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ENHANCEMENT OF ACIDITY AND CATALYTIC ACTIVITY OF ALUMINA BASED METAL ORGANIC FRAMEWORK (MIL-53 Al)

Esra Yilmaz
Ege University

Emine Sert
Ege University

Ferhan Sami Atalay
Ege University

Abstract: Metal organic frameworks are highly porous materials which are formed by combination of metal precursor and salts as inorganic part and ligand as organic part. They have many advantages such as low density, high surface area, tunable pore size and high porosity. Due to peculiar features, such as unsaturated metal active sites, high surface area and easily functionalization, its usage as catalyst are promising.

The MIL-53(Al) structure contains chains of trans corner-sharing [$AlO_4(OH)_2$] octahedra that are connected to each other by 1,4 benzenedicarboxylate (BDC) ligands, and thus 3D net in which one-dimensional channels run parallel to the inorganic backbone of the structure is formed. There are so many studied on usage of aluminium based metal organic framework in adsorption and gas adsorption and separation processes. However, there is very limited number of studies on catalytic properties of this material.

MIL-53(Al) provides several advantages compared with other MOFs such as high thermal stability, cheap, and available raw materials. It is also moisture resistant and has relatively high surface area which makes it an attractive MOF alternative for catalytic processes. In this study, aluminium salt was selected as metal precursor and MIL-53 (Al) was synthesized by solvothermal method.

Then the synthesized material was sulfated to increase the acidity. The characterization of synthesized and sulfated materials were performed by FT-IR, BET, XRD and TGA methods. The catalytic activity of sulfated material was tested in esterification reaction of acetic acid. The effects of time, sulfation, temperature and alcohol type were investigated.

Keywords: MOF, MIL-53(Al), solvothermal, sulfation, and acidity

Introduction

Metal organic frameworks evolved from coordination and solid-state/zeolite chemistry that were labeled as coordination polymers. They were formed by metal ions as nodes and organic ligands as linkers. MOF materials possess tunable pore sizes, structure diversity, low density, high surface area, and high porosity. Due to peculiar features, such as unsaturated metal active sites, high surface area and easily functionalization, its usage as catalyst are promising.

The MIL-53(Al) structure contains chains of trans corner-sharing [$AlO_4(OH)_2$] octahedra that are connected to each other by 1,4 benzenedicarboxylate (BDC) ligands, and thus 3D net in which one-dimensional channels run parallel to the inorganic backbone of the structure is formed. There are so many studied on usage of aluminium based metal organic framework in adsorption [1–4] and gas adsorption and separation processes[5–7]. However, there is very limited number of studies on catalytic properties of this material.

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*Corresponding author: Esra Yilmaz-E-mail: esra.yilmaz@ege.edu.tr

Esterification reaction without catalyst is slower because carboxylic acid gives proton by protolysis. Therefore, esterification should be occurred with help of an acid catalyst that acts protogenic. Even though homogeneous acid catalysts like HCl, H_2SO_4 very effective in esterification reactions, they aren’t preferred due to cause corrosion and byproducts. Also these catalysts have a big disadvantage of separating problems. The advantage of a heterogeneous catalyst is well known, and the use of solid ion exchange resin as the catalyst has the following advantages; (a) the catalyst can be easily separated from the reaction products by decantation or filtration (b) continuous operation in column and reusability are possible (c) the side reaction can be eliminated and the product purity is high.

In this study, alumina based metal organic framework was synthesized and sulfated and then used as catalyst. Using characterization techniques, the effect of sulfation on the structure of MIL-53(Al) was highlighted. Also, the effect of operating parameters on the conversion of acetic acid were investigated.

Methods

The terephthalic acid (TPA, 99%), the $Al(NO_3)_3·9H_2O$ (99%) were purchased from ABCR, N,N-dimethylformamide (DMF, 99.8%), butanol, hexanol were purchased from MERCK. All the chemicals in this study were used without further purification.

Synthesis and sulfation of MIL-53(Al)

In solvothermal method, MIL-53 (Al) was prepared according to the report by[2]. 0.844 gram $Al(NO_3)_3·9H_2O$ and 0.249 gram H_2BDC were mixed in a solvent of 11 mL of N,N-dimethylformamide and 4 mL water. The precursor solution was transferred to a Teflon lined stainless steel autoclave and heated at 130^oC for 48 hours. The synthesized white MIL-53(Al) powder was washed with water to remove the nitric acid produced during synthesis and then washed with DMF to remove the unreacted BDC. The obtained material was activated at 150°C for 12 hour.

Characterization of MIL-53(Al) and sulphated MIL-53(Al)

X-ray powder diffraction patterns of MOFs were obtained with a Rigaku Ultima-IV diffractometer. Measurement of the surface area and adsorption isotherm of nitrogen on the MOFs was obtained at 77 K using a Micromeritics Gemini - 2380 apparatus. Before the nitrogen adsorption was accomplished, the humidity content in the MOFs pores was evacuated for 4h at 150^o C to remove the water molecules from the pores of the MOFs. The specific surface area values of the MOF were calculated with the Brunauer–Emmett–Teller (BET) method and the Langmuir method using the adsorption data of the nitrogen adsorption isotherm. The thermal stability of the MOFs was investigated by thermal gravimetric analysis (TGA), using a Perkin Elmer Pyris 1 thermal analyzer with a range between 30^o C and 500^o C with a heating rate of 5^o C/min. The ATR-Fourier transform infrared (FT-IR) spectrum was determined using FT-IR spectrum 100 with a range of 650–4000 cm^{-1}. To understand whether the materials gain acidic property, N-butylamine titration method was carried out for raw and sulfated MOFs. 0.05 gram of the MOF was suspended in 10 mL acetonitrile and mixed for 3 hours. Then, the suspension was titrated with 0.1N n-butylamine in acetonitrile.

Catalytic Activity Measurement

Acetic acid and butanol were fed to the batch reactor equipped with a condenser to prevent loss of material during experiment. Temperature controller was also used for heating the reaction mixture to reaction temperature. The mixture was stirred at 500 rpm to prevent concentration gradients across the reaction mixture. After the reactants reached to the experimental temperature, catalyst was added. Analyses of the samples were performed using Agilent 7890A gas chromatograph.

Results and Findings

Effect of sulfation on the structure of MIL-53(Al)

Figure 1(a) shows the crystal structure of the synthesized and sulfated MIL-53 (Al). The diffraction peaks matched well with the literature for MIL-53(Al)[1,6] . MIL-53(Al) was sulfated to increase the acidity. As shown from Figure 1(a); the crystal structures of MOFs don't show any difference after sulfation. The surface area decreased after sulfation because of the increment of sulfur content and the volume of the sulfoxy acid groups after sulfation in the MIL-53(Al) (Table 1). This situation causes a decrease in the porosity of MOFs.

The TGA profile shows that MIL-53(Al) is stable up to 400°C (Figure 1 (b)) and a 3-7% weight loss between 50 and 100°C results from water evaporation for MOFs. As shown in Figure 1(b), the weight change starts near 300 °C due to the decomposition of the network and a 10 % weight loss between 300 and 400°C.[1]

According to the FT-IR spectrum of MIL-53(Al) (Figure 4(c)), the strong bonds between 1600 and 1400 cm^{-1} correspond to O-C-O vibrations. This is proof of the presence of dicarboxylate within MIL-53(Al). The bonds at 1040 and 750 cm^{-1} can be attributed to the vibration of the aromatic ring (benzene). Sulfated sample shows an additional peak at 1292 cm^{-1} due to the sulfoxy acid strechings[8].

Surface acidity test for raw and sulfated MIL-53(Al) was performed by N-butylamine titration method. Figure 2 shows the titration results of MOFs. According to this result, acidity of MIL-53Al was increased with sulfation. Initial electrode potential values (Ei) increased from 35 to 83. If Ei is greater than 100 mV, material has very strong sites, if Ei is between 0 and 100 mV, material has strong sites, if Ei is between 0 and -100 mV, material has weak sites, if Ei is smaller than -100 mV, material has very weak acid sites[9]. According to results, sulfation increased the acid strength of material for all MOFs.

Activity of MIL-53(Al) and sulphated MIL-53(Al)

Esterification of acetic acid with butanol was carried out using MIL-53(Al) and sulfated MIL-53 (Al) as catalyst. To determine the optimum operating conditions, different parameters including alcohol chain length, temperature, and catalyst loading and molar ratio of alcohol to acid were studied. To understand the importance of acidic property on catalyst in esterification reaction, the sulfated and non – sulfated materials were also tested. In addition, reusability of catalysts and catalyst leaching were studied. After the esterification experiment which took 7 hours, samples were taken and analysed by Gas Chromatography (GC). Therefore, the conversion of acetic acid were calculated according to the results obtained from GC. The chain length and branching of alcohol and acid effect the yield of ester. Conversion is decreased by increasing of the chain length of alcohol and acid for all MOFs. In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. As the chain length increases, the conversion values decreases because of the difficulty of performing esterification reaction. Conversion decreased from 64.4 to 57.7 when hexanol was used instead of butanol.The effect of temperature on the conversion of acetic acid was studied at three different temperature (353, 358 and 363 K). While three different temperature values were tested, other conditions were kept constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. The conversion increases with increasing temperature because temperature increases the collision between molecules. Similar results were observed in the literature. [10–12] the conversion results were calculated as 57.8, 61, 64.4, respectively. To compare the sulfated and non-sulfated materials activity on esterification reaction, the experiment were repeated before and after sulfation. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. As shown from Figure 3, sulfation increases the catalytic acitivity of catalyst for the esterification of acetic acid with butanol. As shown from results, sulfation increases the catalytic acitivity of catalyst for the esterification of acetic acid with butanol.

Reusability and Leaching of MIL-53(Al) and sulfated MIL-53(Al)

The catalyst could be separated from the reaction mixture by simple filtration, and could be reused without a significant degradation in catalytic activity. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500 rpm. The used catalysts were filtered from reaction mixture then they were used again at the same conditions. The conversions were obtained as 64.4, 62.1 and 60.3 for first, second and third usage of them. It can be concluded that from this results, this material is effective and reusable for liquid phase esterification reactions and could be reused without a significant degradation in catalytic activity. To observe the catalysts leaching, catalysts were filtered after 1 hour, and experiment continued up to 6 hours, the conversions of acetic acid were obtained in absence of catalyst. The results were shown in Figure 4. After catalyst was filtered, conversion values remained constant, so, it can be concluded that there was no catalyst leaching.

Conclusion

In this study, aluminium salt was selected as metal precursor and MIL-53 (Al), was synthesized by solvothermal method. Then the synthesized material was sulfated to increase the acidic property. Characterization of synthesized and sulfated materials were performed by FT-IR, BET, XRD and TGA methods. The sulfated material was used in esterification reaction of acetic acid to test the catalytic activity. Time, sulfation, temperature and alcohol effect were investigated. Also reusability of sulfated MOF was achieved by washing with pure water.

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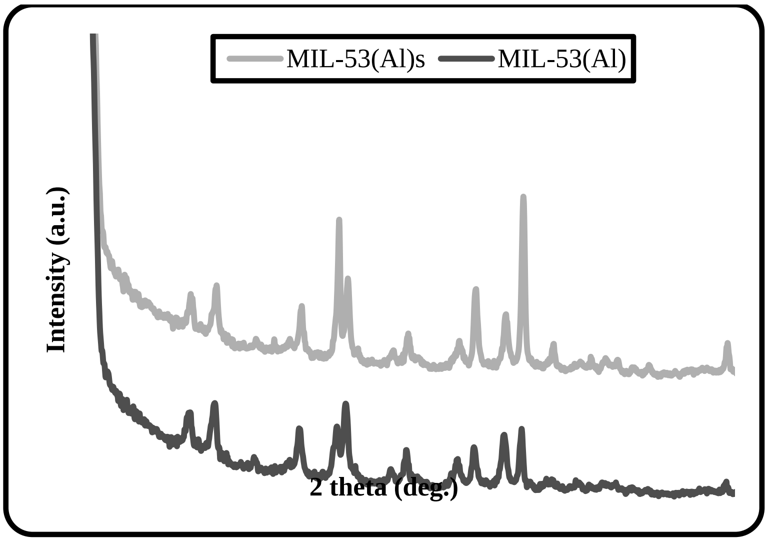
Table and Figures

Table 1. BET analysis results of MOFs

	BET Surface Area, m^2/g	**Langmuir Surface Area, m^2/g**	**Pore Volume cm^3/g**	**Adsorption Average Pore Width, Å**
MIL-53(Al)	578.79	860.36	0.54	37.79
MIL-53(Al)s	66.90	107.56	0.20	122.11



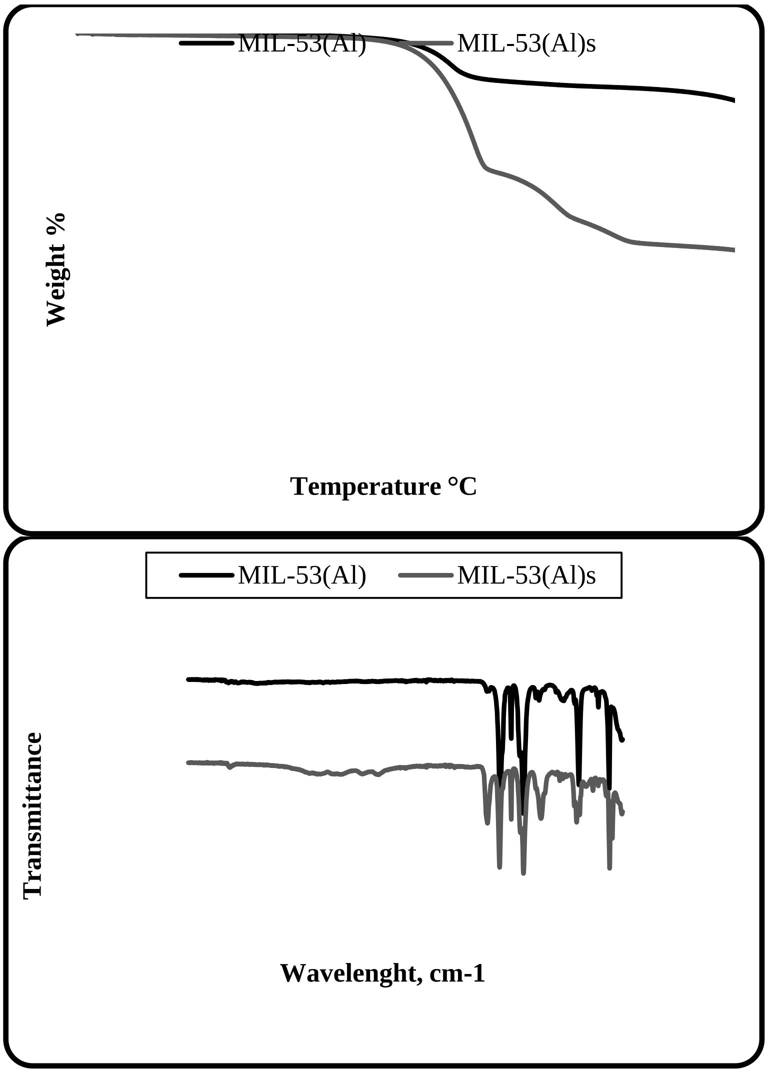


Figure 1 (a) XRD pattern; (b) TGA profile; (c) FT-IR spectrum of MIL-53(Al) and MIL-53(Al)s

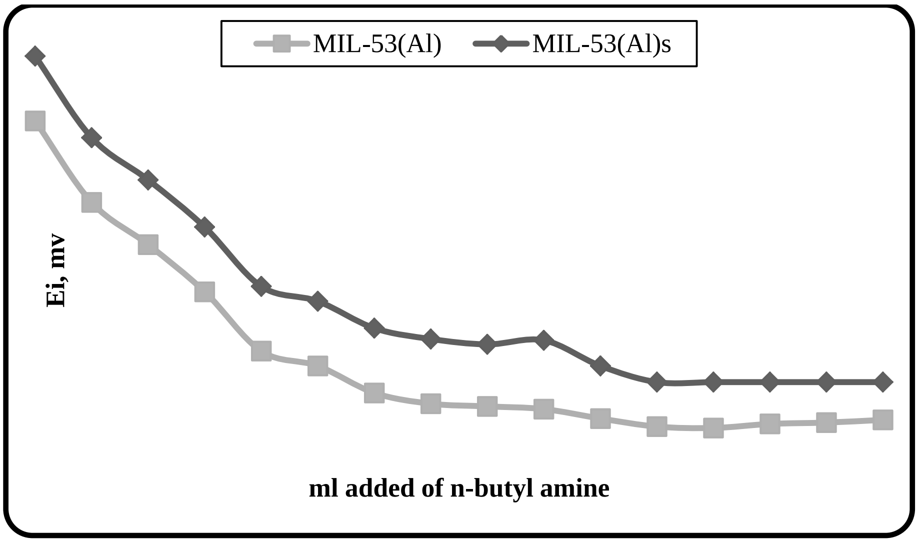


Figure 2. Potentiometric titration of n-butylamine in acetonitrile for MOFs

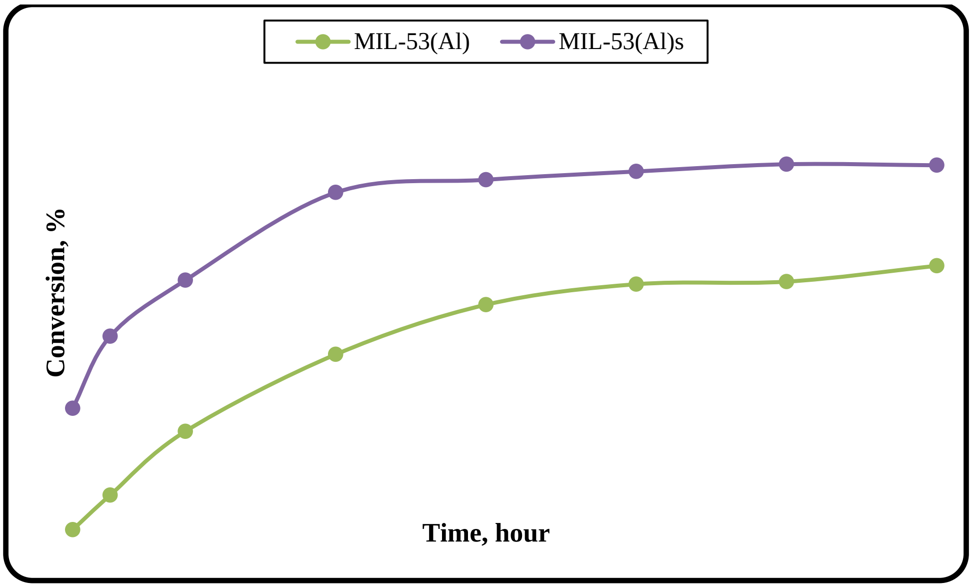


Figure 3. Sulfation effect on esterification of acetic acid

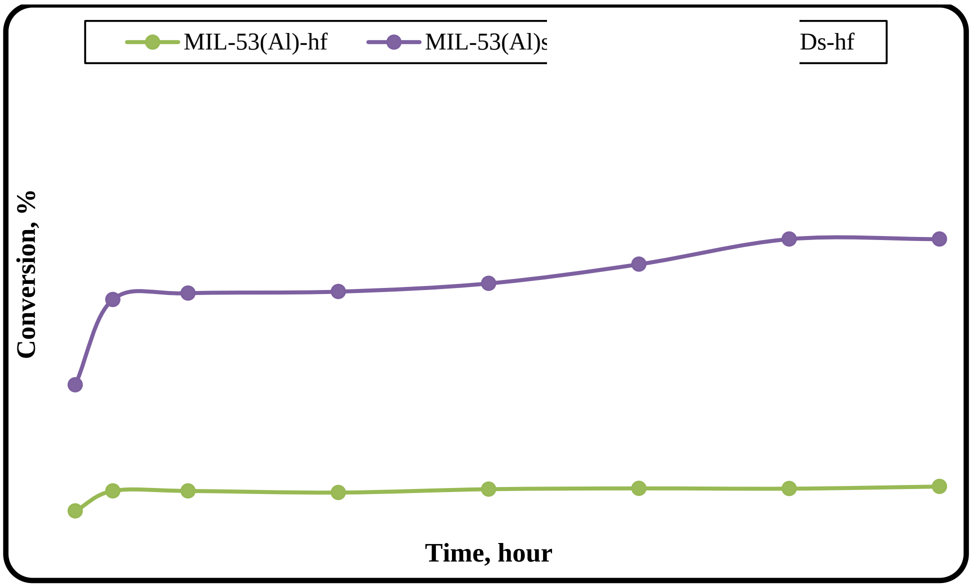


Figure 4. Hot filtration results

References

Patil, D. V.; Rallapalli, P. B. S.; Dangi, G. P.; Tayade, R. J.; Somani, R. S.; Bajaj, H. C. *Industrial and Engineering Chemistry Research* 2011, *50* (18), 10516–10524.

Zhou, M.; Wu, Y. N.; Qiao, J.; Zhang, J.; McDonald, A.; Li, G.; Li, F. *Journal of Colloid and Interface Science* 2013, *405*, 157–163.

Xie, L.; Liu, D.; Huang, H.; Yang, Q.; Zhong, C. *Chemical Engineering Journal* 2014, *246*, 142–149.

Trung, T. K.; Trens, P.; Tanchoux, N.; Bourrelly, S.; Llewellyn, P. L.; Loera-Serna, S. *Journal of the American Chemical Society* 2008, *53* (22), 78035.

Hu, Y. H.; Zhang, L. *Advanced Materials* 2010, *22* (20), 1–14.

Himsl, D.; Wallacher, D.; Hartmann, M. *Angewandte Chemie - International Edition* 2009, *48* (25), 4639–4642.

Maes, M.; Vermoortele, F.; Alaerts, L.; Couck, S.; Kirschhock, C. E. a; Denayer, J. F. M.; De Vos, D. E. *Journal of the American Chemical Society* 2010, *132* (43), 15277–15285.

Goesten, M. G.; Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Sai Sankar Gupta, K. B.; Stavitski, E.; Van Bekkum, H.; Gascon, J.; Kapteijn, F. *Journal of Catalysis* 2011, *281* (1), 177–187.

Hassan, S. M.; Ibrahim, a a; Mannaa, M. a. 2013, *4* (2), 104–116.

Qu, Y.; Peng, S.; Wang, S.; Zhang, Z.; Wang, J. *Chinese Journal of Chemical Engineering* 2009, *17* (5), 773–780.

Sert, E.; Buluklu, A. D.; Karakuş, S.; Atalay, F. S. *Chemical Engineering and Processing: Process Intensification* 2013, *73*, 23–28.

Sert, E.; Atalay, F. S. *Chemical Engineering and Processing: Process Intensification* 2014, *81*, 41–47.