorbed or reacted with silanols during the synthesis. From the TGA study, it can be concluded that TFA/Al-MS, prepared by direct treatment of TFA with Al-MS, do not have aluminium triflate species on silica surface and TFA gets adsorbed on Al-sites grafted on silica surface by making coordinative bond.

The DTG profile of Al(TF)-MS sample showed significant weight loss at 315°C (**Figure 2**). This weight loss can be attributed to decomposition of aluminium triflate species, which is almost close to the decomposition temperature of supported aluminium triflate species (~312°C) present in AlTF/MS sample. This clearly indicates that the Al(TF)-MS sample contains surface aluminium triflate species. In DTG profile of Al(TF)-MS, there are no weight losses attributed to TFA adsorbed on silanol sites or Al-sites, which confirms that there is no adsorbed TFA species in the sample.

The aluminium triflate was synthesized in good yield by reaction of aluminium *iso*-propoxide with TFA (in 3:1 molar ratio; **see ESI**), which also show decomposition of triflate species in almost same temperature range (centered at ~360°C) as pure aluminium triflate procured from Aldrich (**ESI, Figure S1**). It confirms that the reaction of aluminium *iso*-propoxide and TFA gives aluminum triflate in the proposed method. The equimolar reaction of aluminium *iso*-propoxide and TFA might be producing aluminium triflate derivative (probably aluminium mono triflate species; i.e., Al(TfO)(iOPr)$_2$), which will react with surface silanols of MCM-41 to form surface grafted aluminium triflate species (**Scheme 3**). The lower decomposition temperature of supported aluminium triflate species in Al(TF)-MS and AlTF/MS (at 315°C and 312°C, respectively) as compared to pure aluminium triflate (~360°C) may be due to dispersion of aluminium triflate species over silica surface and the presence of plenty of surface hydroxyl groups (silanols) facilitating their thermal decomposition.[3(a), 3(b)] From TGA study, it is clearly evident that the Al(TF)-MS sample contains surface aluminium triflate species.



Scheme 3. Synthesis route for preparation of Al(TF)-MS sample and probable structure of surface grafted aluminium triflate species.

The amount of supported organic species (SOS; adsorbed TFA or aluminium triflate species) in the samples were calculated from C,H,S data as well as from their weight losses (for decomposition of SOS) in TGA.[24,28] The amount of organic species obtained from C,H,S data in the samples were found to be almost similar to the amount calculated from TGA (**Table 1**). This was noticed that TFA/Al-MS has higher TFA loading (0.76 mmol/ g) than TFA/MS (0.40 mmol/ g). In the TFA/Al-MS sample, the molar amounts of SOS (i.e., co-ordinatively bonded TFA) and Al were 0.76 mmol/ g and 0.79 mmol/ g, respectively indicating that around 96% grafted Al might have reacted with TFA. It shows that almost all Al in Al-MS are functionalized with co-ordinated TFA making probably 1:1 complex, i.e., each Al must be having one adsorbed TFA molecule.

There is significant difference in molar amounts of SOS and Al in Al(TF)-MS sample (**Table 1**; SOS and Al contents were 0.31 mmol/ g and 0.70 mmol/ g, respectively; % Al functionalization = 44%) showing that around 44% Al of total Al content could be grafted with triflate group or as aluminium triflate and rest of Al were in un-functionalized form. The less functionalization might have occurred due to condensation reactions of aluminium mono-triflate *iso*-propoxide molecules i.e., Al(TfO)(*i*OPr)$_2$) with aluminium *iso*-propoxide molecules, followed by reaction of resulting molecules with surface silanols.

The amount of SOS and Al in AlTF/MS (**Table 1**; 0.34 mmol/ g and 0.25 mmol/ g, respectively) indicates the loss of triflate groups from aluminum triflate during loading as the molar ratio of triflate or SOS and Al was found to be less than 3 (i.e., triflate/Al molar ratio = 1.36), which may be due to hydrolysis of aluminum triflate during loading. This ratio (triflate/Al molar ratio = 1.36) also indicates that there should be predominantly aluminium mono-triflate species along with some amount of aluminium di-triflate species supported over silica surface.

The ^{27}Al MAS NMR study of synthesized samples revealed the presence of different types of Al species in the samples. The ^{27}Al NMR spectrum of Al-MS sample (**Figure 3**) shows three resonance signals centred at around 3.8 ppm, 32.4 ppm and 56.7 ppm indicating the presence of octahedrally, pentahedrally and tetrahedrally co-ordinated Al species, respectively (**Scheme 4(i)**).[5(c)] The ^{27}Al NMR spectrum of AlTF/MS sample has a sharp resonance signal at 0.50 ppm, which can for octahedral Al mono- and di-triflate species (**Scheme 4(ii)**). The resonance signal at -2.76 ppm in ^{27}Al NMR spectrum of TFA/Al-MS must be for octahedral Al, but it cannot be for octahedral Al triflate species. The octahedral Al species having an adsorbed TFA through co-ordinative bond as shown in **Scheme 4(iii)** may give the resonance signal at -2.76 ppm. The co-ordinative bonding between TFA and Al will increase electron density at Al i.e., shielding on Al, which will cause upfield shifting of signal (at -2.76 ppm) as compared to octahedral Al in Al-MS. Poh et al.,[29] have reported the signal to a more negative chemical shift value (-5 ppm) for octahedral aluminium bonded to silica and sulfate groups as SiO–Al $(OSO_3H)_5^{n+}$ in sulfated Al-MCM-41. The ^{27}Al NMR result shows that all the tetrahedral, pentahedral and octahedral Al species of Al-MS were converted to octahedral Al having coordinated TFA in TFA/Al-MS showing a single peak at -2.76 ppm. Poh et al,[29] have explained that the disappearance of the peak corresponding to tetrahedral aluminium after treatment with sulphuric acid was due to removal of tetrahedrally coordinated aluminium from the framework and transformation to octahedral aluminium, also referred as extraframework aluminium. Similar observation was also reported by Chen et al. for sulphated Al-MCM-41.[30]

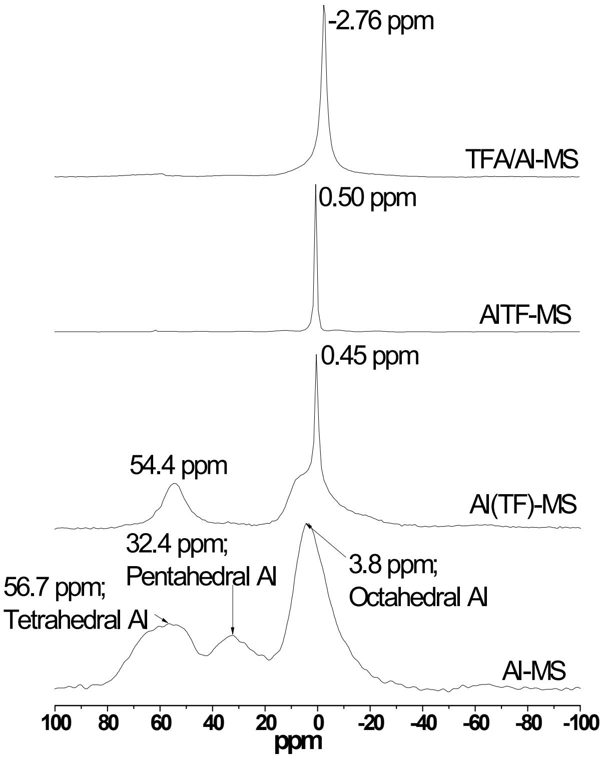
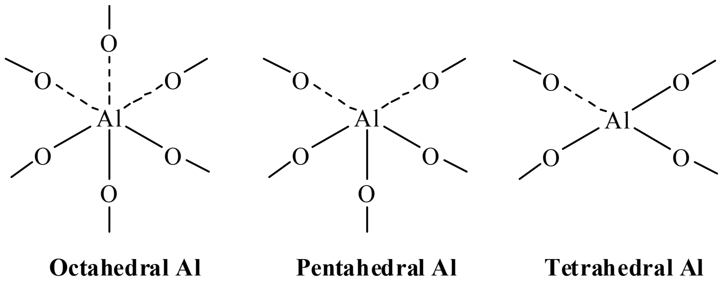
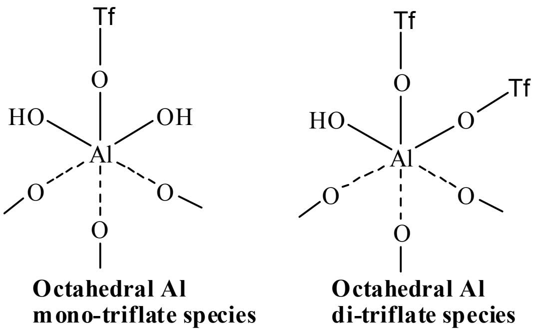


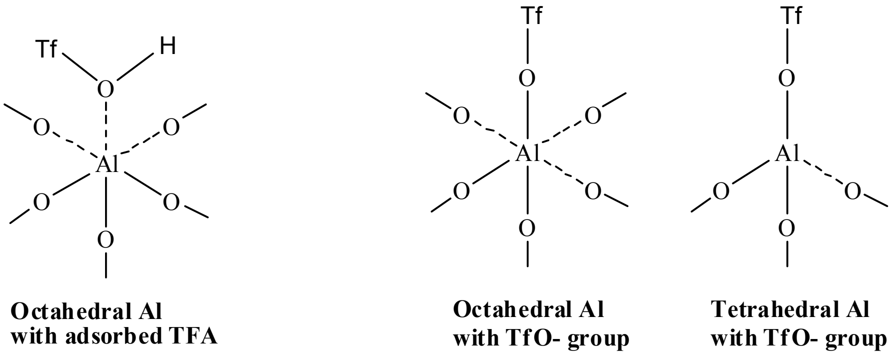
Figure 3. ^{27}Al MAS NMR spectra of synthesized samples.



(i) Al species in Al-MS



(ii) Al species in AlTF/MS



(iii) Al species in TFA/Al-MS **(iv) Al species in Al(TF)-MS**

Scheme 4. Different types of Al species in the samples.

The resonance signal at 0.45 ppm in ^{27}Al NMR spectrum of Al(TF)-MS sample (**Figure 3**) can be attributed to octahedral Al triflate species in the sample (**Scheme 4(iv)**). This is also confirmed from ^{27}Al NMR spectrum of AlTF/MS sample showing a sharp resonance signal at 0.50 ppm for octahedral Al triflate species. The presence of an electron withdrawing group (i.e., TfO- group) on Al must show downfield shifting of signal for octahedral Al in Al(TF)-MS and AlTF/MS samples as compared to octahedral Al signal in Al-MCM-41. The upfield shifting of the signal for octahedral Al in Al(TF)-MS and AlTF/MS samples is possible due to co-ordination of either surface hydroxyl groups (silanols) or water molecules with Al-triflate species populating more electron density at Al. The resonance signal centred at ~54.4 ppm in ^{27}Al NMR spectrum of Al(TF)-MS may be representing presence of some framework tetrahedral Al triflate species (which is at 56.7 ppm for un-functionalized tetrahedral Al in Al-MS sample). The presence of a shoulder in the signal for octahedral Al (at 0.45 ppm) in Al(TF)-MS sample may be for un-functionalized octahedral Al species. From ^{27}Al MAS NMR study, it was confirmed that Al(TF)-MS sample contains supported aluminium triflate species along with some un-functionalized Al, and TFA/Al-MS does not have aluminium triflate species and it has octahedral Al with co-ordinatively bonded TFA.

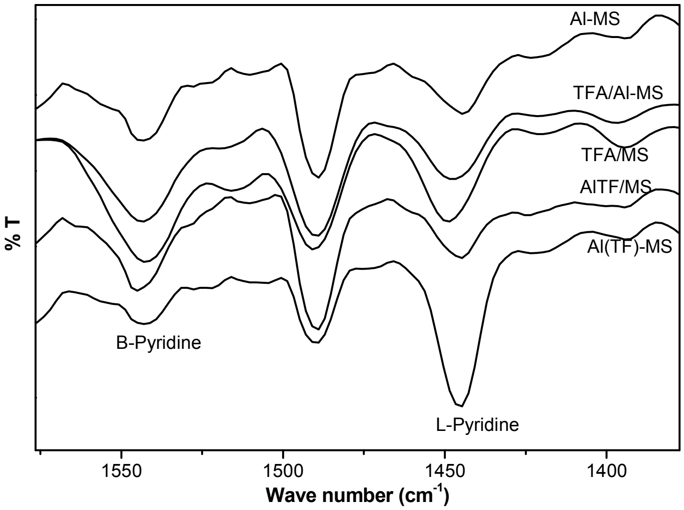
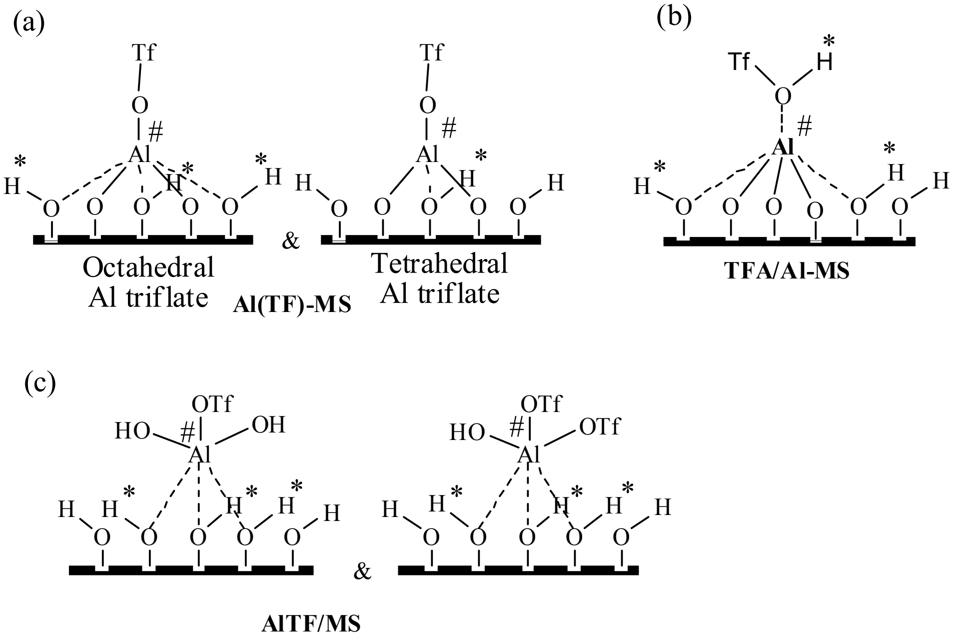


Figure 4. FTIR spectrum of (b) pyridine adsorbed samples (B-Pyridine: pyridine bound to Brønsted acid sites; L-Pyridine: pyridine bound to Lewis acid sites).

The FTIR study of pyridine adsorbed samples (**Figure 4**) reveals the presence of both Brønsted and Lewis acidic sites in the samples showing bands at ~1546 cm^{-1} and ~1446 cm^{-1} assigned to pyridine bound to Brønsted and Lewis acid sites, respectively.[31] The band at 1490 cm^{-1} is representative of adsorbed pyridine at both the acidic sites. The lowest B/L ratio (B/L = 0.7) in Al(TF)-MS sample shows higher Lewis acidity in Al(TF)-MS as compared to other samples (**Table 1**), which may be due to the presence of extraframwork octahedral aluminium triflate species as well as octahedral un-functionalized Al. This is reported that in Al-MCM-41, the octahedral Al species provide Lewis acidity and the tetrahedral Al species are responsible for Brønsted acidity.[5(a),29] The FTIR result of pyridine adsorbed Al(TF)-MS sample supports the ^{27}Al MAS NMR result (**Figure 3**) showing predominant octahedral extraframwork Al species for Lewis acid sites along with tetrahedral octahedral framework Al for Brønsted acid sites. The silanols and water molecules co-ordinated with Al (aluminium triflate species and un-functionalized Al) can also generate Brønsted acid sites (**Scheme 5(a)**). It can be seen that the amount of Lewis acid sites in Al(TF)-MS (calculated from the data given in **Table 1**) is much higher (1.78 mmol/g) than the amount of TfO- moiety (0.31 mmol/g) i.e., aluminium triflate species and even total Al content (0.70 mmol/g) present in the sample. The higher amount of Lewis acidity in Al(TF)-MS in comparison of Al content could be possible due to adsorption of more than one molecules of base (ammonia/ pyridine) on each octahedral Al-sites. Each octahedral Al species (either aluminium triflate or un-functionalized Al) have three co-ordinations with surface vicinal silanols and/ or water molecules. The adsorption of more than one base molecule on an octahedral Al-site can occur by breaking the co-ordinations with silanol/ water. We demonstrated by ^{27}Al MAS NMR study of benzyl amine adsorbed Al-MS sample that the octahedral Al species are converted into tetrahedral Al species due to adsorption of amine molecule on octahedral Al by breaking the co-ordinations with silanols.[5(d)]

The ^{27}Al MAS NMR spectrum of TFA/Al-MS shows the presence of only octahedral Al (no tetrahedral Al), however, FTIR result of pyridine adsorbed sample indicates the presence of significant amount of Brønsted acid sites along with Lewis acid sites in this sample (B/L: 1.3; **Table 1**). The Brønsted acid sites in TFA/Al-MS can be generated due to TFA adsorbed over Al-sites by coordinative interaction as well as co-ordinated surface silanols and water molecules with these Al-sites (**Scheme 5(b)**).



Scheme 5. Structure of the surface Al species and Bronsted and Lewis acid sites in (a) TFA/Al-MS, (b) Al(TF)-MS; (c) AlTF/MS [* = Bronsted acid sites; # = Lewis acid sites].

The aluminum triflate (which is a Lewis acid) supported on MS (i.e., in AlTF/MS sample) contain predominantly Brønsted sites (B/L: 1.2; **Table 1**). In contrast, the ^{27}Al MAS NMR spectrum of AlTF/MS shows the presence of only octahedral Al, and therefore, this sample should have higher Lewis acidity. The higher amount of Brønsted acidity in AlTF/MS could be generated due to co-ordination of aluminium triflate species (in octahedral form) with surface silanols (**Scheme 5(c)**). In TFA/MS, the protonated silanols bonded with triflate ions on the silica surface (**Scheme 1**) act as Brønsted acid sites.[24] The presence of significant amount of both types of acid sites, Brønsted as well as Lewis sites, in silica supported TFA has also been reported by Angelis et al.[27]

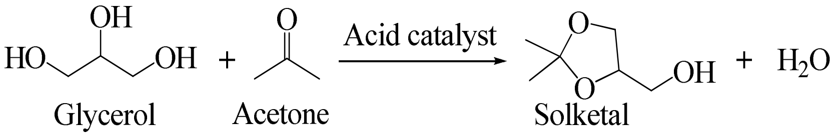
The MCM-41 has negligible acidity (0.1 mmol/ g), which increased after grafting of Al in Al-MS sample to 0.88 mmol/ g (weak strength) (**Table 1**). The TFA/MS, TFA/Al-MS, Al(TF)-MS and AlTF/MS samples have significantly high acidity (2.70 mmol/ g, 4.03 mmol/ g, 3.02 mmol/ g and 5.22 mmol/ g, respectively) with weak, medium and strong strength. It is to be noted that the SOS content (adsorbed TFA or triflate amount) in these samples is in the range of 0.31 to 0.76 mmol/ g, however, the amount of acidity in these samples is significantly higher (2.70 to 5.22 mmol/g). The reason for very high acidity in TFA/Al-MS, Al(TF)-MS and AlTF/MS samples could be the dispersion of adsorbed TFA or aluminum triflate species over large surface and also due to co-ordinations of surface silanols and/ or water molecules with aluminum species as shown in **Scheme 5**. Similarly, the high acidity in TFA/MS sample can be due to the hydration of adsorbed TFA (on silanol sites) by vicinal silanols as well as water molecules generating more number of acidic sites.

The BET surface area (S_{BET}) of the MS sample was 1230 m^2/ g, which decreased to 1156 m^2/ g in Al-MS sample (**Table 1**). The S_{BET} was significantly reduced to 708 m^2/ g in TFA/Al-MS sample after loading of TFA over Al-MS. Similarly, S_{BET} of Al(TF)-MS, AlTF/MS and TFA/MS samples was also decreased (817 m^2/ g, 460 m^2/ g and 580 m^2/ g, respectively). The decrease in S_{BET} of supported samples in comparison of MS is indicative of the loading/ grafting in the internal surface (inside the pores) of MS.

The characterization results reveal that Al(TF)-MS sample, prepared by a two-step single pot synthesis method, contains surface grafted Al with probably one triflate group (along with un-functionalized grafted Al species) generating significant amount of acidity with predominantly Lewis sites. The TFA/Al-MS sample, prepared by treating Al-MS with TFA, does not contain aluminium triflate species and it has TFA adsorbed over Al-sites generating good amount of acidity. The AlTF/MS sample, prepared by using conventional procedure, has also substantial amount of acidity due to supported aluminium triflate species (probably as predominantly mono- and few di-triflate species) on silica surface.

3.2. Catalytic activity of synthesized samples for ketalization of glycerol with acetone to solketal

The catalytic activity of all the synthesized samples was studied for the synthesis of solketal by acid catalyzed reaction of acetone with glycerol, which is also known as ketalization reaction (**Scheme 6**). **Table 2** shows the activity of different samples (in terms of glycerol conversion, in ketalization of acetone with glycerol under given reaction conditions. The selectivity to the desired product (solketal) was ~100% with all the samples, which was observed not to be affected on varying the various reaction variables showing that the reaction does not produce other products such as hemiketal or six membered cyclic ketal. However, the conversion of glycerol varies with sample's acidity and reaction conditions (such as catalyst amount, amount of acetone, reaction temperature, etc.).



Scheme 6. Acid catalyzed ketalization of glycerol with acetone to solketal.

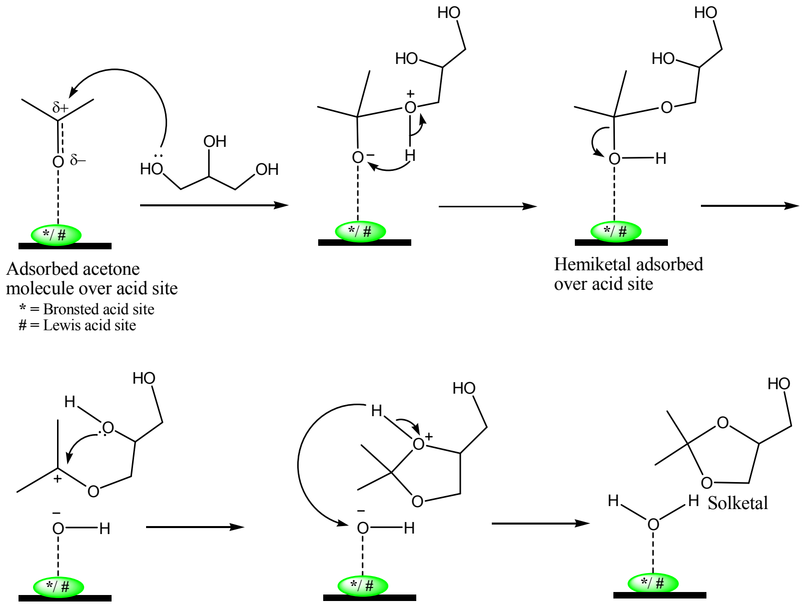
Except MS and Al-MS, all the samples showed good activity in ketalization giving glycerol conversion in the range of 75-89% (**Table 2**, entry 1-7) when 1 mL acetone was used in the reaction. The acidity of samples was observed to be influencing conversion giving highest conversion (89%) with AlTF/MS having highest acidity (5.22 mmol) and lowest conversion (75%) with TFA/MS having lowest acidity (2.7 mmol). The AlTF/MS gave 89% glycerol conversion, which was higher than pure Al(OTf)$_3$ used under homogeneous condition (79% glycerol conversion). Higher activity of the supported sample (i.e., AlTF/MS) may be attributed to dispersion of the aluminium triflate species and generation of more acidic sites on the silica surface. The role of acid catalyst (Brønsted/ Lewis acid sites) in ketalization reaction is to activate the acetone molecule for nucleophilic addition of glycerol (**Scheme 7**) to form hemiketal. The hemiketal (adsorbed over acid site) undergoes dehydroxylation producing a tertiary carbonium ion intermediate,[17] which reacts (nucleophilic attack) with the secondary hydroxyl group to form the five-membered ring ketal (solketal).

Table 2. Conversion of glycerol in ketalization of glycerol with acetone to solketal using different synthesized samples.[a]

Entry	Catalyst	Acetone amount (mL)	Conversion of glycerol (wt. %)	
1	MS	1	0	
2	Al-MS	1	9	
3	Al(TF)-MS	1	84	(80[b], 79[c])
4	TFA/Al-MS	1	89	(78[b], 10[c])
5	AlTF/MS	1	89	(80[b], 6[c])
6[d]	Al(OTf)$_3$	1	79	
7	TFA/MS	1	75	(0[b])
8	Al(TF)-MS	3	92	(90[b])
9[e]	Al(TF)-MS	3	87	
10[f]	Al(TF)-MS	3	93	
11[g]	Al(TF)-MS	3	86	

[a] *5.4 mmol glycerol, 50 mg catalyst, room temperature (30°C), 4 h.*
[b] *First reuse of spent catalyst under similar reaction condition.*
[c] *Second reuse of spent catalyst under similar reaction condition.*
[e] *100 mg catalyst;* [f] *50°C;* [g] *100 mg catalyst, 50°C.*
[d] *Reaction with pure aluminium triflate (20 mg; amount corresponds to Al present in 50mg catalyst), procured from Aldrich, under homogeneous condition.*

For reuse study, all the spent catalyst samples were separated by filtration of reaction mixture, washed with acetone (by stirring in 5 mL acetone) and dried at room temperature for overnight. The spent catalysts were reused for solketal synthesis reaction under similar reaction condition as with fresh catalyst. The spent Al(TF)-MS sample showed good reusability with almost maintained activity in subsequent reaction cycles (**Table 2**, entry 3), whereas TFA/Al-MS, AlTF/MS spent catalysts gave significant decrease in the glycerol conversion in second reactions cycle (**Table 2**, entry 4, 5). The TFA/MS spent catalyst has no activity in even first reuse (**Table 2**, entry 7).



Scheme 7. Plausible reaction mechanism of ketalization of glycerol with acetone to solketal over solid acid catalysts.

The spent catalyst samples, after washing with acetone and drying at 110°C for 2 h, were analyzed by TGA and compared with TGA profile of fresh catalysts to confirm the presence and amount of SOS in the samples. Those spent samples which did not show reusability, did not show weight loss at higher temperature (above 200°C; for decomposition of organic moieties) in TGA profile indicating leaching of loaded organic moieties (adsorbed TFA or triflate species) from the samples during reaction. This clearly shows that non-reusability of the supported samples viz. TFA/Al-MS, AlTF/MS and TFA/MS is due to the leaching of loaded catalytic species. The TGA of Al(TF)-MS sample before and after reaction (second cycle) did not show significant leaching (**Figure 5**) showing that loaded aluminium triflate species were quite stable and therefore, spent catalyst showed almost similar activity as fresh catalyst.

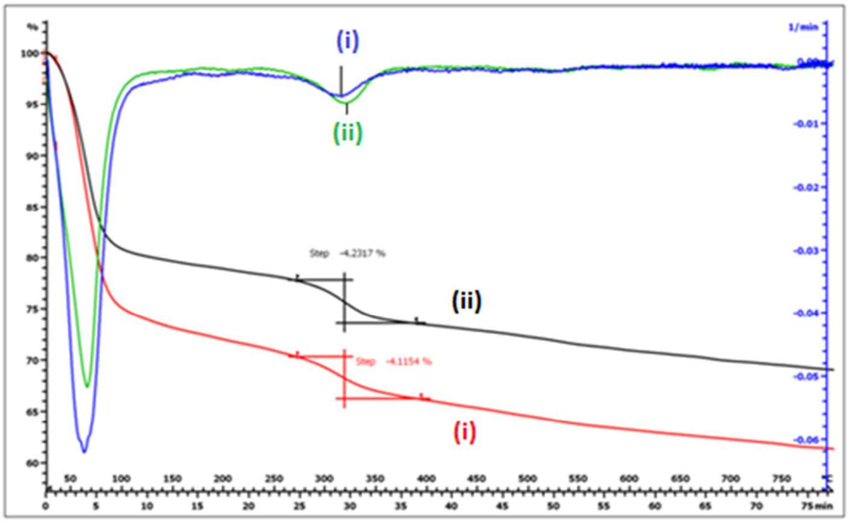


Figure 5. TGA-DTG profiles of Al(TF)-MS (i)before and (ii)after reaction.

The Si/Al ratio in the spent TFA/Al-MS and Al(TF)-MS samples after second reuse were found to be unchanged (Si/Al ration were 20.6 and 24.5, respectively), and there was negligible amount of Al in the spent AlTF/MS. This indicates that in the reaction, TFA/Al-MS lost only adsorbed TFA but grafted Al remained intact, whereas AlTF/MS sample lost the supported aluminium triflate species. The triflate moiety (SOS content) as well as Al content in Al(TF)-MS spent catalyst were not much changed showing that the grafted aluminium triflate species in spent catalyst remained intact.

The water produced during the reaction may attack on Al-stes (i.e., ligand substitution reaction) in TFA/Al-MS sample replacing co-ordinatively bonded TFA. Similarly, the supported aluminium triflate species in AlTF/MS sample can also be replaced from the surface by nucleophilic reaction of water molecules on Al. Kobayashi et al reported higher stability of metal triflates against water hydrolysis than metal halides.[32] In Al(TF)-MS sample, the triflate group seems not to be substituted from Al by nucleophilic reaction of water molecules showing good stability of grafted aluminium triflate species. The aluminium triflate species in Al(TF)-MS sample is covalently grafted on silica surface by Si-O-Al bonding, therefore, the grafted aluminium triflate species could not be removed from silica surface by reaction of water. This result confirms the covalent grafting of aluminium triflate species on silica surface through Si-O-Al linkage. Furthermore, the good reusability of Al(TF)-MS catalyst also indicates that acidic sites are not poisoned/ deactivated by adsorption of water molecules on the sites. The reusability of Al(TF)-MS was studied for five cycles, which did not show significant change in conversion of glycerol (80-84%) and SOS content (by TGA).

On increasing the amount of acetone from 1 mL to 3 mL in the reaction, the conversion of glycerol with Al(TF)-MS increased from 84% to 92% (**Table 2,** entry 3 and 8), which is due to increased concentration of acetone in the reaction mixture for interaction with acidic sites of catalyst and then its reaction with glycerol. The excess acetone in the reaction can also play the role of solvent. The high molar amount of acetone (6 to 8 times to glycerol) has been taken for higher conversion of glycerol in previous studies. [18,20-23] For atom efficient process, acetone should be used in equimolar or at least in lowest possible molar amount in the reaction. It can be seen that Al(TF)-MS gave substantially good conversion of glycerol (84%; **Table 2,** entry 3) when 1 mL of acetone (which corresponds to acetone : glycerol molar ratio of ~2.5 : 1) was employed in the reaction. With mesoporous substituted silicates

(Zr-TUD-1, Hf-TUD-1 and Sn-MCM-41 Lewis acid catalysts), the highest 52% conversion could be obtained with Hf-TUD-1 in equimolar reaction of acetone and glycerol under reflux condition, which increased to 65% conversion at 2:1 molar ratio. The highest glycerol conversion (~90%) was reported with zeolite Beta (Si/Al=16) using 1.2:1 molar ratio of acetone and glycerol under reflux condition.

The spent Al(TF)-MS catalyst of the reaction carried out using higher volume of acetone (3 mL) was recovered by centrifugation and was directly reused, without any solvent wash, after room temperature drying for overnight. The conversion of glycerol with this spent catalyst (without solvent wash) in next cycle was 90%, which showed almost similar activity of the spent catalyst as with the fresh catalyst (92% conversion; **Table 2**, entry 8). This shows that Al(TF)-MS catalyst is directly reusable, without any solvent wash, after room temperature drying. This experiment indicates that there is not poisoning/ deactivation of the active sites by adsorption of reactant(s)/ product and water molecules, so spent catalyst does not require any treatment (washing/ thermal) for regeneration. The spent Al(TF)-MS catalyst from the reaction mixture, in which 1 mL acetone (3 mL) was used in the reaction, could not be recovered by centrifugation due to more viscous reaction mass, which needed to be diluted with acetone (5 mL) to separate the catalyst by filtration or centrifugation. Therefore, the spent Al(TF)-MS catalyst of the reaction using less amount of acetone (1 mL) could not be possible to reuse directly without solvent wash.

We noticed that as compared to the reusability procedure of the reported solid acids in solketal synthesis, the reusability procedure of Al(TF)-MS catalyst is very simple. For the reusability of spent catalyst in solketal synthesis, the spent catalysts have been regenerated to restore the activity either by washing with a solvent followed by drying at high temperature (75-110°C)[20,22] or by calcination at high temperature[19]. The spent sulfonic acid-functionalized mesoporous silica[18] was reused without washing or regenerating the catalyst (acetone/ glycerol molar ratio = 6:1), after overnight drying at 90°C. The reusability of Zr and Hf-TUD-1 and Sn-MCM-41[19] could be possible after washing with pre-heated *tert*-butanol (five times) at room temperature followed by drying at 100°C overnight up to 4th cycle and after that calcination in air above 550°C was employed to restore the activity. These catalysts get deactivated by reaction residues deposited on the active sites and water adsorbed in the pores of the catalysts, so high temperature calcination was required to regenerate the catalyst.

The increase in reaction temperature (from 30°C to 50°C) did not show much improvement in the glycerol conversion (**Table 2,** entry 8 & 10). For the solvent free and selective conversion of glycerol to solketal, the Al(TF)-MS catalyst showed comparable activity to previously reported solid acid catalysts.[17-22] However, it is to be noted that the highest conversion with the reported solid acid catalysts was achieved under reflux conditions (70-80°C), whereas, with Al(TF)-MS, the highest conversion (92%) could be obtained at ambient temperature (room temperature; 30°C).

On increasing catalyst amount from 50 mg to 100 mg (either at 30°C or at 50°C), the conversion was observed to be slightly decreased (**Table 2,** entry 8 & 9 or **Table 2**, entry 10 & 11). The high conversion with less catalyst loading can be due to the increased dispersion of the solid catalyst in a fixed volume of reaction mixture that increases the availability of the catalytically active acid sites to reactant molecules.[31] The most of solid acids[18-23] have been used in 5-10 wt.% of glycerol to have highest conversion; we also found that 10 wt.% is optimum catalyst loading for Al(TF)-MS.

4. Conclusions

A water tolerant aluminium triflate grafted on MCM-41 catalyst with high surface acidity was synthesised by a novel approach and characterized thoroughly. The catalytic potential of the catalyst was demonstrated for solvent free ketalization of glycerol to solketal at room temperature; the catalyst was found to be efficient at room temperature, stable and water tolerant. The catalyst showed excellent reusability by simple procedure without significant loss in its activity in solketal synthesis. This study shows that the aluminium triflate grafted MCM-41 catalyst may also have potential application as water tolerant acid catalyst in other reactions producing water as co-product.

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Graphical abstract

Synthesis of Aluminium Triflate Grafted MCM-41 as Water Tolerant-Acid Catalyst for Ketalization of Glycerol with Acetone

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The aluminium triflate species grafted over MCM-41 (Al(TF)-MS) was synthesized by a novel route as an inexpensive and water tolerant solid acid catalyst for ketalization of glycerol with acetone to solketal (solketal synthesis).