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CHARACTERIZATIONS AND CATALYTIC ACTIVITIES INVESTIGATION OF SYNTHESIZED SOLID-BASED HETEROGENEOUS CATALYSTS IN THE ESTERIFICATION

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ABSTRACT

Mesoporous materials functionalized with STA(Silicotungstic acid) have been proved to be efficient catalysts for esterification reactions. In the investigation, impregnation method was applied for the synthesis of STA/MCM-41 catalysts. MCM-41 and STA(Silicotungstic acid) were used to silica source and active material respectively. The active material was loaded by dry-impregnation method after silica source. Molar ratios of catalysts were determined by 1.25, 2.5 and 5% (W/Si). Actually, this molar ratio values are very low for the impregnation method. But catalysts were successfully synthesized by applying impregnation method. And catalytic activities of STA/MCM-41 catalysts were investigated with an ethyl acetate reaction. On the other hand, the second reaction of STA/MCM-41(2.5%) catalyst was carried out in the presence of under identical conditions after the first reaction. Before and after reactions, the physical properties of the catalysts were determined by XRD, DRIFT, BET, SEM and Mapping analysis methods.

Keywords: Catalyst, Impregnation, STA/MCM-41, Catalytic activity, Characterization

1. INTRODUCTION

A new family of silica based mesoporous materials M41S in 1992 was discovered by scientists at Mobil [1-4]. Recently numerous research concerning the preparation conditions, synthesis methods, characterization and use of these materials as catalysts support by adding catalytic active sites in different reactions about MCM-41 have been reported [5, 6].The catalysts synthesized with these support materials showed excellent properties due to their strong acidity. On the other hand, the pore size of the catalysts synthesized with these templates have a maximum value of 1nm disabling the interaction of the reactants with the active sites located inside the channels of the template [7]. M41S family provided new alternatives to be utilized as templates in catalyst synthesis. The M41S family consists of MCM-48, which has a cubic ordered pore structure, MCM-41, which has a hexagonally ordered pore structure and MCM-50, which has an unstable lamellar structure. In this review we cover the synthesis, modification, characterization and potential applications of these materials [8]. The characteristics of these materials have large surface area, very narrow and ordered pore size distribution [8-10]. with pore diameter adjustable from to 100Å [8]. These materials have high surface area and an ordered pore size distribution [9, 10]. But the pore size of the structure is limited to 80 Å and the hydrothermal stability of the material is low which constitutes difficulties in high temperature applications [8, 9]. The structures of these mesoporous materials are formed of pure silica which shows low activity in reactions. In order to increase the activity, a heteroatom needs to be introduced into the framework of the structure [11, 12]. Among these, aluminum was incorporated to the mesoporous structure to create Bronsted acid sites and the synthesized catalysts were successfully used in degradation of polymers [7, 13, 14]. Heteropoly acid (HPA) compounds are known for their strong Bronsted acidity and high proton mobility and hence being used in a variety of reactions [15-21]. These compounds show high activity in reactions, nevertheless, their low surface areas [19] and solubility in the presence of polar solvents [17, 19] limit their use as catalysts. The investigations in the use of these compounds focused clearly on the chemical interactions of the

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compound with certain support materials. The aim of support utilization is to fix the compound to the career in order to prevent leaching in liquid-phase reactions [17].

Currently, the HPAs are attracting significant interest in biodiesel production. However heteropoly acids have many disadvantages as catalysts such as low surface area, low thermal stability and high dissolutions in solvent. One of the HPAs is STA. HPAs have strong Lewis acids and Bronsted acids sites. HPAs are needed to have high surface area and thermal stability support material to be used efficiently in the production of biodiesel, esterification, adsorption and desorption applications. M41S is one of the best between catalytic materials for the development hydrothermal and thermal stability.

Esterification is performed in the homogenous phase in the presence of acid catalysts such as sulfuric and p-toluenesulforicacids [22]. Alternative approaches have been investigated with regard to heterogeneous catalysts because homogenous catalysts cause corrosion and contamination problems with the final product [22, 23]. Esterification reactions can be performed exclude a catalyst, even though the reaction is carried out extremely slow, for the rate of acetic acid is dependent on the autoprotolysis of the acetic acid. Consequently, esterification needs an acid catalyst, which acts as a proton donor to acid. Mineral acids are typical homogeneous catalysts such as HCl, HF, $ClSO_2OH$, H_2SO4, etc. These catalysts and heterogeneous catalysts are used in the esterification [24].

The activity of MCM-41 supported that the heteropoly acid catalysts are long been investigated for various reactions. The most popular methods of synthesis are sol-gel [25]and impregnation of the active material to readily-prepared support structure [18, 26-28]. Reactions conducted with HPA impregnated catalysts included esterification reactions [25, 26], isopropylation of naphtalene [27] and alkylation of phenol [28]. The loading amounts in syntheses ranged between 10-80% based on the application [26-28]. The method of synthesis is crucial in achieving strong interactions between the active material and the support structure. Impregnation of the active compound to the support has proven to be effective in obtaining high activities. However, some leaching eventually occurred in repeated use of these catalysts. In order to minimize the leaching of the active material, direct hydrothermal synthesis method as a different approach was employed in the present study. The selection of the heteropoly acid compound was thought to be equally important as the selection of synthesis method. The activities of heteropoly acid compounds were recently compared with the works of Degirmenci et.al. for ethyl-tert-butyl ether (ETBE) [15] and Varisli et.al. [20] for ethylene and diethyl-ether productions. Results showed that silicotungstic acid (STA) had illustrated the highest activity among heteropoly acid compounds [19, 20]. Hence STA was selected in the present study as active material of the catalyst. The catalytic activity of the synthesized catalyst was determined by esterification of acetic acid with ethanol selected as model reaction. The parameters applied in reaction were determined based on literature survey [25, 29-31].

In the present paper, STA/MCM-41 catalysts with high surface areas were synthesized by impregnation method for different W/Si mass ratios varying between % 1.25, %2.5 and %5. To illustration that such catalysts have catalytic activity at low loading rates in that the loading rates of active materials were kept low. Catalytic activities of STA/MCM-41 catalysts was investigated with an ethyl acetate reaction and physical properties of the catalysts before and after reaction were determined with XRD, FT-IR, DRIFT, BET, SEM and mapping analysis methods. The applied impregnation method route was thought to enhance the uniform dispersion of the W/Si throughout the structure of catalysts, hence STA/MCM-41 catalysts have attractive properties for potential use in esterification reactions. Moreover, ıt observed that the leaching problem was limited after the recovered of STA/MCM-41 catalyst (%2.5) due to the washing(it was used deionization water) method.

2. MATERIAL AND EXPERIMENTAL SECTION

2.1. Preparation of MCM-41/STA Catalysts

Initially, a solution of 13.2 grams surfactant (CTMABr; Cetyltrimethylammonium bromide Merck) with

87ml deionized water was prepared at 30°C and mixed with 300-400 rpm for 1 hour. Then 11.2 ml and 2.53 M Na_2SiO_3 (containing %27 SiO_3, Merck) was added dropwise before active material STA (tungstosilicic acid, Sigma-Aldrich). STA was added to resulting synthesis mixture as solid. STA/MCM-41 was synthesized modified based on the literature [32]. Then two drops of H_2SO_4 were added. The pH of solution was adjusted with H_2SO_4 to around 11-12. The resulting solution was further stirred for 1 hour and aged at 120°C for 96 hours. The formed crystalline sample was filtered with deionized water, dried at 30°C for 18 hours and finally calcined at 350ºC for 6 hours in a tubular furnace for template removal by flowing air. The amounts of STA added to the catalysts were determined as 1.25, 2.5 and 5% based on the weight(0.081, 0.162 and 0.324g) ratio of tungsten (W) of STA to Silicium (Si) of Na_2SiO_3. Schematic presentation of the synthesis STA/MCM-41 was illustrated in (Figure 1).

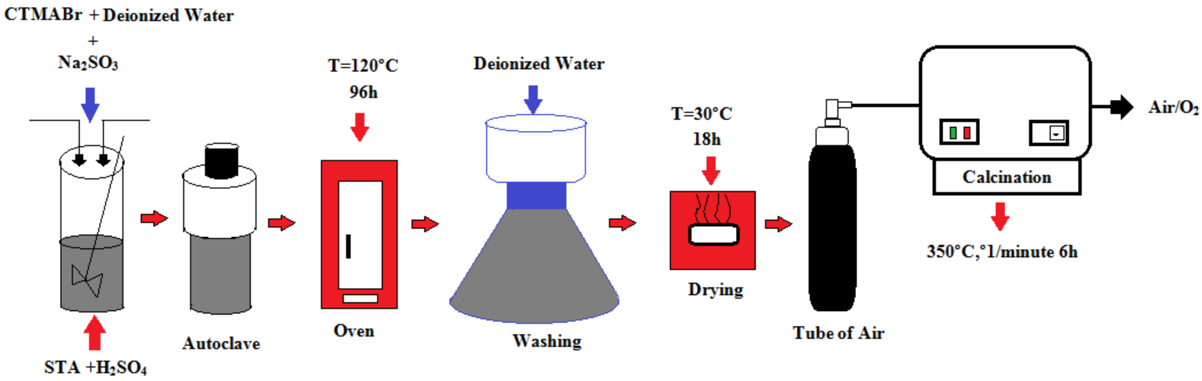

Figure1. Schematic presentation of STA/MCM-41catalysts synthesis

2.2. Catalytic Reaction Experiments

The esterification reaction of acetic acid with ethanol was carried out as the model reaction. The experiments of ethyl acetate were conducted in a batch reactor equipped with a reflux cooler. The reactions were performed at 343K, 1/1 feed molar ratio(ethanol/asetic acid), at 1000rpm stirring speed and the catalyst amounts were determined as 0.4g (reactor size; 80ml). The reactants and product mixture were analyzed in a Shimadzu GC-2010 gas chromatograph equipped with a FID detector operated at 300°C and a TRB Wax; 30m x 0.32mm x 0.5µm capillary column. Calibration factors and acetic acid conversion were determined with Shimadzu GC-2010. N_2 was used as the carrier gas in constant pressure (58,0 kpa) with H_2 and dry air. Manuel was injected 0,5µl of sample value at a split ration 1/1, column flow 1.74 ml/min., injected temperature 280 °C, FID temperature 300°C, column temperature 45-100°C ramped at 30°C /min. The analysis time was 5.33 min. Synthesis of ethyl acetate with ethanol and acetic acid reactants was performed by the following reaction Equation 1.

acetate with ethanol and acetic acid reactants was performed by the following reaction Equation 1.

$$AA + EtOH \rightarrow EtAC + H_2O \qquad (1)$$

The conversion was expressed with acetic acid transformation using the reaction calibration factors(ethanol-acetic acid, ethanol- ethyl acetate) as shown in Equation 2.

$$X_{AA/EtAC}= \frac{\propto_{EtAC}*A_{EtAC}}{(\propto_{EtAC}*A_{EtAC})+((\propto_{EtOH}*A_{EtOH})+((\propto_{AA}*A_{AA})} \qquad (2)$$

Where:
$X_{AA/EtAC}$=Acetic acid conversion(%)
$\propto_{EtAC}$ = Calibration factor of Ethyl acetate
$\propto_{EtOH}$ = Calibration factor of Ethanol
$\propto_{AA}$ = Calibration factor of Acetic acid

A_{EtAC}= Area of Ethyl acetate
A_{EtOH}= Area of Ethanol
A_{AA}= Area of Acetic acid

2.3. Characterization Analyses

DRIFT (Diffuse Reflectance Fouirier-Transform Infrared) analyses of STA/MCM-41 catalysts were conducted on a Perkin Elmer IR instrument in the range 380-4000cm^{-1}. XRD patterns were obtained on a Panalytical Empryan HT-XRD instrument using CuKα (Wavelength of Cu; 1.54060) radiation with 0.066 step size and over the range 0°<2 θ<10°. Pore size distributions and average pore diameter of STA/MCM-41 catalysts were determined by nitrogen adsorption-desorption isotherms in ASAP2020. BET surface areas were obtained from nitrogen adsorption-desorption experiments conducted at 523K after degassing the samples at 363K for 30 minutes. The morphological structure of the catalysts and elemental composition of tungsten (W) and silica (Si) before and after reaction were carried out with SEM and mapping analyses (Zeiss SUPRA V 40). XRD and BET analyses were catalysts recovered after first run of ethyl acetate production. XRD, BET, SEM and mapping analyses were also conducted on the after reaction for the determination changing structures of catalysts.

3. RESULTS AND DISCUSSION

3.1. Catalytic Reaction Experiments

Esterification reaction of acetic acid with ethanol was selected as the model reaction in the present work. Reaction experiments were conducted at 343K, 1/1 molar ratio(ethanol/asetic acid) in the presence of 0.4g STA/MCM-41 catalysts, in a batch reactor equipped with a reflux condenser. Second reaction of STA/MCM-41 (2.5%) catalyst was conducted recovered from the reaction media and used under identical experiment conditions after being washed and dried at the reaction temperature (6h). It indicated that preserved its catalytic activity. Results were illustrated in (Figure 2), in terms of acetic acid conversion obtained with bare 1.25-5% catalysts and run 2.5% catalyst. On the other hand, calibration experiments carried out without catalyst.

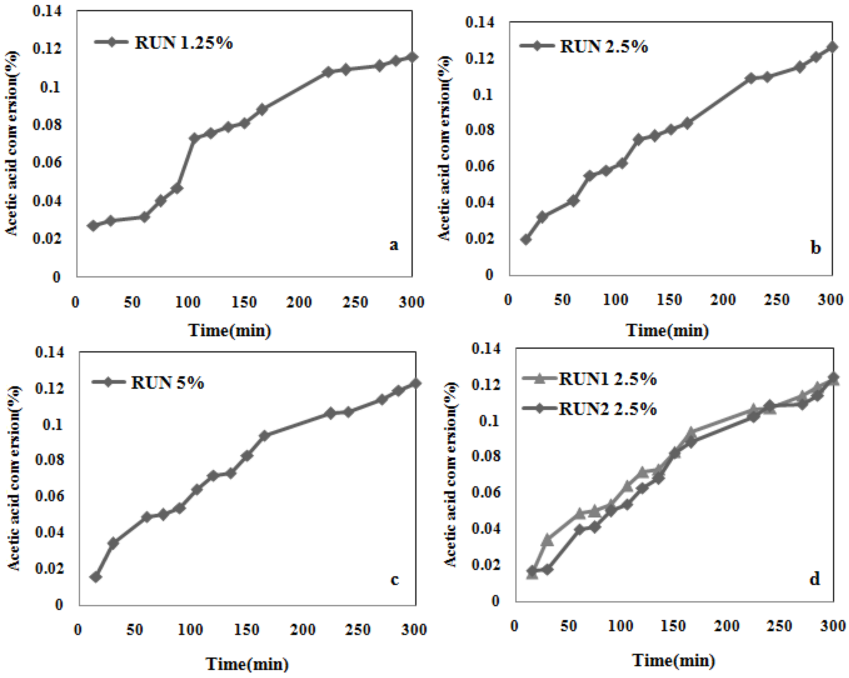

Figure 2. Acetic acid conversions obtained in the presence of bare STA/MCM-41 catalysts synthesized with a) W/Si: 1.25% b) W/Si: 2.5% c) W/Si:5% d) compare of results of the bare(Run1) and reused (Run2) catalyst(2.5%).

3.2. Characterization Analyses

The hexagonal structure of parent MCM-41 was identified by determination of diffraction patterns in the low angle range between 2Ө= 0°-10° with four peaks which corresponded to(100), (110), (200) and (210) reflections of ordered mesophase[31,33]. Before reaction, in the XRD patterns observe that the peaks determining (200) and (210) reflections had disappeared for STA/MCM-41 catalyst synthesized with 1.25% W/Si ratio (Figure 3). However 2.5 – 5 % W/Si STA/MCM-41 catalyst had lost just one (210) (Figure 3).The intensities of the peaks reflections of catalysts decreased and finally disappeared due to blockage of the pores with increasing STA amount without %5 (Figure 4). Because STA is accumulated in the walls of the pores rather than it is deposition inside the pores.

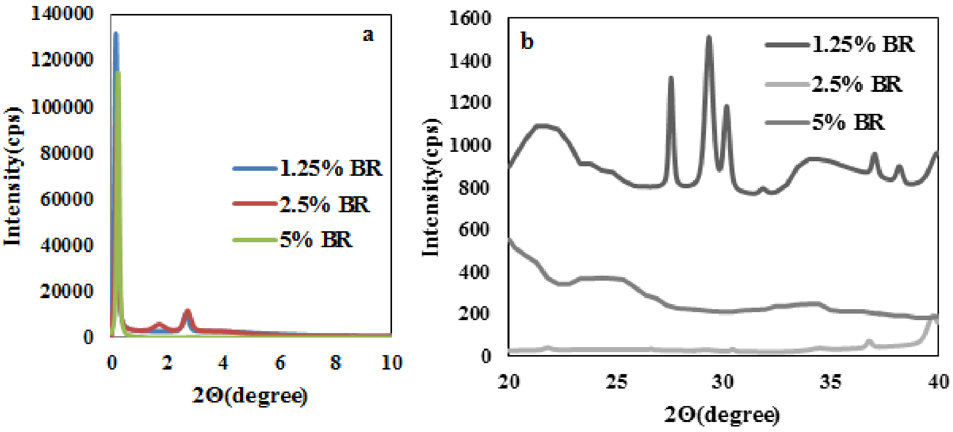

Figure 3. Before reaction(BR) Low-High angles XRD patterns of a) %1.25 -5 W/Si b)%1.25-5 W/Si W/Si synthesized STA/MCM-41 catalysts.

After reaction(AR), the intensities of the peaks reflections decreased and high angle XRD of patterns disappeared due to decomposition of STA amount (Figure5).

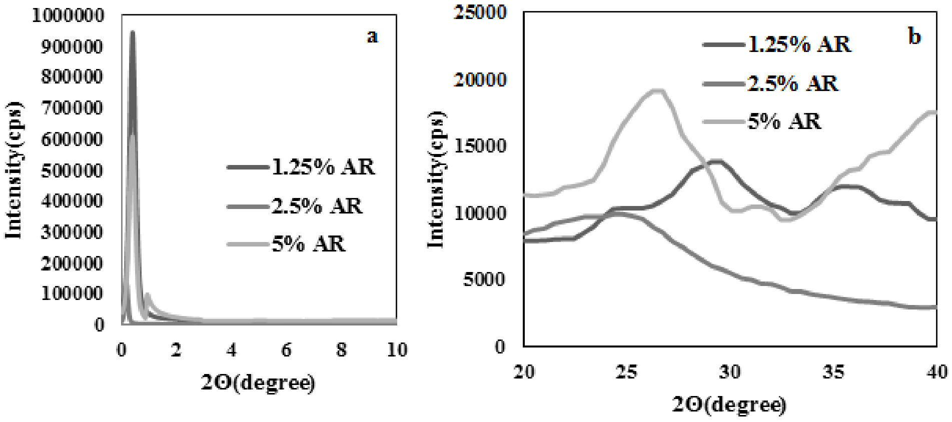

Figure 4. After reaction Low-High angles XRD patterns of a) %1.25 -5 W/Si b) %1.25-5 W/Si W/Si synthesized STA/MCM-41 catalysts.

Before and after reaction, nitrogen adsorption-desorption experiments conducted with STA/MCM-41 catalysts were given in (Figure 5, 6). Physical Properties of MCM-41 support(surfactant) material and STA/MCM-41catalysts were illustrated in (Table1) before and after reaction. MCM-41 exhibited a type IV isotherm with an H1 hysteresis loop characteristic of mesoporous structure [31, 33, 34] (Figure 5) and 6. Results obtained with the catalysts indicated a decrease in pore volumes with STA addition without 5%. Before reaction BET measurements showed a decrease in total surface area of the parent with STA addition without after reaction as expected (Table1). However, it was interesting to observe an increase in total area of the catalyst with increasing amount of STA(5% W/Si) utilized in synthesis. This increase was thought to be due to restructuring of the hexagonal structure of the sample molecule promoted by the impregnation preparation technique. The obtained result was also evidenced by the decrease in the micro pore area by STA addition. BJH pore size distribution was showed (Figure 7). In addition, the irregulations surface areas and pore volumes of the synthesized catalysts were due to the initial value of the P/Po (Table1).

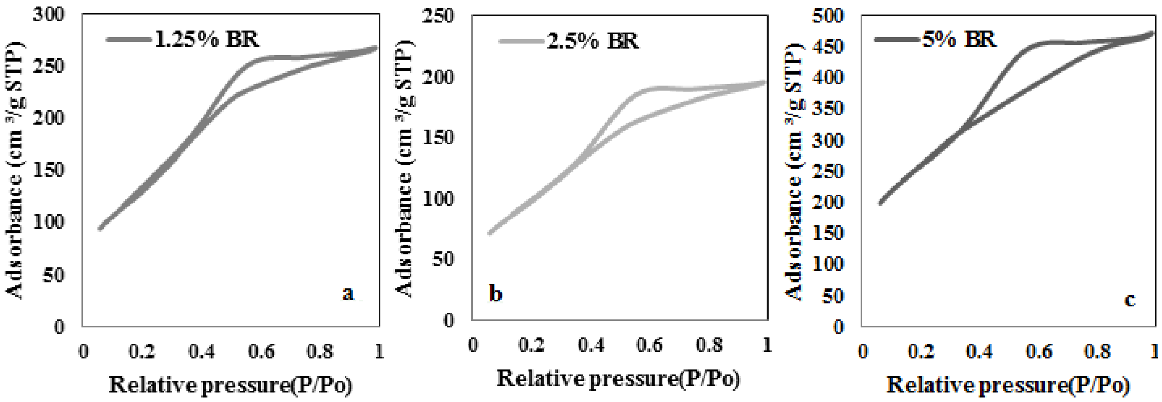

Figure 5. Before reaction N_2 adsorption-desorption isotherms of a) %1.25 W/Si b)%2.5 W/Si c) %5 (W/Si)

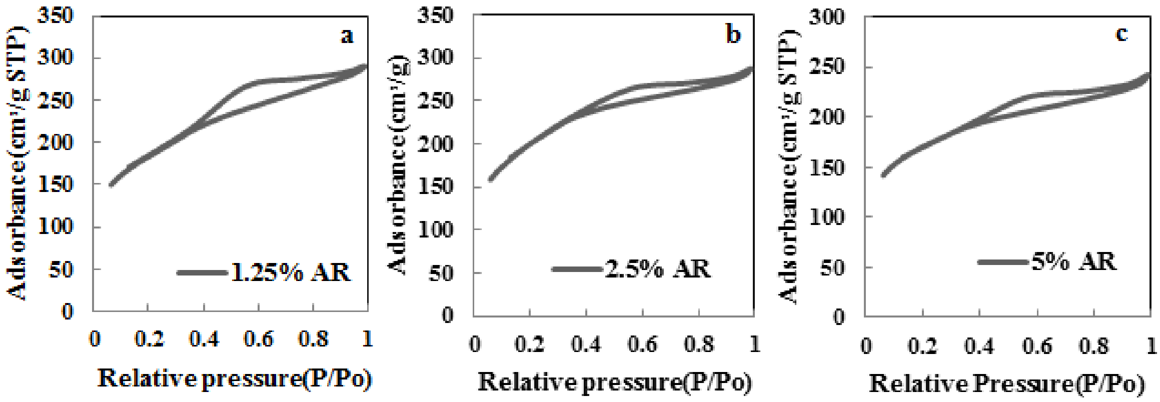

Figure 6. After reaction N_2 adsorption-desorption isotherms of 1.25% (W/Si) b) 2.5 %(W/Si) c) 5% (W/Si)

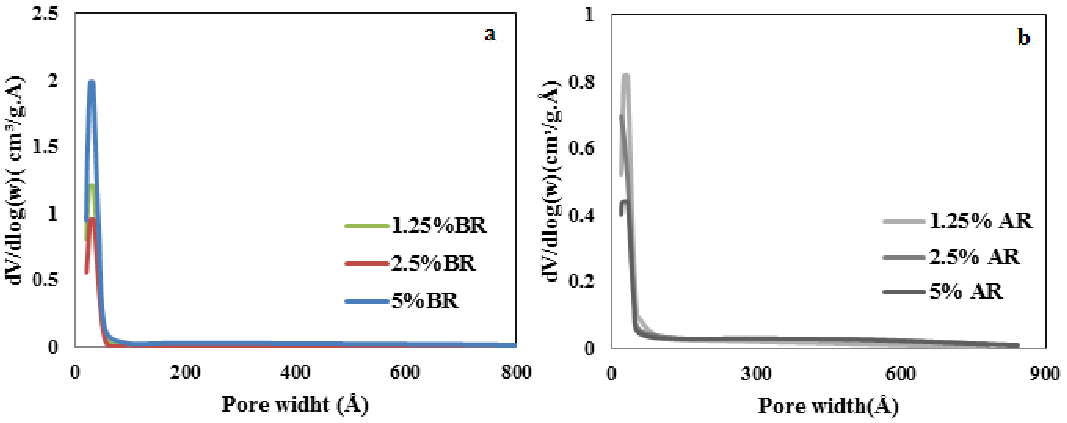

Figure7. Pore size distributions (BJH) of a) before reaction b) after reaction

DRIFT analyses were conducted with pyridine adsorbed STA/MCM-41 catalysts that were illustrated in (Figure 8). The presence of both Lewis acid(LA) and Bronsted acid(BA) sites observed in the wavelengths of 1441 and 1590 cm^{-1} respectively. DRIFT analyses showed that catalysts had acidic characteristics features. These values were determined by identification of peaks at 1456 - 1606, 1450-1604 and 1448-1603 cm^{-1} for the STA/MCM-41 (W/Si: %1.25-5), respectively. The peaks observed at 1488-1490 cm^{-1} were attributed to physically adsorbed pyridine(P) [31, 33, 34].

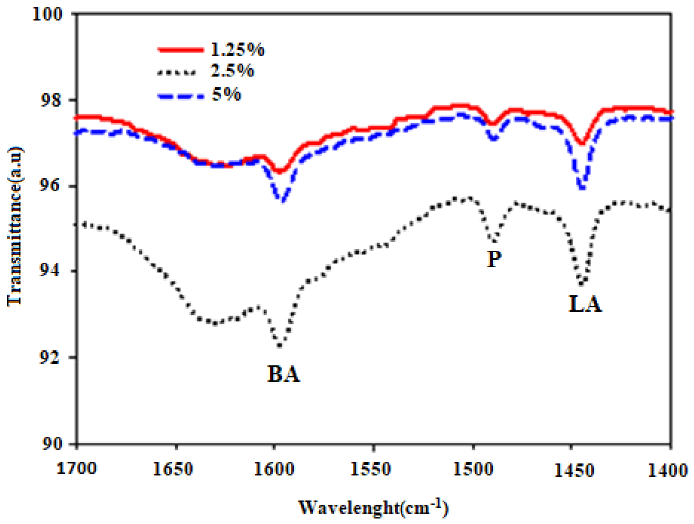

Figure 8. DRIFT analyses of pyridine adsorbed STA/MCM-41 used catalysts (1.25-2.5-5% (W/Si))

The characteristic lattice parameter was calculated from Equation (3) The lattice parameters and the textural properties of samples were measured by BET(N_2 adsorption/desorption) and with X-ray diffraction analysis[31, 33, 34] in the (Table1).

$$a=2d_{(100)}/3^{1/2} \qquad (3)$$

The pore wall thickness "δ" was then estimated from the average pore diameter (BJH adsorption average pore diameter; dp) and the lattice parameter”a” using Equation (3) [31, 33, 34].

$$\delta= a-0.95dp \qquad (4)$$

Table 1. Physical properties of STA/MCM-41 catalysts

MCM-41/STA W/Si (%)	**BET surface area(m²/g) m²/g**		**Pore volume (cm³/g)**		**Pore diameter (nm)**		**d(100) nm**		**Pore Walls Thickness ”δ”(nm)**	
	***B**	****U**	**B**	**U**	**B**	**U**	**B**	**U**	**B**	**U**
1.25	509.6	598.	0.46	0.32	11.8	10.4	56.6	25.4	62.3	26.5
2.5	372.9	647.	0.33	0.29	16.1	9.3	52.7	19.9	57.8	20.4
5	940.9	527.	0.68	0.22	6.4	11.3	41.2	25.4	44.6	26.6

*B: bare catalyst; **U: used catalyst

Deformation of pore structure could not also be seen from SEM images obtained after reaction (Figure 9). These images showed the preservation of pattern structure. After reaction mapping analyses of catalysts were illustrated in (Figure 10). Result of the mapping analysis homogeneous distribution of tungsten(W) and silicate(Si) of STA molecule was observed.

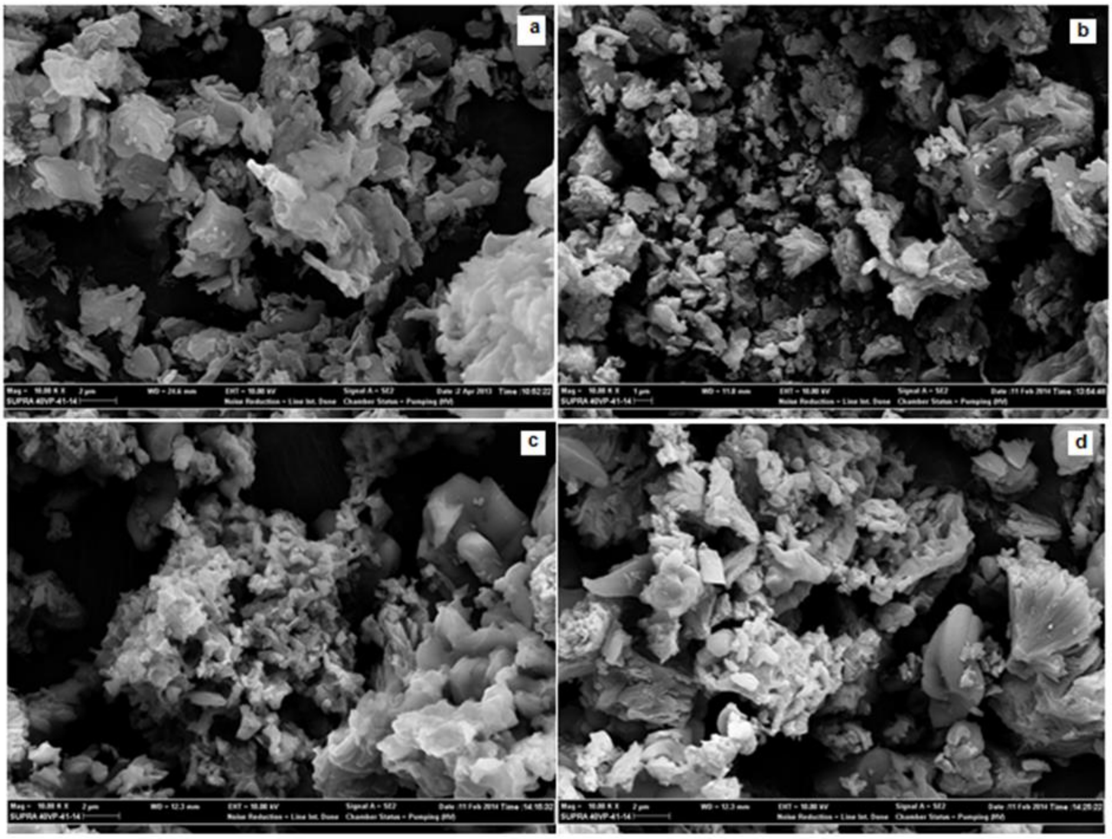

Figure 9. SEM images of parent MCM-41[37] and used STA/MCM-41 catalysts synthesized with a) MCM-41 b) W/Si:1.25% c)W/Si:2.5% d) W/Si:5%.

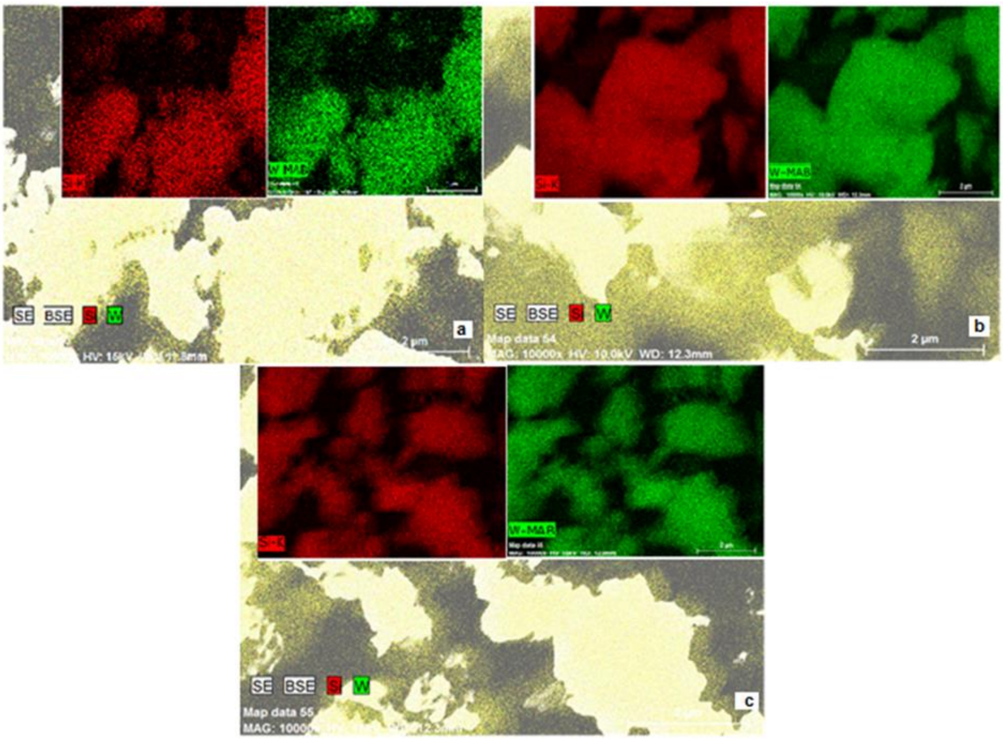

Figure 10. Tungsten (W) and Silicium (Si) EDX mapping of used STA/MCM-41 catalysts synthesized with a) 1.25 % W/Si b) 2.5 % W/Si c) 5 % W/Si

4.CONCLUSION

Results of the characterization analysis and Ethyl acetate reaction showed that the catalysts were active in an acid catalyzed reaction. The fundamental aim of the paper is show that a new catalyst reacts to the reaction. STA is a very active heteropoly acid, however it readily dissolves in the presence of polar compounds. In order to provide a sustainable activity of the catalyst, the leaching of the compound must be prevented. Results obtained in this work clearly showed that these catalysts could have been used effectively in Ethyl acetate reaction.

Results of Ethyl acetate analysis and characterization studies implied that the loading amounts of STA on parent molecule should not exceed 2.5 % W/Si ratio which was determined as the limit in providing monolayer coverage of the active material. Before reaction, increase of %5 surface area was thought to be due to STA incorporation in the pore wall than it is deposition inside the pores. After the reaction, despite the increase in surface area of catalysts(%1.25-2.5), the pore volume was not observed significant modification. However, significant decrease of surface area and pore volume of %5 was observed. In addition this conclusion was reached based on activity comparison of fresh and used catalysts and evaluation of mapping results. Mapping of W and Si revealed a homogenous distribution of active material on the support which is not valid for the BET result of 5%.

Catalytic activity has been limited (%10-13) due to reaction temperature is determinate by the boiling point of ethanol and acetic acid. Catalytic activity of STA/MCM-41(5%) was decreased due to STA incorporation in the pore wall than it is deposition inside the pores. However, it had been observed that catalytic activity was maintained in the reuse of catalyst (2.5%). Although loading rates are very low for the impregnation method, the catalytic activity is expected to rise with temperature. Reason of that STA is entered into the pores of pattern.

REFERENCES

[1] Kaya E, Oktar N, Karakaş G, Mürtezaoglu K. Synthesis and characterization of Ba/MCM-41 Turk J Chem 2010; 34: 935-943.

[2] Blin J L, Flamant R, Su B L. Synthesis of nanostructured mesoporous zirconia using CTMABr-ZrOCl2.8H2O systems: a kinetic study of synthesis mechanism, International Journal of Inorganic Materials 2001; 3: 959-972

[3] Kresge C T, Leonowicz M E, Roth WJ, Vartuli JC, Beck J S. Nature 1992: 359:710.

[4] Beck J S, Vartuli J C, Roth W J, Leonowicz M E, Kresge C T, Schmitt K D, Chu C T W, Olson DH, Sheppard E W, McCulle S B, Higgins J B, Schlender J L, J Am Chem So 1992; 114:10834

[5] Llewellyn PL, Ciesla Y, Decher H, Stadler R, Schüth F, Unger KK. Stud Surf Sci Catal 1994; 84:2013. 1998; 8:219.

[6] Obalı Z, Sezgi N A, Doğu T. The synthesis and characterization of aluminum loaded SBA-type materials as catalyst for polypropylene degradation reaction, Chemical Engineering Journal 2011; 176-177: 202-210.

[7] Øye G, Sjöblom J, Stöcker M. Synthesis, characterization and potential applications of new materials in the mesoporous range, .Advances in colloid and interface science, 2001; 89-90: 439-466.

[8] Tokay K C, Dogu T, Dogu G. Dimethyl ether synthesis over alumina based catalysts, Chemical Engineering Journal 2012; 184: 278-285.

[9] Gucbilmez Y, Dogu T, Balcı S. Vanadium incorporated high surface area MCM-41 catalysts, Catalysis Today 2005; 100: 473-477.

[10] Dai Q, Wang X, Chen G, Zheng Y, Lu G. Direct synthesis of Cerium (III) incorporated SBA-15 mesoporous molecular sieves by two-step synthesis method, Microporous and Mesoporous Materials 2007; 100 : 268-275.

[11] Aktas O, Yasyerli S, Doğu G, Dogu T. Structural variations of MCF and SBA- 15-like mesoporus materials as a result of differences in synthesis solution Ph, Materials Chemistry and Physics 2011;131: 151-159.

[12] Obalı Z, Sezgi N A, Dogu T. Catalytic degradation of polypropylene over alumina loaded mesopours catalysts, Chemical Engineering Journal, 2012; 207-208 : 421-425.

[13] Marcilla A, Gomez-Siurana A, Berenguer D. Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers, Applied Catalysis A: General 2006; 301: 222-231.

[14] Obalı Z, Doğu T. Activated carbon-tungstophoshoric acid catalysts for the synthesis of tertamyl ethyl ether (TAEE), Chemical Engineering Journal 2008; 138 : 548-555.

[15] Degirmenci L, Oktar N, Dogu G. ETBE Synthesis over silicotungstic acid and tungstophosphoric acid catalysts calcined at different temperature, Fuel Processing Technology 2010; 91: 737-742.

[16] El-Wahab M M M A, Said A A. Phosphomolybdic acid supported on silica gel and promoted with alkali metal ions as catalysts fort he esterification of acetic acid by ethanol, Journal of Molecular Catalysis A: Chemical 2005; 240 109-118.

[17] Brahmkhatri V, Patel A. 12-Tungstophosphoric acid anchored to SBA-15: An efficient, environmentally benign reusable catalysts for biodiesl production by esterification of free fatty acids, Applied Catalysis A: general, 2011; 403 161-172.

[18] Ciftci A. Varisli D, Tokay K C, Sezgi N A, Dogu T. Dimethyl ether, diethyl ether & ethylene from alcohols over tungstophosphoric acid based mesoporus catalysts, Chemical Engineering Journal 2012; 207-208: 85-93.

[19] Varisli D, Dogu T, Dogu G. Petrochemicals from ethanol over a W-Si based nanocomposite bidisperse solid acid catalyst, Chemical Engineering Science 2010; 65:153-159.

[20] Varisli D, Dogu T, Dogu G. Ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropolyacid catalysts, Chemical Engineering Science 2007; 62:5349-5352.

[21] Marchetti J M , Miguel VU, Errazu AF. Heterogeneous esterification of oil with high am out of free fatty acids, Fuel 2007; 86: 906-10.

[22] Mbaraka I K , Radu D R, Lin VS-Y, Shanks B H. Organosulfonicacid – funtionalized mesoporous silicas for the esterification of fatty acid, J. Catal. 2003; 219:329-36.

[23] Okuhara T, Mizuno M, Misono M. Adv. Catal. 1196; 41:113.

[24] Yang L, Qui Y, Yuan X, Shen J, Kim J. Direct synthesis, characterization and catalytic application ofSBA-15 containing heteropolyacid H3PW12O40, Journal of Molecular Catalysis A: Chemical 2005; 229 :199-205.

[25] Sawant D P, Vinu A, Justus J, Srinivasu P, Halligudi S B. Catalytic performances of silicotungstic acid/zirconia supported SBA-15 in an esterification of benzyl alcohol with acetic acid, Journal of Molecular Catalysis A: Chemical 2007; 276: 150-157.

[26] Liu Q Y, Wu W L, Wang J, Ren X Q, Wang Y R. Characterization of 12- tungstophosphoric acid impregnated on mesoporus silica SBA-15 and its catalytic performance in isopropylation of naphthalene with isopropanol, Microporous and Mesoporous Materials 2004; 76: 51-60.

[27] Kumar G S, Vishnubarthan M, Palanichamy M, Murugesan V. SBA-15 supported HPW: Effective catalytic performance in the alkylation of phenol, Journal of Molecular Catalysis A: Chemical 2006; 260: 49-55.

[28] Hasanoglu A, Salt Y, Keleser S, Dincer S. The esterification of acetic acid with ethanol in a pervaporation membrane reactor, Desalination 2009; 245: 662-669.

[29] Cavlar N, Gonzalez B, Dominguez A. Esterification of acetic acid with ethanol: Reaction kinetics and operation in a packed bed reactive distillation column, Chemical Engineering and Processing 2007; 46: 1317-1323.

[30] Miao S, Shanks B. H. Mecahanism of acetic acid esterification over sulfonic acid functionalized mesoporus silica, Journal of Catalysis, 2011; 279: 136-143.

[31] Sener C, Dogu T, Dogu G. Microporous and Mesoporous Mater, 2006;94: 89-98.

[32] Shanmugam S, Viswanathan B, Varadarajan T K. Synthesis and characterization of silicotungstic acid based organic–inorganic nanocomposite membrane, Journal of Membrane Science 2006; 275: 105–109.

[33] Simsek V. Synthesis, characterization and investigation catalytic activity in the glycerol esterification reaction of acidic catalyst, Ph.D. Thesis, Gazi university graduate school of natural and applied sciences january 2015.

[34] Simsek V, Değirmenci L, Mürtezaoğlu K. Esterification of lauric acid with glycerol in the presence of silicotungstic acid incorporated STA/MCM-41 catalysts, International Journal of Chemical Reactor Engineering 2016Accepted.