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Research Article

Synthesis and Characterization of Fe/SBA-15 Heterogeneous Catalysts for Methyl Acetate Production

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Abstract

In the present study, the synthesis of SBA-15 (Santa Barbara Amorphous) support material(SPm) was initially carried out with the method determined according to the literature research. The catalytic property of SBA-15 was imparted by the hydrothermal method (HtM), different from the traditionally applied impregnation method. In this method, the active substance (iron III oxide; Fe_2O_3) was added to the solution during the synthesis of the SPm. The amount of active substance in the synthesized catalysts was calculated based on the mass ratios of silicon (Si) in SBA-15 and iron (Fe) in Fe_2O_3. The active substance ratios in the catalysts were determined as 10, 25% Fe/Si. The activities of Fe/SBA-15 catalysts were tested in methyl acetate production (MAP). MAP reaction experiments were carried out in the presence of 0.4g catalyst (Fe/SBA-15), 373K, in autogenous pressure and 2/1 Acetic acid(AA)/methanol(MeOH) feed rate for 48 hours. The effects of active substance loading rate on AA conversion were determined. The structural properties of Fe/SBA-15 catalysts were investigated by XRD, BET, FTIR/DRIFT, SEM/EDX, and MAPPING analysis methods.

Keywords: Fe, SBA-15, Methyl acetate, Hydrothermal, Characterization.

Metil Asetat Üretimi İçin Fe/SBA-15 Heterojen Katalizörlerin Sentezi ve Karakterizasyonu

Öz

Sunulan bu çalışmada ilk olarak SBA-15(Santa Barbara Amorphous) destek maddesinin sentezi, literatür araştırmasına göre belirlenen yöntemle gerçekleştirilmiştir. SBA-15 maddesine katalitik özellik, geleneksel olarak uygulanan emdirme yönteminden farklı olarak, hidrotermal yöntemle(HtM) kazandırılmıştır. Bu yöntemde, aktif madde (demir III oksit ;Fe2O3) destek madde sentezi sırasında çözeltiye eklenerek gerçekleştirilmiştir. Sentezlenen katalizörlerdeki aktif madde miktarı, SBA-15'teki silisyumun (Si) ve Fe2O3 içerisindeki demirin (Fe) kütlece oranları baz alınarak hesaplanmıştır. Katalizörler içerisindeki aktif madde oranları %10, 25 Fe/Si olarak belirlenmiştir. Fe/SBA-15 katalizörlerin aktiviteleri, metil asetat üretiminde (MAÜ) test edilmiştir. MAÜ reaksiyon deneyleri, 373K, 0.4g katalizör(Fe/SBA-15) varlığında, otojenik basınçta ve 2/1 Asetik asit(AA)/metanol(MeOH) besleme oranında 48 saat boyunca gerçekleştirilmiştir. Aktif madde yükleme oranının AA dönüşümü üzerindeki etkileri belirlenmiştir. Fe/SBA-15 katalizörlerinin yapısal özellikleri ise XRD, BET, FTIR/DRIFT, SEM/EDX ve MAPPING analiz yöntemleriyle incelenmiştir.

Anahtar Kelimeler: Fe, SBA-15, Metil asetat, Hidrotermal, Karakterizasyon.

1. Introduction

Recently, the discovery by mobile researchers of silica-derived and metal-containing M41S materials, these materials have attracted the attention of scientists due to their mesopores, homogeneous pore size distribution, and high surface areas, both as a support for catalysts and as adsorption and separation (Şimşek, 2015). Their use as catalysts in fields attracts attention. Nowadays, silica-based support materials(SiBSMs)(such as SBA-15, SBA-16, MCM-41, and MCM-48)widely use synthesis of heterogeneous acidic catalysts (HeACs)(Şimşek, 2015; Şimşek & Avcı, 2018; Şimşek & Şahin, 2019).

Homogeneous acidic catalysts(HoACs) and HeACs are used in industrial-scale ester production. They used in the esterification reactions catalyze the reaction by giving a proton to the carboxylic acid(R-COOH)(Maki-Arvela et al., 1999; De Almeida et al., 2014). Homogeneous catalysts(HoCs) are generally used in esterification reactions(ERs)(Yin et al., 2013) such as HI(hydriodic acid), H_2SO_4(sulfuric acid), HCI(hydrochloric acid) and NaOH(sodium hydroxide), and (Yin et al., 2013; Helminen et al., 1998; Poonjarersilp et al., 2014; Oliviera et al., 2010). Recently, but, interest in heterogeneous catalysts(HeCs) has been intensified because HoCs dissolve quickly in the liquid reaction medium, cause corrosion, environmental pollution, do not easily decompose from the product, and require a separation process (Yin et al., 2013; Oliviera et al., 2010). for re-used. Among the SiBSMs, SBA-15 (Hess, 2009; Cavalleri et al., 2009) and M41S family(Brahmkhatri & Patel, 2011; Sawant, et al., 2007; Liu et al., 2004; Kumar et al., 2006) are the most well-known. Impregnation(Brahmkhatri & Patel, 2011; Sawant, et al., 2007; Liu et al., 2004; Kumar et al., 2006), dry-wet impregnation(Şimşek &Mürtezaoğlu, 2019) and sol-gel(Yang, et al., 2005) methods are widely used in the synthesis of supported mesoporous materials and HeCs (solid catalysts). However, recently, direct HM has come to the forefront as an alternative synthesis method in studies where heteropoly acid catalysts(Fulvio et al., 2005) metals(Jimenez et al., 2010; Laugel et al., 2009) are used as active substances. Because HM has some advantages such as a homogeneous solution media for precursors, low material loss after synthesis procedure, low cost, and easy experiment properties or set up(Şimşek, 2019 ;Senapati & Maiti,2020).

The sieve structure of SBA-15 has larger pore sizes and thicker pore walls compared to the M41S family(Şimşek, 2015; Thieleman et al., 2011). SBA-15 is a mesoporous silica sieve with adjustable pore diameters between 5 and 15 nm and a hexagonal structure with a narrow pore distribution. The fact that the wall frame thickness is between 3.1 and 6.4 nm is one of the main reasons for its higher hydrothermal and mechanical stability than materials such as MCM-41 (Thieleman et al., 2011).

SBA-15 is a suitable material for adsorption and separation in analytical environmental applications due to its high internal surface (400-900m²/g) areas Şimşek, 2015; Thieleman et al., 2011). It is also a suitable SPm in catalysts (Hess, 2009; Cavalleri et al., 2009; Şimşek, 2019). During the synthesis of SBA-15, which has a hexagonal mesoporous structure, it was observed that the pH value of the gel before washing with 300 ml of distilled water was always less than 0. After washing with 300 ml of distilled water, the pH value was obtained between 0-1. In other words, the pH value is very important for the catalytic activity of the SBA-15 SPm. The adjustable pore size in the synthesis of PMs increases the product selectivity. The pore size of the material must also be large then the large size of the organic molecules formed in the reaction. In catalyst synthesis, silica-alumina based materials are preferred because of that pore size ranges can be controlled depending on the synthesis parameters(Clark, 2002; Wilson & Clark,2000).

Due to these properties, it is an important SPm for acidic catalysts used in ERs such as glycerol, which is obtained as a by-product in biodiesel production, and methyl acetate, ethyl acetate. The pH value before synthesis and after washing is important for the SBA-15 SPm to show high catalytic activity. ERs are equilibrium-limited and slow reactions. For this reason, there is a need for the use of catalysts in order to economically produce esters. Studies have shown that ester production increases in the presence of acidic homogeneous and heterogeneous catalysts(Röhnbak et al.,1997).

The heterogeneous catalysts used in the ER are usually homogeneously dispersed on a porous SPm. Natural or artificial solid materials, in which the pores are heterogeneously or homogeneously dispersed in different sizes and dimensions, are generally called porous materials. Their use as SPm in catalyst synthesis is one of the most important application areas of porous materials. The porous structure increases the surface area of the catalysts and increases their activity (Şimşek, 2008). The use of heterogeneous catalysts in ERs has increased in recent years. In reactions with heterogeneous catalysts, the parameters affecting the activity are temperature, stirring speed, catalyst amount, mole ratio of reactant, presence of inert material in the feed and retention time. The most important factors in the preference of solid acidic catalysts are that they reduce the corrosion problems and environmental problems that will occur due to the use of homogeneous acidic catalysts and do not create an additional separation cost in the chemical process (Helwani et al., 2009).

In this study, SBA-15 SPm synthesized by HM and Fe/SBA-15 (10,25% Fe/Si loading ratio) catalyst was synthesized. The catalytic activities of the synthesized materials (SBA-15, Fe/SBA-15) were tested in the MER selected as the model reaction. XRD, BET, FT-IR, DRIFTS, SEM/EDX, and MAPPING analysis methods were used to examine the structural changes of the synthesized materials before the reaction. The main purpose of this study is to investigate the synthesis, characterization, and catalytic activities of heterogeneous acid catalyst synthesized by the HM in the ER.

2. Material and Method

2.1. Synthesis of SBA-15 and Fe/SBA-15 Materials

SBA-15 synthesis was carried out in accordance with the synthesis procedure determined as a result of the literature search(Şimşek, 2019). Pluronic P123 as a surfactant, tetraethyl orthosilicate(TEOS) as silica source, deionized water(DW) as a solvent, and HCl acid for adjusting solution pH were used in the synthesis of porous material. First, pluronic P123 was dissolved in DW and stirred for 4hours at 40°C until the solution became clear. Then, TEOS was added to the prepared clear solution. Within the scope of the study, the TEOS/Pluronic P123 ratio was determined as “2”. After mixing for 2 hours, the solution obtained was placed in an autoclave and kept in an oven at 100°C for 48 hours. Second, the product, which became a gel in the autoclave, was washed with DW and a solid product was obtained after filtration. The solid product was then dried at 80°C for 12 hours. Finally, the sample was calcined at 540°C for 5 hours in order to remove the Pluronic p123 remaining during the synthesis in the SBA-15 structure. The HM was used in the synthesis of the Fe/SBA-15 catalyst used in the study. According to this method, TEOS was first added to the surfactant simultaneously with the active substance Fe_2O_3. The steps the solution goes through until it becomes solid are the same as for SBA-15 synthesis. Unlike the SBA-15 synthesis, the calcination temperature in the Fe/SBA-15 synthesis was determined as 350°C, taking into account the catalyst strength. The active substance ratio in the Fe/SBA-15 catalyst was determined based on the molar ratio of iron (Fe) in the iron (III) oxide structure to silicon (Si) in the TEOS structure. Within the scope of the study, this rate is Fe/Si: 10,25 %. The synthesis steps of the Fe/SBA-15 catalyst are shown schematically in Figure 1.

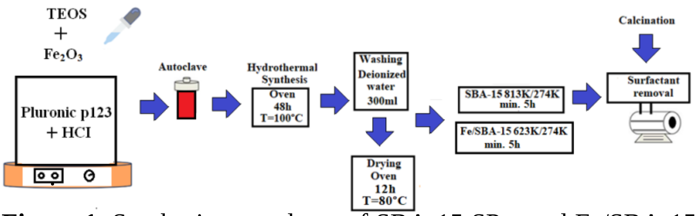
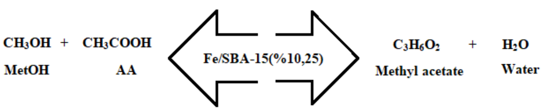


Figure 1. Synthesis procedures of SBA-15 SPm and Fe/SBA-15 catalyst.

2.2. Product of Methyl Acetate

The ERs were carried out in a batch reactor at autogenic pressure. The amount of Fe/SBA-15 catalyst was determined as 0.4g, the stirring speed was determined as 1000 rpm, and the mole ratio of AA/MetOH was determined as 2/1 during the experiments carried out in a reactor with methyl acetate production. Samples were taken at certain time intervals during the reaction and analyzed using Shimadzu gas chromatograph (GC-2010) instrument. In the gas chromatograph(GC) operation conditions are given in Table 1. MetOH and AA reactants with ethyl acetate synthesis and acetic acid conversion (Eq.1-2.)



(1)

$$XA =: \frac{AC*\alpha AC}{AC*\alpha AC+AB*\alpha AB+AA*\alpha AA} \quad (2)$$

Here: The AAC(%) is $X_{AA/MtAC,}$ the calibration factor of methyl acetate is $\propto_{MtAC}$, the calibration factor of MetOH is $\propto_{MtOH,}$ the calibration factor of AA is $\propto_{AA}$, the area of methyl acetate is A_{MtAC} , the area of MetOH is A_{MtOH} and $A_{AA}$is the area of AA.

2.3. Characterization studies

Fourier transform infrared spectroscopy(FT-IR) analyses of SBA-15 SPm and Fe/SBA-15 catalysts(10,25%) were performed using Perkin Elmer IR device between 380-4000 cm^{-1} wavelengths. In order to determine the Brønsted acid acidity of the Fe/SBA-15 catalysts, multiple internal reflection(DRIFT) analyses were carried out using the pyridine(C_5H_5N) adsorbed samples in the same instrument and wavelength range, and the acid sites of the catalyst were determined. X-ray diffraction(XRD) analyses to identify structural phases of SBA-15 and Fe/SBA-15 catalysts: Panalytical Empryan HT-instrument; using CuKα radiation, 0.066 step pitch (sensitivity) and between 0°<2 θ<60° range were performed. In order to determine the surface area(SA), pore size distribution(PSD), and average pore distribution, multi-point Brunauer-Emmett-Teller(BET) and Barrett-Joyner-Halenda(BJH) analyses methods were carried out using the ASAP2020 device in the range of N2 gas and 363-523K degas temperature for 3hours. The surface morphologies of the SPm and catalyst were determined by SEM/EDX (scanning electron microscope/energy dispersive x-ray, Zeiss SUPRA V40 instrument) analysis. Moreover, the MAPPING analysis method was used to determine the distributions of Fe and Si elements in the catalyst and support structure.

Table 1. Operation properties of GC[22].

Column	TRB Wax, 30mx0.32mmx0.5 µm Capillary column
Detector	FID (flame ionization detector)
Carrier gas and flow rate	N_2(99.9%), 1.5 ml/min.
Column operated temperatures	80°C (1 minute) $\xrightarrow{15^0 C/min.}$ 330°C (2 minutes)
Detector temperature	380 °C
Injection temperature	280 °C

N_2 constant pressure	(58,0 kPa)
Hydrogen (H_2)	(99.9%)
Dry air	(99.9%)
Injection sample volume	0.2µl

3. Results and Discussion

3.1. Characterization Analyses

Figure 2 (a) shows N_2 adsorption/desorption experiments of SBA-15 SPm and Fe/SBA-15 (10, 25% Fe:Si). And BJH pore volume distribution is given in Fig 2(b). SBA-15 and 10, 25% catalysts have shown a type IV isotherm curve with an H1 hysteresis loop its characteristic of mesoporous structure[30]. The surface area and pore volume decreased as a result of the addition of Fe_2O_3. These reductions are thought to be due to the accumulation of Fe_2O_3 on the pore walls, as well as some of it entering the pore. Changes in the structure of the 10% Fe/SBA-15 catalyst can be explained by the changes in the SBA-15 structure of the Fe added to the structure rather than the reaction effect.

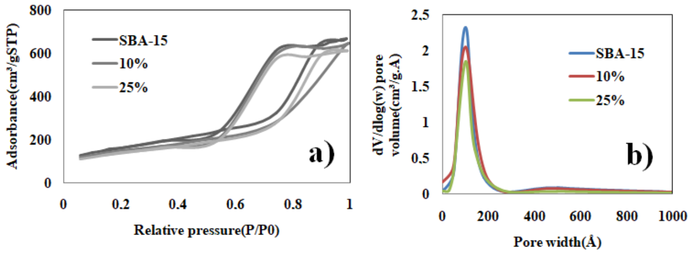


Figure 2. a) BET isotherm curves, and b) BJH desorption pore volume distribution of materials.

Figure3 shows SBA-15 has a regular mesoporous and hexagonal structure(Şimşek & Avcı, 2018; Helwani et al., 2009; Huang et al., 2010; Baskarana et al., 2014) with d100, d110 main peaks(Quach et al.,2020). Furthermore, in the characteristic peaks of SBA-15 SPm were observed shifts and losses after loading Fe(Figure 3)(Şimşek, 2015; Şimşek, 2019; Baskarana et al., 2014). According to the XRD analysis results of the SBA-15 SPm, it was observed that Bragg peaks at 1.12° and 2.94° 2θ values were obtained. Moreover, the characteristic peaks of SBA-15 were obtained in accordance with the literature(Şimşek, 2015; Şimşek, 2019) Figure 3(a). Although there were shifts in the basic Bragg peaks of SBA-15 after the active substance loading, 200 and 210 peaks were observed Figure 3(a,b) (Magdalena et al., 2019). It was assumed that this was due to the fact that the active substance did not cause significant changes in the structure during synthesis. As expected, no significant changes were observed in wide-angle XRD analyses (Figure 3(c)). These results are supported by the SEM analysis image of the Fe/SBA-15 catalyst before the reaction (Figure6,7).

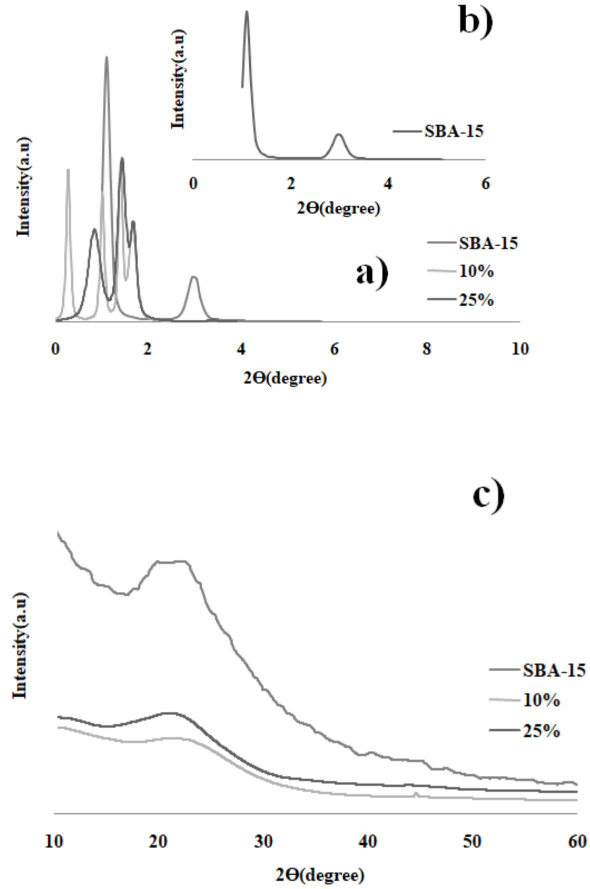


Figure 3. XRD analyses(low angle (a,b) and c) high angle) of SBA-15 and Fe/SBA-15(10,25%) materials.

Table 2. Physical properties of SBA-15 and Fe/SBA-15(10, 25%) materials.

Material	BET surface area(m²/g)	Pore volume (cm³/g)	Micro surface area (m²/g)	Average pore diameter(dp) (Å)	d(100) nm	Lattice parameters (a:nm)
SBA-15	636.7	1.27	48.6	95.4	8.85	9.87
Fe/SBA-15*	537.5	1.07	36.8	103.5	8.14	9.38
Fe/SBA-15**	289.4	0.40	14.4	112.7	7.76	8.96

*10% Fe/Si, **25% Fe/Si

The characteristic lattice parameters "a" of SBA-15 and 10,25% catalysts were obtained using Eq. (3) "$a=2d_{(100)}/3^{1/2}$". The lattice and d(100) parameters of materials were measured using BET and XRD analyses methods.

$$a = 2d(100)/\sqrt{3} \qquad (3)$$

Here: a; lattice parameters, d(100): dspace(distance between planes).

Figure4 illustrates FTIR analysis results of SBA-15 SPm and Fe/SBA-15 catalysts. 447-1045cm^{-1} wavelengths indicate SBA-

15 characteristic structure peaks. Si-O and SiO2 tensile and flexible vibrations (symmetrical and asymmetrical) peaks of it were obtained 1045, 940, 787cm^{-1} wavelengths, respectively(Junhong et al., 2020). Moreover, the 447cm^{-1} peak corresponds to Si-O-Si bending vibration in the structure of SBA-15(Bhuyan et al.,2017).

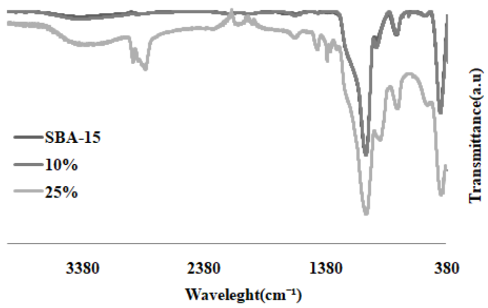


Figure 4. FTIR analyses of SBA-15 and Fe/SBA-5 (10,25%) materials.

Figure 5 shows DRIFT analyses peaks of Fe/SBA-15(Fe/Si:10,25%) catalysts. Lewis acid site (LeAs) and Brønsted acid site(BrAs) was obtained at between 1300-1500cm^{-1} wavelengths (Figure 5). LeAs and BrAs site of Fe/SBA-15(Fe/Si:10,25%) catalysts were obtained at 1347-1346, 1458-1458 cm^{-1} wavelengths, respectively (Cavlar et al., 2007). 1372 and 1373 peaks corresponded to pyridine physically adsorbed in the catalyst structure(Cavlar et al., 2007).

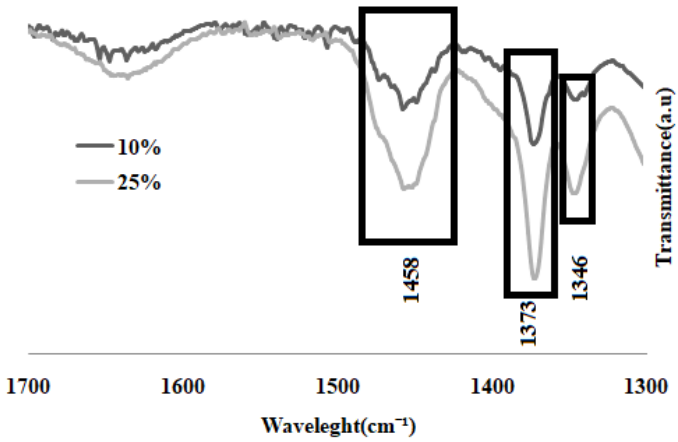


Figure5. Drift analyses of Fe/SBA-15 (10,25%) materials.

The p6mm space groups and wheat structures of the SBA-15 SM (Thieleman et al., 2011)were indicated in the SEM analysis results (Fig.6,7 (a, b)). Moreover, these structures were preserved after active compound(Fe) loading (Fig.6,7(a,b)). The results of SEM/EDX and MAPPING analyses, it were determined that the distribution of Fe and Si elements on the support material(SBA-15) surface was homogeneous (Fig.8,10;a,b). the EDX results of catalysts indicated that the increase in the amount of Fe (active compound) loading in the SBA-15 has been proven(Fig.9,11).

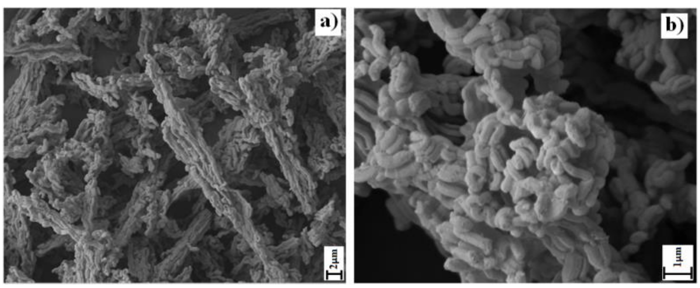


Figure 6. SEM images of parent Fe/SBA-15 (10% Fe/Si ; a, b; 5-20kx)).

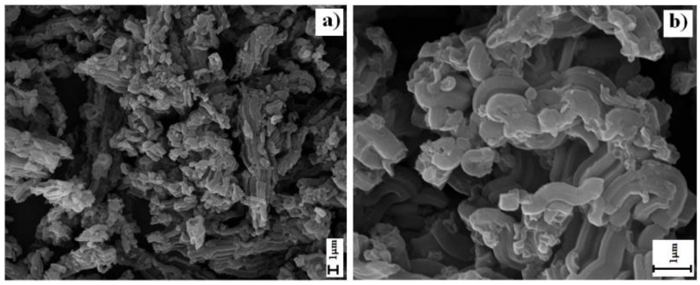


Figure 7. SEM images of parent Fe/SBA-15 (25% Fe/Si ; a, b; 5-20kx))

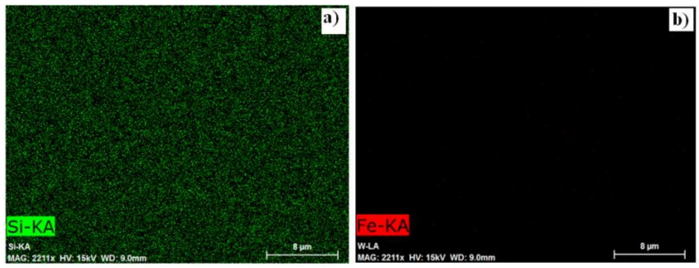


Figure 8. MAPPING images of parent Fe/SBA-15 (10% Fe/Si ; 2.211kx)).

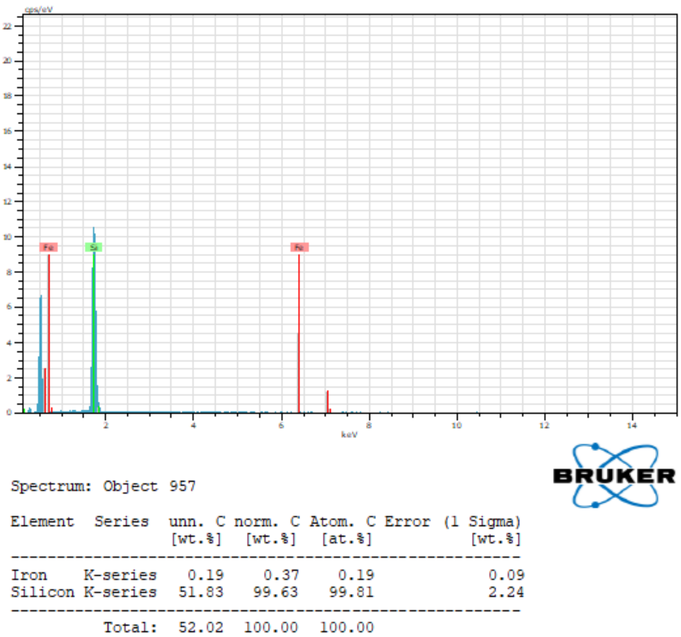


Figure 9. EDX analysis of parent Fe/SBA-15 (10% :Fe/Si).

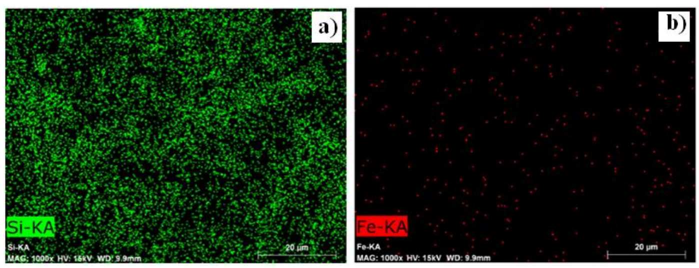
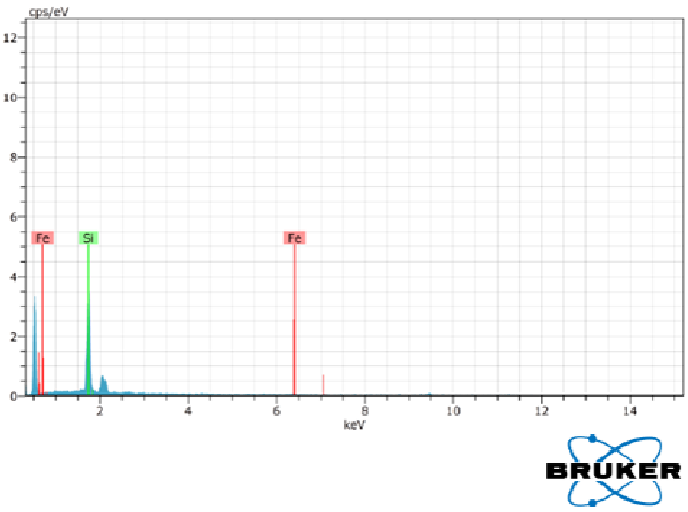


Figure10. MAPPING images of parent Fe/SBA-15 (25% Fe/Si ; 1kx)).



Spectrum: 503

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Silicon	K-series	11.77	96.79	98.36	0.56
Iron	K-series	0.39	3.21	1.64	0.10
	Total:	12.16	100.00	100.00	

Figure 11. EDX analysis of parent Fe/SBA-15 (25% : Fe/Si).

3.2. Catalytic Analyses

Catalytic activities of synthesized Fe/SBA-15 catalysts within the scope of the study; It was investigated by methyl acetate synthesis with MetOH and AA reactants at 373 K. Reaction experiments were carried out in a batch reactor. Experiment conditions have been determined as catalyst amount of 0.4g, stirring speed of 1000 rpm, the mole ratio of AA/MetOH 2/1, and analysis time 48 hours. AA conversion values were obtained as 43-48, 55-61 and 64-72%, respectively after 6, 24 and 48hours(Fig. 12(a,b,c)). However, the reaction was not reached to balance limitation. On the other hand, the initial reaction rates of catalysts at different temperatures were calculated. The calculations were obtained at the end of 1 hour and using the batch reactor equation. Parameters: Volume of the batch reactor; V, and V=V0(volume batch reactor=initial volume). the IRR (initial reaction rates), and the SRR(specific reaction rate) of Fe/SBA-15 catalysts(%10,25) are shown in Table 3.

Table 3. IRR and SRR values of Fe/SBA-15 catalysts(%10,25).

Materials	Temperature (K)	SRR (k;L/mol.min)	IRR(-rA) mol/L.min
Fe/SBA-15*	373	1.159×10^{-4}	0.013459
Fe/SBA-15**	373	1.27×10^{-4}	0.014525

*10% Fe/Si, **25% Fe/Si

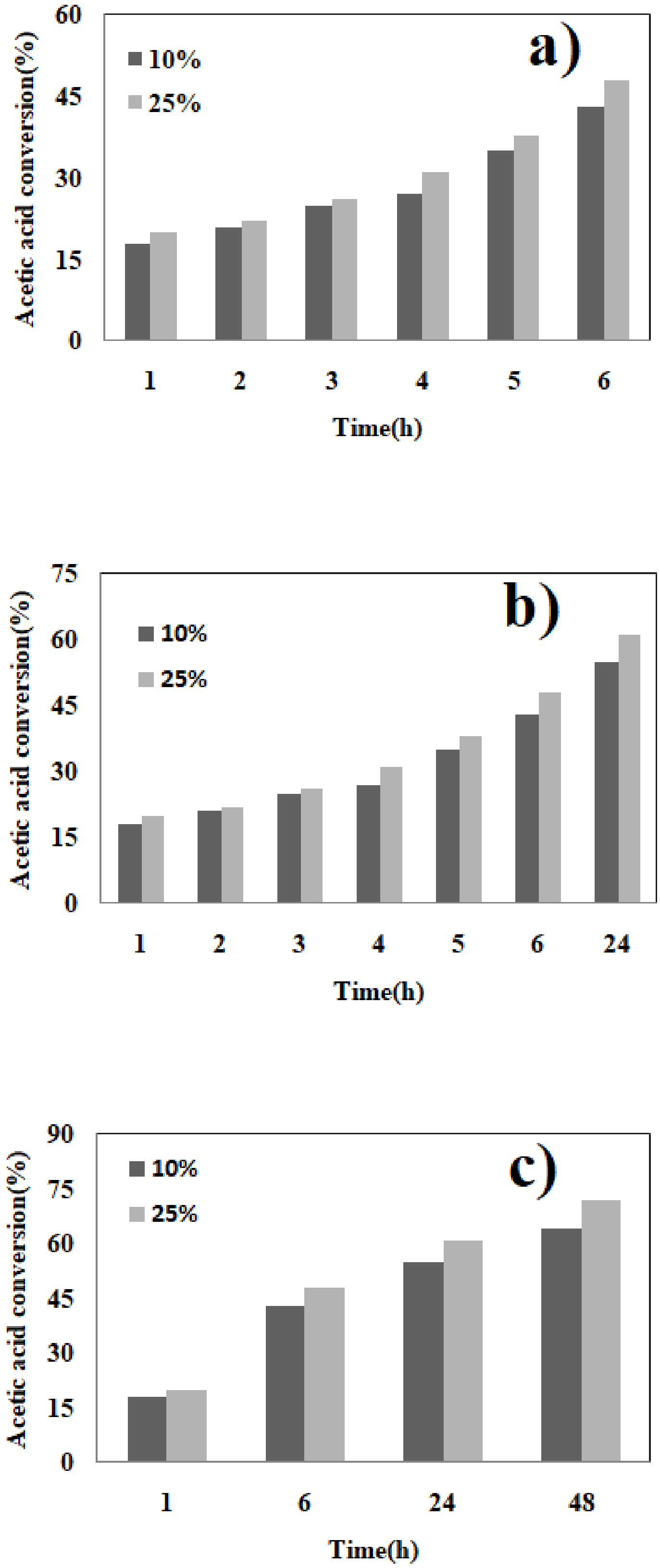


Figure 12. Acetic acid conversion (a)6h, (b)24 and (c) 48h.

4. Conclusions and Recommendations

SBA-15 SPm and Fe/SBA-15 catalysts were successfully synthesized with HM. Moreover, the characterization studies carried out on the materials proved that the synthesis of SBA-15 was carried out successfully in accordance with the literature. By the way, it was observed that Fe added to the structure during the synthesis not caused structural deterioration in the Fe/SBA-15 catalyst.

By adjusting the synthesis conditions, the active substance was homogeneously added to the catalyst structure and the activity of the catalyst was adjusted depending on the parameters applied in the synthesis procedures. Catalytic activity values of 10, 25% catalysts were calculated as 64 and 72%, respectively after 48hours.

It is estimated that Fe/SBA-15 catalysts synthesized by the HM will be more efficient in higher temperature reactions. This is because the SBA-15 SPm has high thermal stability and thick wall thicknesses.

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